AN ABSTRACT OF THE DISERTATION OF

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Abstract approved:

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Many pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons are persistent, bio-accumulative, and toxic. These semi-volatile organic compounds (SOCs) can undergo atmospheric transport and deposition in cold, remote ecosystems. A better understanding of their accumulation in the fish of these ecosystems is important to better predict the human and ecosystem health risks of these and other SOCs. This dissertation describes the development of analytical methods to measure 91 of these SOCs at concentrations <1 ng/g in fish tissues, and determination of fish and ecosystem characteristics affecting their distributions throughout western US lakes. To measure PBDEs in extracts, a gas chromatography low resolution mass spectrometric method was developed for the selective and quantitative isotope dilution analysis of 39 PBDEs. PBDE specific high mass ion production was optimized, selectivity enhanced, and accuracy was improved with the use of ^{13}C surrogates. An analytical method was developed and validated to measure 91 target compounds at <1 ng/g in fish. The method was sensitive (0.2-990 pg/g detection limits), efficient (61 % recovery), reproducible (4.1 %RSD), and accurate (8 % deviation, NIST SRM #1946). SOC concentrations in 136 fish from 14 remote lakes were compared to human health contaminant screening values. Most fish concentrations were 1-6 orders of magnitude below screening values, however average fish concentrations of dieldrin and/or p,p’-DDE in 8 lakes exceeded lifetime cancer screening values for subsistence fishers. Because fish SOC concentrations varied several orders of magnitude within and between lakes, statistical models were developed to explain the influence of 7 fish and 12 ecosystem characteristics on fish

SOC concentrations. Fish characteristics that best explained SOC concentrations were fish age and lipid concentration. Average air temperature, measured winter SOC deposition, and lake elevation were ecosystem characteristics that best explained fish concentrations of historic use pesticides, current use pesticides, and PCBs and PBDEs, respectively. This suggests that human health impacts are possible from some atmospherically deposited SOCs, and that fish SOC concentrations in western US lakes can be explained by combinations of fish lipid concentration and/or age, and air temperatures, elevations, proximity to sources, and/or winter SOC deposition.

Analysis of Semi-Volatile Organic Contaminants and Their Accumulation in Remote Aquatic Ecosystems of the Western U.S.

by

Luke K. Ackerman

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APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Luke K. Ackerman, Author

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CONTRIBUTIONS OF AUTHORS

Dr. Staci Simonich and Glenn Wilson assisted with the experimental design and writing for Chapter 2.

Dr.’s Dixon Landers, Carl Schreck, Mike Kent, and Staci Simonich, were responsible for project design related to the fish, and Adam Schwindt for coordinating and conducting sample collection in Chapter 3. Dan Koch was responsible for most of the sample preparation for chemical analysis. Adam Schwindt was responsible for discussions of wildlife fish consumption in Chapter 3. All assisted in the edits of Chapter 3.

Dr.’s Dixon Landers, Carl Schreck, Mike Kent, and Staci Simonich, and Adam Schwindt assisted in the edits of Chapter 4.

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Dedication

This dissertation is dedicated first to the hard working and (often) underpaid people of the state of Oregon, who paid in a sizeable part for my studies. It is dedicated to the especially hard working and underpaid graduate assistants of OSU, UO, and the greater graduate employee labor movement, to whom I am eternally grateful for the solidarity and inspiration they have shared with me. It is also dedicated to those who helped me grow, learn, and accomplish, my scholarly mentors Debbi Woodard and Lynn MacAusland, Fr. Michael Trealevan SJ, Dr. Joanne Smieja, and lastly Dr. Staci Simonich. Finally, and mostly, it is dedicated to my loving partner in life, without whose love and support, this would not have been possible, Michaela Lindahl.

Analysis of Semi-Volatile Organic Contaminants and Their Accumulation in Remote Aquatic Ecosystems of the Western US

1. Introduction

1.1 Background on SOCs

Anthropogenic semi-volatile organic compounds (SOCs) such as pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), have resulted in improved crop yields(*1*), longevity and efficiency of dielectric fluids(*2*), and flame resistance of polymeric materials(*3*). Some SOCs, such as polycyclic aromatic hydrocarbons (PAHs), result from inadvertent production during power generation, manufacturing, and goods transport due to incomplete combustion of hydrocarbon fuels(*4*).

Many pesticides(*5*), PCBs(*6*), PBDEs(*7*,*8*), and PAHs(*9*) have been demonstrated to cause cancer(*10*), chronic health(*11*), reproductive(*12*), and developmental problems(*13*) in humans(*14*) and animals(*15*), at part-per-billion tissues concentrations. These same anthropogenic organic compounds are often persistent in the environment(*16*) and can accumulate in biota(*17*). For these reasons, persistent organic pollutants (POPs) such as these have been targeted for regulation and phase out by international treaties(*18*), as well as health and environmental agencies.

These persistent, bioaccumulative, and toxic (PBT) compounds are semi-volatile and partition between the atmosphere and condensed media, depending on the ambient temperature and the nature of the surfaces. Some SOCs such as these undergo atmospheric transport(*19*), condense in cold locations(*20*), and accumulate in remote(*21*) or previously unexpected locations across the globe(*22*). It is important to develop an accurate understanding of the accumulation and fate of SOCs in order to better predict the fate and potential risk from these, and other yet to be identified SOCs. Understanding accumulation and fate of SOCs in cold remote ecosystems is important because of their atmospheric transport ability, temperature sensitivity, bioaccumulation, and human and wildlife toxicity.

The transport mechanisms and the fate of SOCs are often dependent on their mode of emission(*23*), environmental processes(*24*), and the physical chemical properties of the compounds(*25*). SOCs such as pesticides, PCBs, PBDEs, and PAHs, have a wide range of chemical structures and physical-chemical properties. Many physical-chemical properties are a measure of a chemical's distribution between two phases at equilibrium, such as air and water (K_{aw}), octanol and water (K_{ow}), or air and pure liquid chemical (P_L, or vapor pressure). SOCs' vapor pressures, hydrophobicities (K_{ow}), and air water partition coefficients (K_{aw}) range over several orders of magnitude (Table 1.1) and thus dramatically affect the tendency of SOCs to reside in and move between air, soil, water, and biota.

These SOCs also exhibit a large range of persistence, with environmental half-lives ranging from hours to years(*26*). Degradation mechanisms include hydrolysis(*27*), photolysis(*28*), hydroxyl radical oxidation(*29*), reductive dehalogenation(*30*), and metabolization transformations(*31*). The relative rates of these degradation processes and the presence of the SOC in the relevant environmental compartment where these degradation processes occur can result in dramatic differences in environmental fate and persistence(*26,32*). The physical chemical properties of the SOCs can affect their residence time in an environmental compartment, and therefore, their persistence and concentrations(*23*).

How an SOC enters the environment can also affect the fate(*23*) and potential human and ecological risks of the SOCs. Emission of some hydrophobic SOCs to water systems can result in significant partitioning to sediments and uptake by aquatic biota(*33*), while emissions to the atmosphere can result in faster reaction with hydroxyl radical (*29*) or photo-degradation(*34*). However, atmospherically persistent SOCs emitted to the atmosphere can travel large distances(*19*) and accumulate up food chains(*35*), affecting remote wildlife health(*36*).

Environmental processes can often play a large role in the fate of SOCs, especially in areas remote from their emission or where large environmental changes take place in the relevant environmental compartment. For example, snow has been shown to effectively scavenge SOCs out of the atmosphere(*24*), Because higher elevations tend to be colder and receive more snow, deposition of more volatile SOCs via snow packs has been observed to increase with elevation(*37*). Similarly, biological processes, such as animal migrations(*38*), and vegetation changes(*39*) can result in large scale movement of organic contaminants.

Previous work has demonstrated that SOCs have accumulated in high mountain snow and fish in Europe(*40-42*) and the Canadian Rockies(*37,43*), likely due to mountain cold trapping. Similar studies of high elevation European lakes suggested elevation affected lake SOC concentrations(*44*), and that elevational accumulation might only be significant for SOCs within a certain vapor pressure range, depending upon ambient temperatures. This has been supported by studies of snow in the Canadian Rockies(*37*). Neotropical montane forests(*45*), and South American mountain vegetation have also shown elevational concentration gradients for some SOCs(*46*). However, there is little wide scale information about the concentrations of SOCs in western US mountains(*47-55*), or whether elevation plays the same role with SOC concentrations in the western US. Also, only recently have some analyses been conducted to explore whether other factors besides elevation might explain differences in SOC accumulation between high elevation locations(*49*). It has been suggested that SOCs may be deposited by snow but may also revolatilize leading up to, or upon snow-melt(*24,56-58*), potentially affecting high elevation SOC fate. Other ecosystems factors, such as proximity to source regions or meteorological patterns may also play a large role in governing SOC accumulation in mountain ecosystems(*49*).

Fish are often at or near the top of aquatic food webs in high elevation lakes(*59*), have been demonstrated to accumulate high concentrations of SOCs(*60*), and can be the largest single source of contaminants in many human and wildlife risk profiles(*61*). It has been shown that fish contaminant concentrations can vary widely within and between populations, and are not easily predicted(*60,61*). Numerous factors have been shown to affect individual fish concentrations within a population, but few do so consistently. Additionally, few studies have reported factors affecting SOC concentrations across fish populations(*60*). Some studies from high elevation lakes have reported no observable elevational trends for fish concentrations of some

SOCs(*62*), and others have suggested that observed elevational trends might be due to other, covariate factors(*63*).

1.2 Data Gaps and Obstacles

Studies of SOCs across western US high elevation ecosystems are needed to assess present concentrations, to investigate ecosystem fate and transport of SOCs, to determine individual and ecosystem factors controlling SOC concentrations in fish, as well as to assess potential or realized impacts of these contaminants on human and ecosystem health. Studies such as these require rigorous analytical techniques that are sensitive, specific, reproducible, and accurate. Gas chromatography-mass spectrometry (GC-MS) is almost exclusively used to separate, identify, and quantitate SOCs in the organic extracts of environmental samples. Sample preparation techniques are needed to remove co-extracted interferants from solid sample extracts, but often limit the list of analytes in a single method to one or two chemical classes. Some SOCs, such as PBDEs have been measured using either exceedingly expensive high resolution mass spectrometry, or insufficiently specific bromide ion monitoring, low resolution-electron capture negative chemical ionization mass spectrometry (LR-ECNI/MS). Also, few organic analytical methods for complex biological matricies, such as fish, are sensitive enough to measure SOCs at the <1 part-per-billion (ppb) concentrations expected in many high elevation fish tissues(*64*).

1.3 Analyses Conducted

This dissertation describes the development and validation of an analytical method to conduct selective measurement of a broad range of pesticides, PCBs, PBDEs, and PAHs in fish tissues at concentrations <1 ng/g, as well as an analysis of fish SOC concentrations across western US high elevation National Parks, their potential effects, and the factors governing their distribution and accumulation. The development and optimization of a selective and sensitive GC-MS technique for the isotope dilution analysis of PBDEs is described in Chapter 2. Optimizations of ion source parameters are described and sensitivity and selectivity of optimizations tested.

The adjusted technique was just as sensitive, and more selective than previous bromide ion monitoring methods. The adjusted technique permitted the use of isotope labeled standards and therefore yielded increased accuracy.

The application of these GC-MS techniques to the analysis of a broad range of 91 current and historic use pesticides, PCBs, PBDEs, and PAHs in fish tissues is discussed, and the resulting methods validation and analytical figures of merit are described in Chapter 3. Additionally, the analysis of 136 fish from 14 remote lakes in 7 western US National Parks is described and determined fish SOC concentrations are compared to previous work as well as human health fish contaminant consumption screening values. The method validation showed the method to be sensitive at low pg/g concentrations in whole fish tissues, with good accuracy, precision, and a wide linear range. Additionally, fish contaminant results demonstrated that fish in high elevation throughout the western US have higher PBDE concentrations than fish in comparable lakes in Europe or in Pacific ocean salmon, and that atmospherically deposited dieldrin and p,p’-DDE accumulated in some fish to concentrations relevant to human health.

In Chapter 4, the concentrations of SOCs in these high elevation fish are compared, and multiple linear regression models, developed to determine which fish and lake characteristics explained the most variability in the SOC concentrations, are presented and discussed. Additionally, interaction between fish and lake characteristics and their affects on SOC accumulation in fish is evaluated and discussed.

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Table 1.1 Physical-Chemical Properties of Selected Analytes

	log K_{ow}	log K_{aw}	log K_{oa}	Log $C_{w,sat}$ (mol/m^3)	Log P_L (Pa)
Endosulfan sulfate	3.66	-4.75	8.41	-0.95	-4.43
HCH, gamma	3.83	-0.51	7.74	-0.61	-1.12
HCH, alpha	3.94	-0.13	7.46	-0.48	-0.61
Dacthal	4.40	-3.99	8.30	-2.82	-3.48
Endosulfan II	4.78	-4.74	9.52	-1.05	-2.40
Endosulfan I	4.94	-3.55	8.49	-2.20	-2.35
Heptachlor epoxide	5.42	-3.17	8.59	-1.88	-1.65
Dieldrin	5.48	-3.36	8.84	-1.88	-1.84
Chlordane, oxy	5.48	-2.48	7.96	-3.94	-3.03
HCB	5.64	-1.58	7.21	-2.85	-1.03
Nonachlor, trans	6.08	-2.20	8.28	-4.73	-3.54
Chlordane, cis	6.20	-2.61	8.83	-2.89	-2.14
Chlordane, trans	6.27	-2.56	8.83	-2.82	-1.99
Nonachlor, cis	6.35	-2.07	8.42	-5.07	-3.88
PCB # 118	6.69	-2.23	9.36	-4.17	-3.00
PBDE #49	6.77	-3.46	10.23	-3.52	-4.49
PBDE #47	6.81	-3.22	10.53	-2.51	-3.73
PCB # 153	6.87	-2.09	9.44	-4.51	-3.22
Mirex	6.90	-1.67	8.57	-4.89	-4.00
PCB # 187	6.92	-2.49	9.41	-4.00	-3.52
p,p'-DDE	6.93	-2.77	9.70	-3.10	-2.47
PCB # 138	7.22	-1.91	9.66	-4.73	-3.25
PBDE #100	7.24	-4.55	11.13	-2.15	-4.54
PBDE #99	7.32	-4.03	11.31	-2.78	-4.75
PBDE #154	7.82	-4.01	11.92	-3.87	-5.42
PBDE #153	7.90	-4.57	11.82	-3.87	-5.68
PBDE #183	8.27	-5.52	11.96	-3.92	-6.33
PCB # 183	8.27	-2.01	10.28	-4.15	-3.76

Quantitative Analysis of 39 PolyBrominated Diphenyl Ethers by Isotope-Dilution GC/Low Resolution MS

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2. Quantitative Analysis of 39 PolyBrominated Diphenyl Ethers by Isotope-Dilution GC/Low Resolution MS

2.1 Abstract

A GC low resolution MS method for the quantitative isotope dilution analysis of 39 mono to hepta brominated diphenyl ethers was developed. The effects of two different ionization sources, electron impact (EI) and electron capture negative ionization (ECNI), and the effects of their parameters on production of high mass fragment ions $[M\text{-}xH\text{-}yBr]^-$ specific to PBDEs were investigated. Electron energy, emission current, source temperature, ECNI system pressure, and choice of ECNI reagent gases were optimized. Previously unidentified enhancement of PBDE high mass fragment ion $[M\text{-}xH\text{-}yBr]^-$ abundance was achieved. Electron energy had the largest impact on PBDE high mass fragment ion abundance for both the ECNI and EI sources. By monitoring high mass fragment ions of PBDEs under optimized ECNI source conditions, quantitative isotope dilution analysis of 39 PBDEs was conducted using nine $^{13}C_{12}$ labeled PBDEs on a low resolution MS with low pg to fg instrument detection limits.

2.2 Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardant chemicals used as additives in polymeric materials ranging from polyurethane foam cushioning, to printed circuit boards and casings for electronics, to textile backings(*1*). Use of PBDEs has risen sharply over the last 20 years and in 1999 PBDE global production was more than double the peak annual global production of PCBs at 67,000 metric tons of PBDEs (*2,3*). PBDEs have been measured at part-per-million (ppm) to sub ppb concentrations in biotic and abiotic samples from around the globe(*1,4*). Since first being measured in environmental samples in 1979(*5*), concentrations of PBDEs in environmental samples have been steadily increasing. Temporal concentration trends from multiple matrices, including mothers milk, indicate rapid increases with doubling times of less than 6 years(*6-8*). In addition, it has been predicted that PBDEs will soon be the most concentrated organohalogen in some animal species(*4*). The observed bioaccumulation of PBDEs is likely the result of their lipophilicity. PBDEs are hydrophobic (log K_{ow} 5.0 - 8.3)(*9,10*) and range from semi-volatile, to fairly non-volatile (0.3 Pa – $2.3x10^{-9}$ Pa)(*11,12*). Similar to PCBs, PBDEs are chemically and microbiologically resistant to degradation under ambient conditions(*13*). These factors combine to make PBDEs persistent in the environment(*14*).

A wide range of PBDE concentrations have been measured in human and abiotic samples(*15*). This variation in concentration is not well understood, and human and wildlife exposure pathways are not fully understood(*14*). Analysis of human diets for PBDEs indicates the food chain is a significant route of human exposure(*16*). Inhalation may also be a major and much more variable route of human exposure to PBDEs(*17*). Some studies have shown that some PBDE congeners and their metabolites can be potent thyroid hormone competitors(*18,19*). Other studies suggest that PBDEs can also act as neurodevelopmental disruptors(*20,21*). These effects have the possibility of being realized in humans and wildlife as these compounds continue to accumulate in tissues.

Studies of the environmental fate and transport of PBDES have measured concentrations over several orders of magnitude in multiple environmental matrices(*15,17*). PBDEs have been shown to accumulate in environmental samples as a complex mixture of multiple congeners(*22,23*), with some congeners debrominating to lower brominated PBDE congeners(*24*). In addition, a number of other naturally occurring and anthropogenic brominated organic compounds have been identified in environmental samples(*25*) and may cause misidentification or misquantification of PBDEs if nonspecific analytical techniques are used(*26*). These challenges require that analytical methods measuring PBDEs in complex environmental matrices have a high degree of selectivity, sensitivity and precision. To meet these needs many previous environmental PBDE studies utilized gas chromatographic isotope dilution high resolution mass spectrometry with electron impact ionization (GC-IDHRMS)(*27-30*). Other studies have investigated the use of electron impact (EI)(*17*), electron capture negative ionization (ECNI)(*8*), inductively coupled plasma (ICP)(*31*), and metastable atom bombardment (MAB)(*32*) ion sources, coupled with low resolution (LRMS)(*8,17*), time-of-flight (TOF MS)(*33*), or tandem (MS/MS) mass spectrometers(*34*). These studies suggest that GC-IDHRMS is the best method to both unambiguously identify and precisely quantitate PBDEs in environmental extracts using isotope dilution because highly specific molecular ($[M]^{+\bullet}$) or high mass fragment ions ($[M - yBr]^{+}$) are typically monitored. However, the expense and limited availability of GC-HRMS may be driving the increased use of GC-ECNI/LRMS for PBDE analysis because the majority of environmental PBDE studies within the last year have utilized GC-ECNI/LRMS and quantitated on the bromide ions ($[Br]^{-}$, m/z 78.9 and 80.9). Although it has been shown that GC-ECNI/LRMS analysis for PBDEs is more sensitive than GC-EI/LRMS(*35*), and more selective than GC/ECD, concern exists over its specificity because the ECNI mass spectra are dominated by the non-specific bromide ions, which are not present in the EI mass spectra(*26,35*).

Various analytical techniques have been used to avoid interferants in GC-ECNI/LRMS analysis of PBDEs in environmental samples. Some of these techniques include extract fractionation to isolate PBDEs from potential interferants(*36*) and use of longer (60 m) GC columns for improved chromatographic separation(*37*). However, by quantitating PBDEs based on bromide ions, these methods cannot perform isotope dilution analysis of PBDEs (only ^{13}C labeled PBDE standards are commercially available). Some of these methods attempt isotope dilution analysis by using different classes of compounds, such as ^{13}C polychlorinated biphenyls (PCBs)(*38*), or ^{13}C polychlorinated diphenyl ethers (PCDEs)(*36*), or they simply employ similar halogenated compounds such as polybrominated biphenyls as internal standards(*39*). These practices eliminate the precision and specificity advantages of compound or class specific stable isotope dilution analysis that might help offset the more involved sample preparation or lengthy chromatographic separation employed to avoid brominated interferants. Isotope dilution analysis of PBDEs is needed to account for the very large range of physical chemical properties(*9-12*) and MS response among the PBDE congeners and their respective degrees of bromination(*35*).

For methods without compound or class specific stable isotope labeled standards, large differences in relative MS responses or analytical method recoveries could skew PBDE congener profiles and lead to misinterpretation. Similarly, using a longer GC column risks PBDE congener profile skewing because of on-column degradation of higher brominated PBDEs to lower brominated congeners(*40*).

An instrumental technique more commonly available and less expensive than GC-HRMS and more specific and precise than current GC-ECNI/LRMS methods, would be useful for environmental PBDE analysis. This need has been intermittently addressed by inclusion of low abundance (relative to the dominant bromide ions) PBDE high mass fragment ions as qualitative ions monitored in some of the GC-ECNI/LRMS methods(*25,41,42*). However, to take advantage of the precision of isotope dilution, these specific PBDE high mass fragment ions would need to be used as quantitation ions in order to allow mass differentiation of stable isotopically labeled standards (^{13}C), because the native and stable isotope labeled PBDEs co-elute chromatographically. Quantifying these specific PBDE high mass fragment ions is challenging because they have historically been present in the ECNI mass spectra at low absolute and relative abundances (~0.1-15% of $[Br]^-$). If these specific PBDE high mass fragment ions were present at higher levels in the mass spectrum, the inherent selectivity and sensitivity of ECNI might allow these higher mass fragment ions to be quantified in a LRMS method utilizing isotope dilution. Similar high mass fragment ions of chlorinated diphenyl ethers(*43*), dioxins(*44*), and biphenyls(*45*) were found to be highly sensitive to ECNI source parameters such as temperature, pressure, electron energy and emission current. In addition, previous optimizations of ECNI source parameters for PBDEs were only conducted on a few congeners, only optimized bromide ions(*35*) (or the ether fragment ion, $[OC_6Br_5]^-$, for decabromo diphenyl ether)(*46*), and only investigated ECNI system pressure and source temperature(*35*).

The goal of this research was to optimize ECNI source parameters in order to obtain significant increases in PBDE molecular and high mass fragment ion abundance, previously disregarded for lack of sensitivity, in order to permit quantitation of PBDEs with these specific ions by isotope dilution GC-ECNI/LRMS. We investigated and optimized electron energy, emission current, source temperature, ECNI system pressure, and choice of ECNI reagent gases to improve instrument specificity and sensitivity, characterized their relative effect on sensitivity, and determined the resulting method's linearity, detection limits, and suitability for isotope dilution analysis of 39 PBDE congeners.

2.3 Experimental Section

2.3.1 Materials.

All experiments were conducted with 39 congener native (EO-5113-7.5x) and/or 9 congener $^{13}C_{12}$ labeled (EO-5100) PBDE standards (CIL, Andover, MA) at 0.1-1.4 ppm, Optima grade solvents (Fisher, Pittsburgh, PA), Grade 5 Helium, Grade 4 Methane and IsoButane, and Pre-pure Nitrogen (BOC, Murray Hill, NJ). See Table 2.1 for a list of the specific PBDE congeners used in this study.

2.3.2 Instrumental Parameters.

PBDEs were analyzed using Agilent 6890 gas chromatographs coupled with 5973N mass spectrometers. A DB-5-MS (0.25 μm film thickness) 30 m x 250 μm (i.d.) fused silica capillary column (Agilent Technologies, Palo Alto, CA) was used to separate the PBDE standard mixtures. The injection was a pulsed splitless injection of 1 μL with 20 psi of helium for 0.5 min in a 280 °C injection port (2 mm gooseneck liner with wool plug) and lowered to a constant flow of 1.1 ml/min. The GC oven temperature program was as follows: isothermal at 157 °C for 1 min, pseudo-exponential with 1.89 °C/min to 180 °C, 2.08 °C/min to 206 °C, 2.36 °C/min to 223 °C, 2.82 °C/min to 252 °C, 3.69 °C/min to 268 °C, 4.68 °C/min to 300 °C and held for 10 min. The transfer line was held at 300 °C. The mass spectrometers were operated in both electron impact (EI) and electron capture negative ionization mode (ECNI). Helium was used as the GC carrier gas and methane or isobutane was used as the reagent gas for the ECNI source. Automated MS source tuning with perfluortributylamine and perfluorodiethyltrimethyldodecane (EI and ECNI, respectively) by the Agilent MSD Chemstation 1701 DA software, along with rough optimizations of select MS source parameters, yielded the following starting points for further optimization experiments. In ECNI mode, the ion source temperature was started at 150 °C, the emission current at 150 µA, the electron energy at 125 eV, and the methane reagent gas flow at 1 mL/min (~$1.8x10^{-4}$ torr system pressure). In EI, the optimization starting point (based on previous optimization experiments(*35*)) was a source temperature of 200°C, electron energy of 70 eV, and emission current of 35 µA. Masses of characteristic ions for each congener (Table 2.1), including the bromide ions ($[Br]^-$, m/z 78.9 and 80.9) for ECNI (not listed in Table 2.1), were monitored in selected ion monitoring mode for 100 ms. It should be noted that the most abundant m/z in the isotopic clusters of each congener's high mass fragment ion was monitored (ie A+3, or A+4 …etc, not A).

To be recorded, each compound's characteristic ions were required to maximize within 0.05 min of the standard's retention time (R.T.), within 0.01 min (or one scan) of each compound's other characteristic ions, and with an intensity ≥ 3 times the peak to peak noise of that ion signal. Data were acquired with Agilent MSD Chemstation 1701 DA.

2.3.3 Optimization Experiments.

MS ion source type (ECNI vs EI), ECNI reagent gas (CH_4 vs Isobutane), and source parameters were adjusted during a randomized analysis sequence of the standard PBDE solution, and the areas of each congener's specific ions recorded. These parameters and their ranges are listed in Table 2.2. Ion source temperature, electron energy, emission current, (and for ECNI, reagent gas flow rate or system pressure) were adjusted one-at-a-time to discrete values during the random sequence, and the areas for the PBDE high mass fragment ions ($[M\text{-}xH\text{-}yBr]^-$) and bromide ($[Br]^-$) ions were tabulated. Peak to peak noise immediately adjacent to the peak was measured for each congener. Scattered throughout the randomized sequence, the standard solution was analyzed under the same starting point conditions three times to determine run-to-run variation which was typically less than 10%.

In order to reduce the large variability in absolute response between PBDE congeners (see Figure 2.1), the response for each congener was recorded as the percent difference from the mean response for that congener across the experimental points of a given parameter. For example, the bromide ions' responses for hepta BDE #181 at different ECNI source temperatures (125-250 °C) were averaged, and it was determined that at a source temperature of 150 °C, BDE #181's bromide ion abundance was 68% above its average. This eliminated absolute abundance variation between congeners, turning PBDE responses for specific MS conditions into percentage differences from average. Each parameter was optimized independently to reduce the experiments to a manageable number. Source parameters were assumed not to interact and their effects on PBDE response were assumed to be additive, although this assumption was tested and is discussed later in the text. The optimum value for a given parameter was identified as the value yielding the largest sum of all congeners' relative response (the largest sum of the percent difference from average) and did not give weight to any particular congener or degree of bromination.

Once optimum source parameters were determined, an 8-point calibration curve with the 39 native and 9 $^{13}C_{12}$ labeled PBDE congeners was constructed from 0.5-1429 pg/uL, and analyzed to determine the instrument's linear range ($r^2 > 0.95$) and limits of detection (concentration equal to 3 times the peak to peak noise of the blank over the same time as the peak).

2.4 Results and Discussion

2.4.1 Chromatographic Separation.

Good chromatographic separation was achieved for all but four of the 39 PBDE congeners (see Figure 2.1). Tri BDE congeners # 28 and 33 co-eluted chromatographically but only # 28 produced a unique high mass ion and so # 33 was not reported. Penta BDE # 85 partially co-eluted with hexa BDE #155 using bromide ($[Br]^-$) and high mass fragment ions ($[M-xH-yBr]^-$). However, because hexa BDE #155 produced a unique molecular ion ($[M]^{-\bullet}$, m/z 643.6), penta BDE # 85 and hexa BDE #155 were co-reported, and hexa BDE #155 was also reported separately. The degree of separation achieved with this work is similar to previous work on 30 m columns for similar mixtures of PBDEs(*35*).

2.4.2 Mass Spectra.

Examples of the mass spectra obtained by EI, ECNI-CH_4 and ECNI-Isobutane for hepta BDE #181 are shown in Figures 2.2A, B, and C respectively. The mass spectra obtained for the 39 PBDEs matched mass spectra reported previously in the literature(*35*). Bromide ($[Br]^-$) ions (m/z 78.9, 80.9) were the base peaks, and high mass fragment ions ($[M\text{-}xH\text{-}yBr]^-$) were the second most abundant ions for almost all ECNI mass spectra. Molecular ($[M]^{-\bullet}$) ions were the second most abundant ions (after bromide) for ten penta through hepta PBDE congeners in their ECNI-Isobutane mass spectra, but for only three hexa and hepta PBDE congeners in their ECNI-CH_4 mass spectra. On average, molecular or high mass fragment ions were 20% more abundant in ECNI-Isobutane mass spectra than in ECNI-CH_4 mass spectra. However, during 12 hours of isobutane use as a reagent gas, the MS sensitivity steadily decreased to 50% of the sensitivity prior to isobutane use (as measured by ion abundance of the source calibrant, PFDTD). Upon removal, the source was observed to be fouled, and required cleaning. Use of Isobutane as a reagent gas was discontinued and no further optimization experiments were conducted.

2.4.3 ECNI Optimization.

Figure 3 shows that optimizing for PBDE high mass fragment ($[M\text{-}xH\text{-}yBr]^-$) ion led to different optimum ECNI source temperatures than optimizing for bromide ($[Br]^-$) ion. Of the ECNI source parameters investigated, high mass fragment ion was most sensitive to electron energy, followed by system pressure, source temperature, and emission current respectively. Of the source parameters investigated, bromide ions were most sensitive to electron energy followed by system pressure, emission current, and source temperature respectively. Source temperatures yielding the largest abundances of high mass fragment ions (125 °C) were significantly different from the temperatures yielding maximum bromide ions' abundances (250 °C). The relative high mass fragment ion abundance for each congener decreased as a function of increasing ECNI source temperature, while the relative bromide ions' abundances increased with increasing source temperature. This trend for bromide ions is in accordance with previous work(*35*). These opposite trends for bromide and high mass fragment ion abundances were unique to source temperature. Optimization experiments of ECNI electron energy and emission current resulted in statistically significant positive linear correlations with abundance of both bromide and high mass fragment ions (least squares, $p<0.01$) (Figure 2.3). ECNI system pressure showed a negative quadratic correlation with both relative bromide and relative high mass fragment ions' abundances (least squares, $p<0.01$), as seen in Figure 2.3. However, optimal ECNI source temperature and system pressure values (experimental value with largest sum of all congeners' relative response) for high mass fragment ion abundance calculated from this work (~150 °C and ~2.5×10^{-4} torr, respectively) were different than previously reported optimal values for bromide ions' abundance (~250 °C and ~2.7×10^{-4} torr)(*35*). The optimal ECNI source temperature and system pressure values for the bromide ions' abundances calculated from this work (~250 °C and ~3×10^{-4} torr) matched closely with previously reported optimum values(*35*). Optimal ECNI electron energy and emission current for high mass fragment ion abundance were the same as the optimal values for bromide ions' abundances (~200 eV and ~225 μA respectively). Optimal values for ECNI electron energy and emission current have not been previously reported.

For all ECNI source parameters, we observed that congener-to-congener variability in high mass fragment ion response was much larger than variability in bromide ions' responses (Figure 3). This can be seen by the larger range in the different congeners' high mass fragment ion profiles as compared to bromide ions' profiles in Figure 2.3. However, this large variability in high mass fragment ion response (as high as 157% relative abundance) is not due to run-to-run variation. Run to run variability (% RSD) of relative fragment ion abundance at the initial ECNI source parameter settings (source temperature of 150 °C, system pressure of 2.1×10^{-4} torr, electron energy of 125 eV, emission current of 150μA) was calculated to be less than 10% for every congener, with an average of 5.6% for high mass fragment ions and 3.5% for bromide ions. For each ECNI source parameter investigated, at least 25 of the 39 individual PBDE congeners' ion abundances (both bromide and high mass fragment ions), at optimum parameter values, were significantly larger than adjacent parameter values (one sided t-test $p<0.05$). In addition, the average PBDE ion abundances (both bromide and high mass fragment ions), at optimum parameter values, were significantly larger than average PBDE ion abundances adjacent parameter values (one sided t-test $p<0.05$), suggesting that the range of high mass fragment ion responses observed in the different congeners was likely due to congener to congener differences in high mass fragment ion response profiles, not random variation.

Because other ECNI source and instrumental parameters were held constant during the randomized experiment, each source parameter's influence on ion abundance is not due to covariance of the parameters. Although experiments were not conducted to measure the interaction between the different parameters and their effects on individual PBDE congeners' high mass fragment ion abundance, we assumed that the different parameters likely had an additive effect on the average PBDE high mass ion abundances. This additive assumption was tested by comparing our observed increases in relative ion abundance, (using all the optimum parameter values), to increases predicted from the sum of the individual source parameter optimization experiments. Although relative (%) increases in absolute high mass fragment ion abundance were substantial, (as high as 16,700 % increase) absolute increases in relative abundances were used to test additivity since relative abundances were used to optimize parameters. Baseline ECNI source parameter values were taken from previous work optimizing bromide ions (~250 °C and ~2.7×10^{-4} torr)(*35*). Where parameters were not reported in the literature, the most recent source tune values were used (electron energy of 125 eV, and emission current of 150 μA). The average congener specific observed increase in the relative high mass fragment ion abundance was found to exceed the predicted additive-model increase by 127%. However, this difference between the predicted and observed changes in the relative high mass fragment ion abundance ranged from -367% (BDE #153) to 2672% (BDE #71) of expected changes. As a chemical class, the observed increase in the mean relative high mass fragment ion abundance matched the mean expected relative abundance increase to within 8%, indicating individual source parameters effect's were additive for the PBDE class of compounds, if not for specific PBDE congeners. This is consistent with previous work which suggests that some ECNI source parameters can have interactive effects on some decomposition ion's abundances for similar halogenated aromatics(*43*).

2.4.4 EI Optimization.

As shown in Figure 2.4A, and B, EI source temperature and electron energy showed a positive trend with average relative molecular ($[M]^{+\bullet}$) and high mass fragment ion ($[M\text{-}yBr]^{+}$) abundance. However, EI source emission current showed a negative trend (Figure 4C) with average relative molecular and high mass fragment ion abundances. All EI parameters investigated showed statistically significant linear correlations with both individual congener's and mean PBDE molecular and high mass fragment ion abundances ($p<0.0001$). Electron energy had the largest effect on PBDE molecular and high mass fragment ion abundances, followed by source temperature, and emission current, respectively. In addition, trends in EI source temperature's and emission current's effects on molecular and high mass fragment ion abundances (Figure 2.4A and C) were opposite of their effects in ECNI (Figure 2.3A and D). However, a direct comparison between ECNI and EI emission current is difficult because different ranges of values were investigated (Figures 2.4C and 2.3D and Table 2.2) due to different auto-tune starting positions and source calibrants.

Optimal EI source parameter values for electron energy, source temperature, and emission current within the range accessible on this HP 5973N MSD were determined to be 70 eV, 250 °C, and 27 μA, respectively. Only an optimum EI electron energy (35 eV) and source temperature (250 °C) have been previously reported(*35*). Our optimum EI electron energy value was significantly different than previous work because this study optimized only for molecular and high mass fragment ions (Table 2.1) instead of total ion chromatogram(*35*). Trends in molecular and high mass fragment ions with EI source parameters were not compared to previous work due to these differences in ions optimized(*35*).

Because there was no previous baseline (no optimum EI emission current was previously reported for PBDEs molecular or high mass fragment ions) with which to compare this study's combination of optimum EI source parameters, we did not test for additivity or interactivity of the EI source parameters(*35*). Similar to the variability observed with high mass fragment ions in ECNI, variability in EI molecular and high mass fragment ion abundances between different parameter values was much higher (as high as 90% relative abundance) than average run-to-run variability (7.3%) of a single congener (Figure 2.4). In addition, as with ECNI, at least 25 of the 39 congeners' abundances at optimal EI source parameter values were statistically significantly different than their abundances at all adjacent source parameter values. On average, run-to-run variability was slightly greater (7.3%) for EI high mass fragment ion abundance than in ECNI (5.6%).

2.4.5 Method Performance.

The limits of detection (LOD), by congener, and the linear range of the 39 PBDEs studied are listed in Table 2.3 and compared against previous optimization work(*35*) for the three investigated quantitation methods: EI high mass fragment ion ($[M\text{-}yBr]^{+}$), ECNI high mass fragment ion ($[M\text{-}xH\text{-}yBr]^{-}$), and ECNI bromide ($[Br]^{-}$) ion. Quantitating on the bromide ions using ECNI resulted in the best sensitivity, with a mean LOD of 192 fg, followed by ECNI high mass fragment ion at 1240 fg, and EI high mass fragment ion at 2.01 pg (Table 2.3). A general trend of decreasing LOD with increasing level of bromination was observed for all ECNI methods, including previous work ($p<0.015$)(*35*). This trend was not observed in EI. Compared with previous work, the mean EI LODs of our optimized method were statistically significantly lower (paired t-test, one sided $p<0.0001$), and our mean ECNI bromide method LODs were slightly higher than previous studies (paired t-test, one sided $p<0.015$)(*35*) (see Table 2.3). Although the mean LOD for our ECNI high mass fragment ion method (122 fg) was slightly higher than the previous ECNI bromide method (89 fg), the LODs for 14 of the 39 PBDE congeners, using our method, were equal to, or lower than previous ECNI bromide methods (Table 2.3)(*35*). Most importantly, the LODs of our optimized ECNI method quantitating on the high mass fragment ion were not statistically significantly different from previous work which optimized for, and quantitated on the bromide ions (paired t-test, one sided

$p<0.407$)(*35*). This demonstrates that the ECNI source parameter optimization performed in this study allowed us to quantitate on highly specific, stable isotope dilution compatible, PBDE high mass fragment ions, while maintaining the sensitivity of previous ECNI methods which quantitated on the bromide ion(*35*). This is likely due to decreases in instrument noise associated with switching from quantitating on the low m/z bromide ions to quantitating on the high m/z high mass fragment ions, as well as increases in high mass fragment signal from previously unexplored optimizations of ECNI source parameters. Seven mono-tri BDE congeners had lower LODs with our optimized EI method than our optimized ECNI high mass fragment ion method. This was caused by lower high mass fragment ion abundance in the ECNI spectra of these lower brominated BDE congeners. Finally, each quantitation method was shown to be linear ($R^2 \geq 0.95$, $p<0.01$) over almost 3 orders of magnitude (Table 2.3). Our optimized isotope dilution GC-ECNI/LRMS method, quantitating on a high mass fragment ion, is the preferable LRMS method because of its selectivity and sensitivity.

The suitability of the optimized ECNI/LRMS high mass fragment ion method for isotope dilution analysis is demonstrated in Figure 2.5 where the selected ion chromatograms of three native and one stable isotope labeled hepta PBDE congeners are shown. The enhanced sensitivity of the optimized method can be seen in the abundance of the high mass fragment ions (m/z 481.7 and 493.7), which are approximately ~25% of bromide (m/z 78.9, 80.9). The enhanced selectivity of this optimized method can be seen in the co-elution and mass discrimination of the native and $^{13}C_{12}$ labeled hepta BDE #181.

Our optimized GC-ECNI/LRMS method shows that GC-ECNI/LRMS instruments can be used for reliable quantitation of 39 PBDE congeners with low pg to fg instrumental LODs while using $^{13}C_{12}$ PBDEs for isotope dilution analysis. By optimizing high mass fragment ion abundance over a wide range of ECNI source parameters and values, we report instrumental LODs for the selective PBDE high mass fragment ions comparable to LRMS methods quantitating on the bromide ion, as well as the ability to use $^{13}C_{12}$ PBDE standards for reliable isotope dilution quantitation in complex environmental samples.

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Table 2.1. PBDE congeners, Retention Times, Quantitation Ions, m/z, Surrogates, and SIM Windows. Br- ions (m/z 78.9 & 80.9), monitored (ECNI) for all congeners, are not listed.

BDE congener	R.T. (min)	ECNI Ion	m/z	EI Ion	m/z	surrogate standard	R.T. (min)	ECNI m/z	EI m/z
				SIM Window 1					
mono #1	8.48	$[M - Br]^{-}$	169.1	$[M]^{+\bullet}$	248.0	mono ^{13}C #3	9.44	180.9	259.9
mono #2	8.94	$[M - Br]^{-}$	169.1	$[M]^{+\bullet}$	248.0	mono ^{13}C #3	9.44	180.9	259.9
mono #3	9.44	$[M - Br]^{-}$	169.1	$[M]^{+\bullet}$	248.0	mono ^{13}C #3	9.44	180.9	259.9
				SIM Window 2					
di #10	15.72	$[M - Br]^{-}$	247.0	$[M - Br_2]^{+\bullet}$	168.1	di ^{13}C #15	21.81	258.8	339.8
di #7	18.36	$[M - Br]^{-}$	247.0	$[M - Br_2]^{+\bullet}$	168.1	di ^{13}C #15	21.81	258.8	339.8
di #11	19.75	$[M - Br]^{-}$	247.0	$[M - Br_2]^{+\bullet}$	168.1	di ^{13}C #15	21.81	258.8	339.8
di #8	19.76	$[M - Br]^{-}$	247.0	$[M - Br_2]^{+\bullet}$	168.1	di ^{13}C #15	21.81	258.8	339.8
di #12	20.48	$[M - Br]^{-}$	247.0	$[M - Br_2]^{+\bullet}$	168.1	di ^{13}C #15	21.81	258.8	339.8
di #13	20.77	$[M - Br]^{-}$	247.0	$[M]^{+\bullet}$	327.9	di ^{13}C #15	21.81	258.8	339.8
di #15	21.81	$[M - Br]^{-}$	247.0	$[M]^{+\bullet}$	327.9	di ^{13}C #15	21.81	258.8	339.8
				SIM Window 3					
tri #30	26.38	$[M - Br]^{-}$	326.9	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #32	29.89	$[M - Br]^{-}$	326.9	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #17	30.77	$[M - Br]^{-}$	326.9	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #25	31.19	$[M - Br]^{-}$	326.9	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #28	32.39	$[M - Br]^{-}$	326.9	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #33	32.59	-	-	$[M - Br_2]^{+\bullet}$	248.0	tri ^{13}C #28	32.39	338.8	259.8
tri #35	33.52	$[M - Br]^{-}$	326.9	$[M]^{+\bullet}$	407.8	tri ^{13}C #28	32.39	338.8	259.8
tri #37	34.60	$[M - Br]^{-}$	326.9	$[M]^{+\bullet}$	407.8	tri ^{13}C #28	32.39	338.8	259.8
				SIM Window 4					
tetra #75	39.28	$[M - HBr_2]^{-}$	324.9	$[M - Br_2]^{+\bullet}$	325.9	tetra ^{13}C #47	41.21	336.7	337.8
tetra #49	40.04	$[M - HBr_2]^{-}$	324.9	$[M - Br_2]^{+\bullet}$	325.9	tetra ^{13}C #47	41.21	336.7	337.8
tetra #71	40.27	$[M - HBr_2]^{-}$	324.9	$[M - Br_2]^{+\bullet}$	325.9	tetra ^{13}C #47	41.21	336.7	337.8
tetra #47	41.21	$[M - HBr_2]^{-}$	324.9	$[M - Br_2]^{+\bullet}$	325.9	tetra ^{13}C #47	41.21	336.7	337.8
tetra #66	42.43	$[M - HBr_2]^{-}$	324.9	$[M - Br_2]^{+\bullet}$	325.9	tetra ^{13}C #47	41.21	336.7	337.8
tetra #77	44.15	$[M - HBr_2]^{-}$	324.9	$[M]^{+\bullet}$	485.7	tetra ^{13}C #47	41.21	336.7	337.8
				SIM Window 5					
penta #100	46.29	$[M - HBr_2]^{-}$	402.8	$[M - Br_2]^{+\bullet}$	405.8	penta ^{13}C #100	46.29	414.7	417.7
penta #119	46.92	$[M - HBr_2]^{-}$	402.8	$[M - Br_2]^{+\bullet}$	405.8	penta ^{13}C #100	46.29	414.7	417.7
				SIM Window 6					
penta #99	47.77	$[M - HBr_2]^{-}$	402.8	$[M - Br_2]^{+\bullet}$	405.8	penta ^{13}C #99	47.77	414.7	417.7
penta #116	48.15	$[M]^{-\bullet}$	565.6	$[M - Br_2]^{+\bullet}$	405.8	penta ^{13}C #99	47.77	414.7	417.7
				SIM Window 7					
penta #118	48.91	$[M - Br]^{-}$	484.7	$[M - Br_2]^{+\bullet}$	405.8	penta ^{13}C #118	48.91	496.6	417.7
penta #85	49.94	$[M - HBr_2]^{-}$	402.8	$[M]^{+\bullet}$	565.6	penta ^{13}C #118	48.91	496.6	417.7
hexa #155	50.02	$[M]^{-\bullet}$	643.6	$[M]^{+\bullet}$	643.6	hexa ^{13}C #153	52.54	574.5	495.6
penta #126	50.50	$[M]^{-\bullet}$	565.6	$[M]^{+\bullet}$	565.6	penta ^{13}C #118	48.91	496.6	417.7
				SIM Window 8					
hexa #154	50.95	$[M - HBr]^{-\bullet}$	563.6	$[M - Br_2]^{+\bullet}$	483.7	hexa ^{13}C #153	52.54	574.5	495.6
hexa #153	52.54	$[M - Br]^{-}$	564.6	$[M - Br_2]^{+\bullet}$	483.7	hexa ^{13}C #153	52.54	574.5	495.6
hexa #138	54.33	$[M - HBr]^{-\bullet}$	563.6	$[M - Br_2]^{+\bullet}$	483.7	hexa ^{13}C #153	52.54	574.5	495.6
hexa #166	54.48	$[M - HBr]^{-\bullet}$	563.6	$[M - Br_2]^{+\bullet}$	483.7	hexa ^{13}C #153	52.54	574.5	495.6
				SIM Window 9					
hepta #183	56.33	$[M - Br_2]^{-\bullet}$	561.6	$[M - Br_2]^{+\bullet}$	563.6	hepta ^{13}C #183	56.33	573.5	575.5
hepta #181	58.77	$[M - HBr]^{-\bullet}$	641.5	$[M - Br_2]^{+\bullet}$	563.6	hepta ^{13}C #183	56.33	573.5	575.5
hepta #190	59.31	$[M - HBr]^{-\bullet}$	641.5	$[M - Br_2]^{+\bullet}$	563.6	hepta ^{13}C #183	56.33	573.5	575.5

Table 2.2. MS Source Parameters Optimized

Parameter	EI	ECNI
Source Temperature (°C)	150 - 250	150 - 250
Electron Energy (eV)	10 - 70	30 - 225
Emission Current (µA)	15 - 105	100 - 225
System Pressure (torr)	9.5×10^{-6}	$0.9 - 4.8\times10^{-4}$

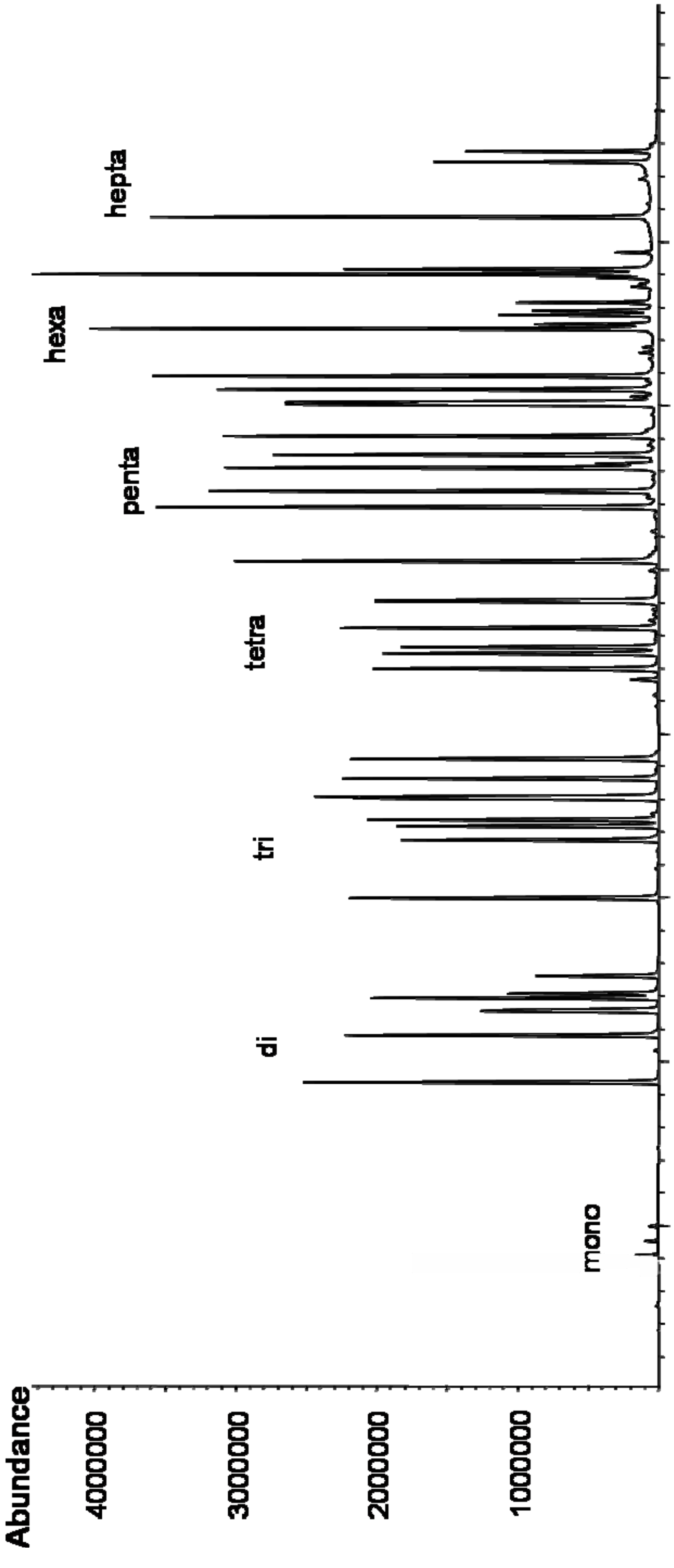

Figure 2.1. GC/ECNI-LRMS Multiple Selected Ion Chromatogram of 39 PBDE congeners (Table 2.1).

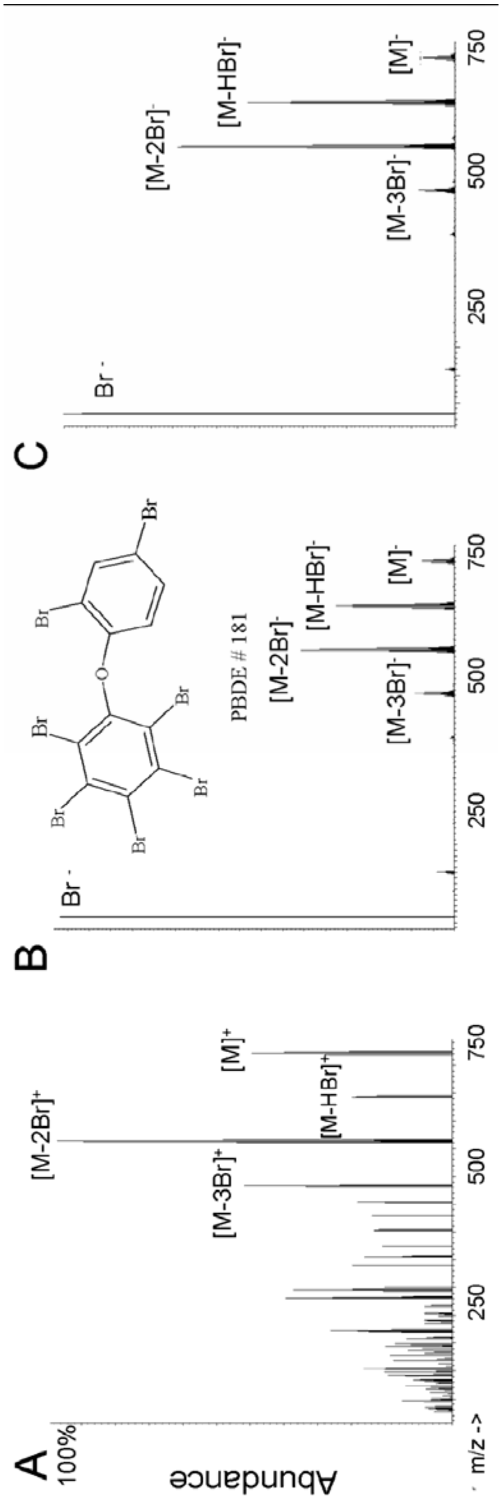

Figure 2.2. Mass Spectra of hepta PBDE #181 A - EI, B - ECNI(CH_4), & C - ECNI(Isobutane)

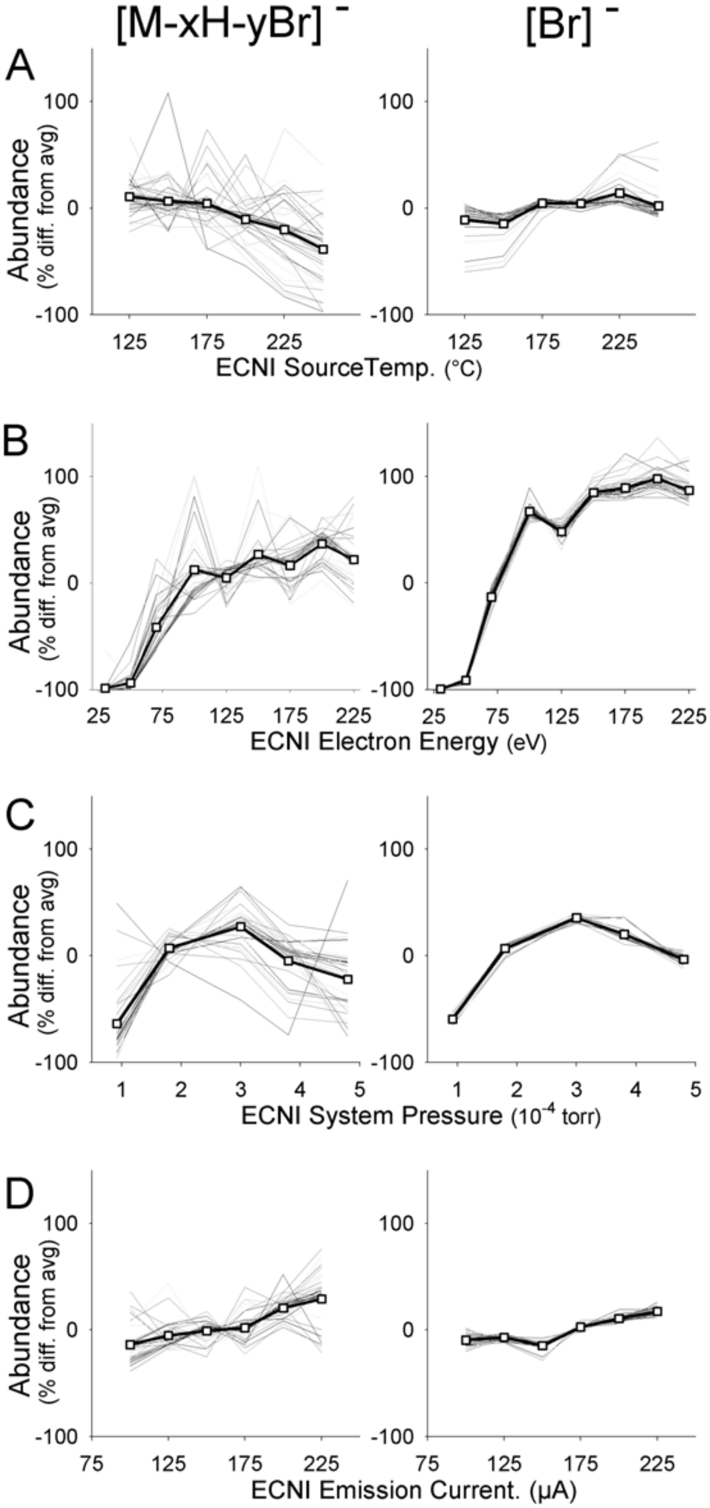

Figure 2.3. Profiles of ECNI Source Parameter Optimization for 39 PBDEs (–) and the average PBDE response (–□–) of high mass fragment ions [M-xH-yBr] ⁻ and bromide ions [Br] ⁻ to: A – Source Temperature; B – Electron Energy; C – System Pressure; and D – Emission Current.

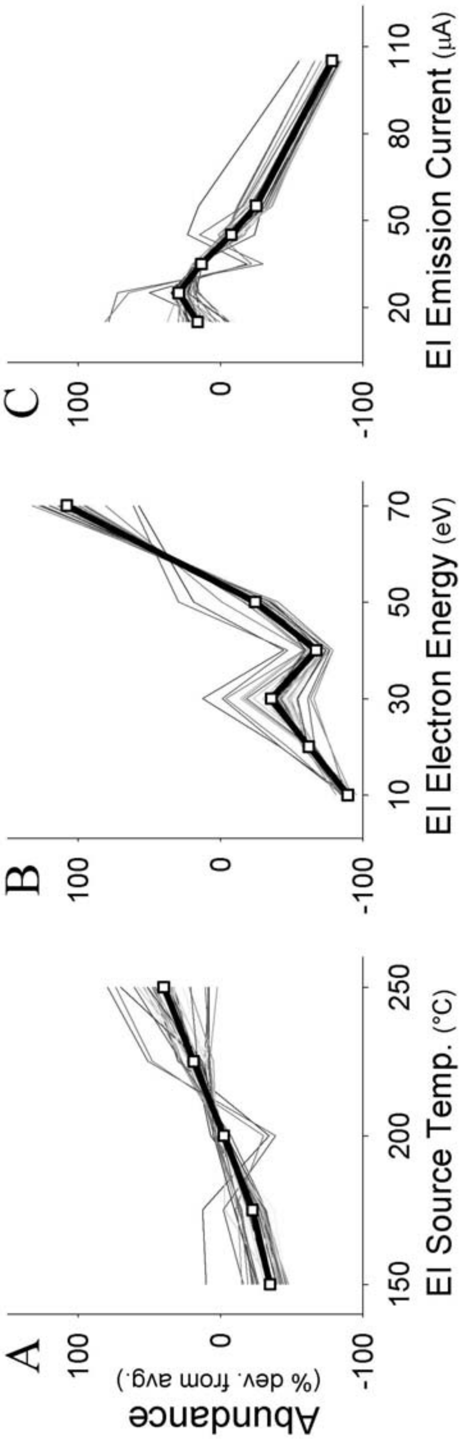

Figure 2.4. Profiles of EI source parameter optimization on 39 PBDEs (–) and their average response (–□–) using molecular [M] + • and high mass fragment ions [M-yBr] + to: A – Source Temperature; B – Electron Energy; and C – Emission Current.

Table 2.3. Limits of detection (fg), and linear range of 39 PBDE congeners using optimized GC-MS methods. ‘-’ – not applicable.

BDE congener	EI		ECNI		
	$[M-yBr]^+$	$[M-yBr]^+$	$[Br]^-$		$[M-xH-yBr]^-$
	This study	Ref.#35	This study	Ref.#35	This study
	fg	fg	fg	fg	fg
mono #1	715	860	793	528	3.7E+03
mono #2	1.0E+03	610	2.6E+03	1.1E+03	1.0E+04
mono #3	878	560	401	1.4E+03	1.2E+03
di #10	358	1.0E+03	33.4	64.0	735
di #7	554	1.2E+03	40.8	56.0	162
di #11	—	950	—	106	—
di #8/11	2.0E+04	—	179	—	334
di #8	—	1.3E+03	—	102	—
di #12	1.1E+03	—	44.3	—	4.9E+03
di #12/13	—	530	—	108	—
di #13	1.3E+03	—	221	—	1.4E+04
di #15	1.0E+03	860	21.0	163	1.1E+03
tri #30	4.4E+03	1.6E+03	28.1	89.0	34.4
tri #32	1.4E+03	2.1E+03	69.1	75.0	24.1
tri #17	1.7E+03	1.7E+03	92.8	86.0	122
tri #25	1.3E+03	2.3E+03	133	71.0	387
tri #28	2.9E+03	—	—	—	7.4E+03
tri #28/33	—	690	366	91.0	—
tri #33	1.0E+03	—	—	—	—
tri #35	2.1E+03	2.1E+03	7.42	66.0	29.5
tri #37	2.0E+03	1.8E+03	44.8	92.0	102
tetra #75	1.9E+03	1.5E+03	38.7	60.0	35.5
tetra #49	2.2E+03	2.8E+03	238	64.0	250
tetra #71	1.3E+03	2.3E+03	130	63.0	330
tetra #47	1.6E+03	2.0E+03	118	92.0	111
tetra #66	979	3.4E+03	98.3	89.0	272
tetra #77	1.2E+03	1.8E+03	87.7	74.0	339
penta #100	1.7E+03	4.3E+03	62.6	75.0	20.2
penta #119	1.5E+03	3.9E+03	28.5	69.0	27.1
penta #99	1.6E+03	6.6E+03	146	96.0	167
penta #116	1.3E+03	8.6E+03	7.46	80.0	17.7
penta #118	1.3E+03	—	42.3	—	153
penta #85	3.0E+03	1.2E+04	—	106	42.3
penta # 105	—	2.2E+04	—	118	—
hexa #155	1.7E+03	5.2E+03	—	—	93.3
penta #126	1.3E+03	1.7E+04	89.5	—	262
hexa #154	860	2.6E+03	28.8	99.0	17.6
hexa #153	732	4.8E+03	97.2	76.0	102
hexa # 140	—	4.0E+03	—	62.0	—
hexa #138	895	6.4E+03	181	89.0	203
hexa #166	704	8.2E+03	89.0	158	131
hepta #183	1.5E+03	1.4E+04	10.4	117	5.36
hepta #181	2.4E+03	2.9E+04	17.4	177	10.8
hepta #190	2.5E+03	3.2E+04	19.8	165	18.9
mean ± (s.d.)	1320 (779)	2290 (7710)	78 (487)	89 (301)	122 (1935)
Linear Range	500 - 1430x10^3		9 - 1430x10^3		5 - 1430x10^3

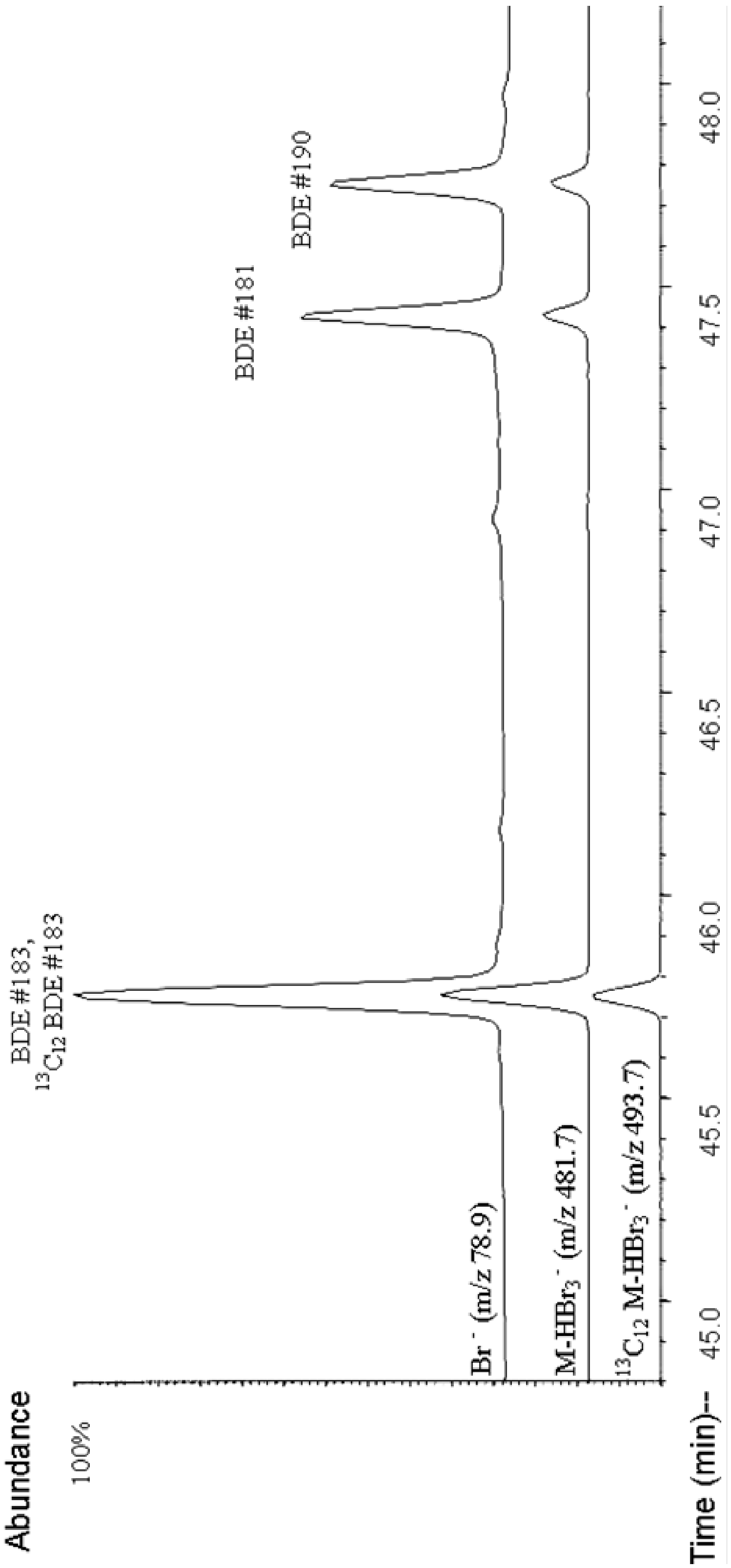

Figure 2.5. – Selected GC-ECNI/LRMS Ion Chromatograms for a mixture of Native (#183, 181, 190) and $^{13}C_{12}$ labeled (#183) hepta PBDEs.

Atmospherically Deposited PBDEs, Pesticides, PCBs and PAHs in Western US National Park Fish: Measurements, and Consumption Guidelines

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3. Atmospherically Deposited PBDEs, Pesticides, PCBs and PAHs in Western US National Park Fish: Measurements, and Consumption Guidelines

3.1 Abstract

An analytical method was developed and validated for the measurement of polybrominated diphenyl ethers, organochlorine, phosphate, sulfate, and nitro pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in fish. This broad range of analytea (log K_{ow} 2.6-9.4) was measured at concentrations <1ng/g (LODs of 0.2-990 pg/g, 70 analytes < 60 pg/g) in individual fish extracts. The method was efficient (average 61% recovery at 8 ng/g ww), reproducible (average 4.1 %RSD), and accurate (19 compounds within NIST SRM 1946 confidence intervals, average 8 % deviation, n=31). Concentrations of these compounds were measured in 136 fish from 14 remote lakes in 7 western US National Parks and compared to human health contaminant screening values calculated from EPA fish advisory guidelines. Of the 28 most frequently measured analytes, average concentrations in fish were highest for p,p'-DDE, followed by dieldrin (6.4 and 1.0 ng/g ww). ΣPBDEs were consistently measured in these Western US fish (1.6 ng/g ww) at concentrations higher than fish in Europe. Although lake average concentrations of most contaminants in fish were 1-6 orders of magnitude below screening values, average fish concentrations of dieldrin and/or p,p'-DDE exceeded human lifetime cancer screening values for subsistence fishers in 8 of 14 lakes. Lake average concentrations of contaminants in fish did not exceed health screening values for recreational fishers, however, concentrations of dieldrin in 12 individual fish from 5 of the 14 lakes exceeded lifetime cancer screening values for recreational fishers (in Glacier, Sequoia, and Rocky Mountain National Parks). These results indicate that atmospheric deposition of organic contaminants to high elevation ecosystems can result in fish concentrations relevant to human health.

3.2 Introduction

Chemical environmental fate and process studies benefit from the measurement of multiple contaminants with different sources and physical-chemical properties. The ratios of these different contaminants in a sample, as well as their relative distribution, can yield important clues about chemical transport and fate(*1*). Measurements of multiple contaminants in environmental samples aid in understanding mechanisms of chemical emission, distribution, transport, and degradation(*2,3*).

Fish often contain the highest concentrations of organic contaminants in aquatic ecosystems due to bioaccumulation and magnification(*4*). In addition, their relevance to benthic, pelagic, human, and ecosystem food webs make fish a good sample matrix for environmental fate and process studies.

To date, most multi-contaminant methods for fish have focused on similar classes of contaminants(*5,6*) or are used as food screening methods with high part-per-billion (ppb) detection limits(*7,8*). Multi-contaminant methods, with ppb detection limits, can fail to detect analytes in a large number of fish samples(*9,10*). In addition, few methods have been shown to quantify more than two classes of contaminants at concentrations <1 ng/g in fish (*11*). Because current and historic use pesticides and other contaminants are often estimated to be present at less than 1 ppb in fish tissues, analytical methods are needed to quantify contaminants in fish at concentrations <1 ng/g (*2,3,7,12*).

Organic contaminant measurements in environmental compartments such as snow(*13-15*), water(*16-19*), sediment(*20-22*), vegetation(*23,24*), and fish(*2,3,25-32*), have demonstrated that cold, high elevation ecosystems can selectively accumulate some semi-volatile and persistent organic contaminants(*16*). Semi-volatile contaminants, which tend to spend more time in the gas phase at warmer temperatures, can condense or be scavenged to the earth's surface, and magnified across elevational and temperature precipitation gradients(*14,33*). The lower temperatures, higher precipitation rates, and proximity of many US mountain ranges to agricultural activity has been shown to affect pesticide contaminant concentrations in annual snowpacks of remote US high elevation ecosystems(*15*). Although enhanced accumulation of contaminants in high elevation fish has been observed in European mountains(*2,3,25,28*) and the Canadian Rockies(*29*), there is very limited data on the accumulation of contaminants in high elevation fish across the US (*32*), and what, if any, risks these contaminants may pose.

The objectives of this research were to develop and validate an analytical method to measure PBDE, current and historic use pesticide, PCB, and PAH concentrations remote fish, to measure these 91 SOCs in 136 fish from 14 lakes of 7 US National Parks, and to assess if measured concentrations were relevant to human health.

3.3 Experimental

3.3.1 Chemicals

Chemical standards, in mixes and individually, were purchased from Cambridge Isotope Labs (CIL, Andover, MA), the US EPA repository, Chem Services Inc. (West Chester, PA), Restek (Bellefonte, PA), Sigma-Aldrich Corp. (St. Louis, MO), and AccuStandard (New Haven, CT). Isotopically labeled standards were purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada) or CIL (Andover, MA). All standards were stored at 4°C and remade as needed, or at least once a year to ensure stability. The organophosphate standards were stored separately from other chemical classes in ethyl acetate (EA) to minimize degradation. The target analytes measured by electron capture negative chemical ionization (ECNI) and their corresponding recovery surrogates and internal standards are listed in Table 3.1, while those measured with electron impact ionization (EI) have been listed previously (*34*).

3.3.2 Samples

Standard Reference Material (SRM) #1946, Lake Superior Lake Trout (1997), was purchased from the National Institute of standards and Technology (NIST) (Gaithersburg, MD) for method validation. 136 fish from 14 lakes in 7 U.S. National Parks and one National Preserve were caught with hook and line methods and/or gill-nets (Table 3.2, Figure 3.1). Fish were collected from lakes in Sequoia-Kings Canyon (SEKI), Rocky Mountain (ROMO), Mt Rainer (MORA), Olympic (OLYM), Glacier

(GLAC), Denali (DENA), and Gates of the Arctic (GAAR) National Parks, as well as Noatak National Preserve (NOAT). Upon capture, 100 μL of blood was removed, the fish euthanized, weighed, measured, and an immediate field dissection was performed with baked and solvent rinsed foil, scalpels, and forceps. Pathological slices (1 cm^3) of kidney, spleen, liver, gills, and gonads, as well as gut contents, were removed, and the carcass wrapped in solvent rinsed foil or aluminized poly-bags, double-bagged, and shipped to the laboratory on dry ice. Fifteen to twenty fish per lake were captured, dissected, and packaged as explained above, and following the results of age, histopathological, and hormone analysis, 10 fish of even age and sex distribution were selected for SOC analysis. Field blanks were obtained by exposing foil, bags, and scalpels to air and water in the same manner and time of sample collection. The samples were stored in a -25 °C freezer until analysis. During sample processing, a power failure lead one freezer's air temperature to reach 2.8 °C. 12 whole fish samples and homogenates of 6 samples were present in this freezer and showed varied signs of thawing. Two large samples' frozen homogenates, which had been split into multiple jars, had been split between the freezer that 'thawed', and another freezer, where power was maintained and temperatures remained at -25 °C. The 'thawed' and non-thawed aliquots of these two samples were analyzed in triplicate. There were no consistent or significant differences in analyte concentrations between the 'thawed' and non-thawed aliquots of either of these two samples ($p>0.05$).

3.3.3 Sample Preparation

Whole fish were prepared to assess predator's contaminant exposure, especially those that may not eat only muscle tissues. Whole fish were homogenized with liquid nitrogen in a stainless steel food processor (Robot Coupe USA, Jackson, MS) until fish particles of ~0.1 cm^3 or less were obtained. Frozen homogenate was transferred to cleaned jars, sealed, weighed and stored at -25 °C until extraction. Method blanks consisted of 150 g baked sodium sulfate, ground with the liquid nitrogen and spiked with recovery surrogates. Also, a subsample of fish homogenate was gravimetrically analyzed for moisture content by baking for 24 hrs at 105 °C and reweighing. Samples (~20 g ww, 1.8 g SRM) and method blanks were weighed, ground with sodium sulfate until free flowing, and transferred into 100mL stainless steel Accelerated Solvent Extractor (ASE) cells (Dionex, Sunnyvale, CA). Isotopically labeled recovery surrogates (12.5-150 ng) were distributed equally among the sample or blank cells. The samples were extracted with dichloromethane (DCM) (100 °C, 1500 psi, 2 cycles of 5 minutes, 150% flush volume). The extract was dried with sodium sulfate, and lipids measured gravimetrically in a 5 ml aliquot of the 250mL extract by allowing the solvent to evaporate and weighing the remaining non-volatile fatty residues. The main extract was concentrated to 0.5 mL (TurboVap II, Zymark, Hopkinton, MA) and exchanged to hexane. Polar interferences were removed from the extract with silica chromatography. Analytes were eluted from a 20g silica cartridge (MegaBondElut, Varian, Torrence, CA) with 125 mL solvent (25 ml hexane, 25 mL 65:35 hexane:DCM, 75mL 70:30DCM:hexane). The combined eluate was reduced, solvent exchanged to DCM, and analytes separated from high molecular weight interferences using gel permeation chromatography (EnviroGel, Waters, Milford, MA) with 19x150 and 30 mm EnviroGel columns, (10-100 Ǻ), operated at 5 mL/min) and a fraction collector, calibrated (corn oil and analyte standards) to collect distinct, large bio-molecule (first), and target analyte (second) fractions. The target fraction was reduced to 0.3 mL under nitrogen and spiked with 150 ng isotopically labeled internal standards. Method blank extracts were carried through the entire method with batches of 3 to 5 samples.

3.3.4 Analysis

Purified extracts were analyzed by gas chromatographic isotope dilution mass spectrometry (GC-ID/MS) on an Agilent 6890 GC coupled with an Agilent 5973N MSD, using selected ion monitoring mass. Both electron impact (EI) ionization and electron capture negative ionization (ECNI) modes were used. The contaminants monitored, their SIM windows, and characteristic ions, column characteristics and GC oven temperature program are listed previously for the EI analysis(*34*) and in Table 3.1 for ECNI analysis. The GC oven temperature program for ECNI analysis was modified as follows to permit quantitation of PBDEs: 120 °C for 1 min, ramped at 4

°C/min to 275 °C, ramp 6 °C to 320, held 6.75 min for a total runtime of 54 minutes. Internal standard calibration curves (5+ points, r^2 >0.98) were prepared from standard solutions, ranging from 2.5 fg/uL to 5 ng/uL. Quality assurance and control procedures were followed and included frequent (≥10% each) calibration checks, blanks, duplicate injections and SRMs. Target analytes were identified only when a peak with > 3:1 signal to noise was observed for all three characteristic ions within 0.01 min or one scan of each other, retention time matched the standard within 0.05 min, and the relative response of characteristic ions was within 20% of the standard. Measured values were eliminated from the dataset if method blanks' concentrations exceeded 33% of the measured concentration in the sample. Method quantitation limits were set as the lowest point on the calibration curve for each analyte, normalized to each sample's mass extracted. Although variable, method quantitation limits on average were 4.3 times higher than method detection limits. All reported concentrations reported were method and/or field blank subtracted (whichever was higher), and surrogate recovery corrected.

3.3.5 Method Detection Limits

Estimated method detection limits (EDLs) were calculated for three representative fish samples (Lake Trout, Brook Trout, and Rainbow Trout) collected from remote lakes in Denali, Sequoia and Rocky Mountain National Parks. The procedure described in EPA Method 8280A was used to calculate EDLs(*35*). The height of noise in an analytes ion signal in a representative fish extract was compared to the target analyte peak heights in the lowest level calibration solutions to estimate a concentration at which a target analyte's peak height would be at least 3 times the height of the noise. This was repeated for three fish samples spanning species, age and lake to assess the consistency of the estimation method.

3.3.6 Method Recoveries

A lake trout sample from Wonder Lake in Denali NP was selected for method recovery experiments due to its representative fat content (10%), relatively low concentrations of the target analytes, and sufficient sample mass to permit multiple analyses. Three 20g aliquots of the homogenized fish were first analyzed according to the method described above to measure background concentrations of target analytes in the fish. Then ~8 ng/g ww of target analytes were spiked into three additional aliquots of the fish homogenate prior to extraction. These three aliquots were processed according to the analytical method and the final extracts were spiked with recovery surrogates and internal standards just prior to GC/MS analysis. The concentrations of target analytes in the three spiked aliquots were method blank and background concentration subtracted. The analyte background concentrations in the fish, prior to fortification, were less than 5% of the recovered amount, except for BDE 47 in which the method blank and background concentration totaled 16%.

3.3.7 Method Reproducability & Accuracy

Method precision and accuracy was assessed using five aliquots of ~1.8g of NIST SRM 1946, analyzed over a 4 month period of time. Less fish tissue mass was analyzed for the SRM than in the National Park fish because of higher target analyte concentrations in the SRM. The average analyte concentrations measured in NIST SRM 1946 aliquots were compared to certified values for 30 comparable analytes.

3.3.8 Fish Contaminant Screening Values

Fish contaminant screening values for health risks associated with fish consumption were calculated for recreational and subsistence fishers in accordance with EPA guidance(*35*) due to the relatively complete toxicological database(*36*) and uniformity of EPA risk methodology. Calculated screening values were compared to the measured concentrations in western national park fish. A formal human health risk assessment was not conducted due to numerous and poorly defined target populations. Cancer and non-cancer chronic health screening values were calculated for frequently detected contaminants from cancer slope factors and reference dose data in EPA's IRIS database. We used EPA default consumption rates of 17.5 g, and 142 g of fish per day for recreational and subsistence fishers, respectively(*35*) to estimate individual contaminant concentrations in fish tissue sufficient to exceed lifetime contaminant consumption limits for humans. These calculations assume a 70 kg individual, a 1 in 100,000 acceptable lifetime excess cancer risk. Screening values for recreation fishers were adjusted to account for the whole fish contaminant concentration measurements made here by increasing the screening value by 32%, which is equivalent to the 32% reduction from whole fish contaminant exposure estimated to be achieved by recreational fishers due to trimming and cooking(*35*). Subsistence fisher screening values were not adjusted for whole fish contaminant concentrations since consumption patterns are highly variable and often include the whole fish (soups, stews, etc.)(*35,37*).

3.4 Results and Discussion

3.4.1 Chromotography/Blanks

This analytical method resulted in fish extract chromatograms with baseline separation of a large majority of the target analytes (Figure 3.2). In the few cases where baseline separation wasn’t achieved, mass-spectral separation was achieved. Sample cleanup procedures were sufficient and rolling or high chromatographic baselines were not observed for samples, spikes, SRMs or blanks. Most analytes were not detected in method or field blanks or measured concentrations were below the quantitation limit (lowest calibration point). However, phenanthrene, BDE 47, and BDE 99 were measured in most method blanks with variable concentrations corresponding, on average, to 300, 14, and 30 pg/g in a 20 g sample, respectively. In all cases, if an analyte’s concentration in the blank exceeded 33% of the sample’s concentration, the measured concentration was discarded. Analyte concentrations in the method blanks were less than 5% of sample concentrations for all method recovery and SRM experiments.

3.4.2 Method Detection Limits

Estimated method detection limits (MDL) ranged from 0.2 to 900 pg/g ww, with a median of 18 pg/g ww. Estimated MDLs were fairly consistent across the three samples, with an average 11 %RSD (Table 3.3). With the exception of seven PBDES and endrin, every target analyte had an EDL of less than 100 pg/g ww (Table 3.3). There were no statistically significant correlations between method detection limits and analyte physical chemical properties such as vapor pressure, log K_{ow}, Henrys Law

Constant (K_h), or molecular surface area, suggesting method detection limits were driven by GC/MS signal to noise ratios, not sample preparation.

3.4.3 Method Recovery Experiments

Analyte recovery over the entire method ranged from 31.4 to 98.3%, with an average recovery of 61.4% at target concentrations of 8 ng/g ww, an environmentally relevant tissue concentration (Table 3.3). Analyte recoveries were reproducible, with an average standard deviation of 4.1% (Table 3.3). The comparison of target analytes' recovery to the recovery of their respective surrogates revealed that target analyte and surrogate recoveries differed by less than 12% on average, indicating the general suitability of most recovery surrogates to represent their respective target analytes' method recoveries. Analyte recoveries showed no statistically significant correlation with log K_{ow}, K_h, molecular surface area, or photo-oxidation half-life. However, there was a weak negative correlation ($r^2 = 0.32$ $p=0.1$) with analyte vapor pressure, suggesting that extract blowdown might have systematically contributed to the loss of some analytes.

3.4.4 SRM Method Validation

Measured concentrations of 19 of 31 comparable analytes with certified concentrations in NIST SRM 1946 were measured within the NIST confidence intervals. The concentrations of all 31 certified analytes averaged within 7% and ranged less than 30% deviation from NIST certified values (Table 3.3). Additionally, 7 contaminants not previously reported in SRM 1946 (b-HCH, heptachlor, endrin, dacthal, endosulfan I, endosulfan sulfate, BDE 155), and one analyte previously reported(*38*) but not certified (BDE 183), were quantitated and are reported here (Table 3.3). The measurement of lower log K_{ow} compounds such as dacthal, endosulfan I, and endosulfan sulfate, as well as higher log K_{ow} compounds such as BDE 183 in SRM 1946, demonstrates the utility of this analytical method for measuring a broad range of analytes, at low concentrations, in fish samples.

3.4.5 SOCs in National Park Fish

The most concentrated and frequently measured contaminants in western national park fish were p,p'-DDE, dieldrin, dacthal, BDE 47, 99, and endosulfan sulfate, respectively (Figure 3.3). In general, current use pesticide concentrations were highest in Sequoia, Rocky Mountain, and Oldman Lake in Glacier, and lower in Olympic and the Alaskan park fish (Figure 3.3). Alaskan park fish had historic use pesticide concentrations comparable to most fish from contiguous US western parks. The variation in the fish contaminant concentrations within lakes was almost as large as the variation in concentrations between most lakes (Figure 3.3). A majority of the 91 analytes are not shown here because they were detected in less than 1/3 of all fish samples. All PAHs were infrequently detected, likely due to their rapid transformation and or elimination in fish(*39,40*).

When compared to similar high elevation lakes throughout Europe, PBDE concentrations measured in western US national park fish were, on average, 4 times higher in concentration(*41*)(Table 3.4). Fish from US national parks were 3-6 times lower in concentration than European mountain fish(*2*) for most historic use contaminants such as, DDTs, PCBs, and HCHs(Table 3.4). It should be noted that the PCB concentrations reported here likely underestimate total PCB concentrations since this study measured seven select PCB congeners (out of 209). A previous study in 1992 of contaminants in fish from Alaskan lakes near those measured here, showed comparable DDT, HCH, and PCB concentrations (2 times or less)(*12*). Fish HCH and chlordane concentrations in these previously measured Alaskan fish were 6 and 12 times higher in concentration(Table 3.4) (*12*). Fish from high elevation lakes in the Asian Tibetan Plateau(*31*) had comparable concentrations of DDTs and 3-10 times higher concentrations of HCB and HCHs compared to these US high elevation fish (Table 3.4).

Average concentrations of DDTs , dieldrin, and PBDEs were 3-8 times higher in these western US National Park fish than the anadromous, wild Pacific salmon, although individual concentrations overlapped (Table 3.4) (*42,43*). These differences in contaminant concentrations between fish from isolated high elevation western US National Park lakes, and wild Pacific salmon were likely not due to differences in lipid content, size, age, tissue sampled, trophic level, catch date, or methodology. A majority of the lake fish were 3-10 times leaner and smaller than the Pacific salmon(*44*), both of which would suggest lake bound fish would likely have much lower concentrations. A majority of lake bound fish were within 1-2 years of age of a typical ocean caught Pacific salmon(*45*), a difference unlikely to account for 3-8 fold concentration differences. Most lake bound fish are likely lower in trophic level than the Pacific salmon as high elevation lake food chains are often short(*26*) and gut contents revealed most lake fish to be omnivorous, suggesting lake fish would likely have lower contaminant concentrations. Tissues sampled, date of fish collection, or methodology likely do not account for contaminant differences since muscle and whole fish organic contaminant concentrations typically differ by less than 30%, most samples were collected within a 2.5 year period, and methods were similar, including the use of isotope dilution (*35,43*). Additionally, concentrations of PCBs, HCB, and HCHs were 2-8 times higher in the Pacific salmon(*42,43*)(Table 3.4). As a whole this suggests that DDTs, dieldrin, and PBDEs, in particular, are present at higher concentrations in aquatic ecosystems of western US high elevation lakes than the adjacent rivers and Northeast Pacific Ocean habitats of Pacific salmon.

3.4.6 Fish Consumption Screening Values

Just over half (77 of 136) of the individual fish from 11 of the 14 lakes had whole body concentrations exceeding the calculated subsistence fisher screening value for dieldrin and/or p,p'-DDE. Lake average dieldrin and/or p,p'-DDE fish concentrations exceeded the individual contaminant screening values for subsistence fishers in 8 of 14 lakes located in Sequoia, Rocky Mountain, and Glacier National Parks (Figure 3.3 C,D). Fish concentrations for the other 11 contaminants ranged 1 to 6 orders of magnitude below these screening values (Figure 3.3). Additive lifetime cancer risks from lake average fish contaminant concentrations exceeded the acceptable risk level in all but three lakes at the subsistence fisher consumption level (Olympic and Glacier National Parks).

Lake average concentrations in fish were below recreational fisher screening values for all 13 contaminants that were measured in >66% of samples and present in EPA IRIS toxicity database. However, lake average fish dieldrin concentrations in 4 of the 14 lakes were within a factor of 1.5 of the screening values, and concentrations of dieldrin in 13 individual fish exceeded the lifetime cancer screening value for recreational fishers (Figure 3.5, D). No other fish contaminant concentrations measured in western US national parks exceeded recreational fisher screening values, and the remaining contaminants' concentrations in fish ranged 1 to 7 orders of magnitude below these screening values (Figure 3.4). Additive cancer risks did not exceed acceptable risk thresholds at recreation fisher consumption levels for any of the 14 lakes average fish.

Calculated screening values for subsistence fishers were about one order of magnitude lower than recreational fishers' due to higher estimated consumption rates and whole fish consumption/exposure methods (stews, soups, etc)(*35,37*). It should be noted that the likelihood of the above risks being realized at these sites is limited by the remote locations, limiting the number of people exposed and their duration of exposure. Also, the confidence in the cancer slope factor for dieldrin, has been classified as "low"(*36*), and there is some debate about the accuracy in use of upper-bound cancer slope factors and additive cancer risks employed in the EPA risk assessment methods(*46*). On balance, the risk methodology does not fully include potential interactions (beyond cancer additivity) in the multiple contaminants present, but remains the sole health based consumption advice that uniformly treats lifetime health risk due to contaminants from fish consumption. Separately, these risk calculations did not characterize nutritional or health benefits potentially associated with salmonid consumption that may balance risks, such as increased omega-3 fatty acid consumption or potential dietary reduction in unhealthy fats.

This multi-contaminant method was validated for the measurement of a broad range of atmospheric contaminants in fish. The method was shown to be efficient, sensitive, and accurate at the part per trillion concentration level. The application of this method to measure contaminants in fish from remote western US national park lakes identified several current use contaminants, such as dacthal, endosulfans, and PBDEs, as ubiquitous and important atmospheric contaminants. Contaminant concentrations in western US national park fish were higher for PBDEs, but lower or comparable in concentration for most historic pesticides, when compared to similar

European fish or Pacific ocean wild salmon. Lake average fish concentrations of dieldrin and/or p,p'-DDE in Rocky Mountain, Sequoia, and Glacier National Parks exceeded lifetime cancer screening values for subsistence fish consumption. These results indicate that atmospheric deposition to high elevation ecosystems and food web magnification can result in contaminant concentrations in fish relevant to human health.

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Table 3.1 - ECNI Target Analytes, Surrogates, Internal Standards, & SIM Windows

Electron Capture Negative Ionization

Analytes, & Surrogates	Surrogate for Quantitation	Internal Standard for Quantitation	Retention Time (min)	Quantiation Ion m/z	Confirmation Ion m/z	2nd Confirmation Ion m/z
SIM Window 1						
d_{14} Trifluralin		$^{13}C_{12}$ PCB 138	13.69	349.2	350.2	319.2
Trifluralin	d_{14} Trifluralin		13.90	335.1	336.1	305.1
SIM Window 2						
HCH, alpha	d_6 gamma-HCH		14.61	71.0	73.0	70.0
$^{13}C_6$-HCB		$^{13}C_{12}$ PCB 138	14.69	291.8	293.8	289.9
HCB	$^{13}C_6$ HCB		14.70	283.8	285.8	281.8
SIM Window 3						
HCH, beta	d_6 gamma-HCH		15.94	71.0	73.0	70.0
d_6 gamma-HCH		$^{13}C_{12}$ PCB 138	16.01	72.0	74.0	263.0
HCH, gamma	d_6 gamma-HCH		16.19	71.0	73.0	70.0
SIM Window 4						
HCH, delta	d_6 gamma-HCH		17.70	71.0	252.9	254.9
Triallate	d_6 gamma-HCH		17.72	160.0	161.1	104.1
SIM Window 5						
PBDE #10	$^{13}C_{12}$ PBDE 28		19.05	167.1	80.9	78.9
Metribuzin	d_6 gamma-HCH		19.15	198.1	199.1	184.1
Heptachlor	d_6 gamma-HCH		19.61	265.9	267.9	299.9
PBDE 7	$^{13}C_{12}$ PBDE 28		20.51	167.1	80.9	78.9
SIM Window 6						
Chlorpyrifos oxon	d_{10} Chlorpyrifos		21.14	297.0	298.0	299.0
d_{10} Chlorpyrifos		$^{13}C_{12}$ PCB 138	21.19	322.0	324.0	214.0
Aldrin	d_6 gamma-HCH		21.24	167.1	78.9	80.9
PBDE #8	$^{13}C_{12}$ PBDE 28		21.28	237.0	239.0	329.9
Chlorpyrifos	d_{10} Chlorpyrifos		21.37	313.0	315.0	214.0
SIM Window 7						
Dacthal	d_6 gamma-HCH		21.54	332.0	330.0	334.0
PBDE 12	$^{13}C_{12}$ PBDE 28		21.65	167.1	80.9	78.9
PBDE 13	$^{13}C_{12}$ PBDE 28		21.79	167.1	80.9	78.9
PBDE 15	$^{13}C_{12}$ PBDE 28		22.33	167.1	80.9	78.9
SIM Window 8						
Chlordane, oxy	d_4 Endosulfan I		23.12	423.9	425.9	351.9
Heptachlor epoxide	d_4 Endosulfan I		23.13	389.8	387.8	391.8
PCB 74	$^{13}C_{12}$ PCB 101		23.28	291.9	293.9	289.9
SIM Window 9						
Chlordane, trans	d_4 Endosulfan I		24.26	409.9	407.9	411.8
SIM Window 10						
PBDE 30	$^{13}C_{12}$ PBDE 28		24.67	246.9	80.9	78.9
$^{13}C_{12}$ PCB 101		$^{13}C_{12}$ PCB 138	24.68	337.9	335.9	339.9
PCB 101	$^{13}C_{12}$ PCB 101		24.69	325.9	327.9	323.9
d_4 Endosulfan I		$^{13}C_{12}$ PCB 138	24.72	377.9	375.9	373.9
Endosulfan I	d_4 Endosulfan I		24.82	403.9	371.9	369.9
Chlordane, cis	d_4 Endosulfan I		24.83	265.9	263.9	267.9
SIM Window 11						
Nonachlor, trans	d_4 Endosulfan I		24.98	443.8	445.8	441.8
SIM Window 12						
Dieldrin	d_4 Endosulfan I		26.07	345.9	347.9	379.9
PBDE 32	$^{13}C_{12}$ PBDE 28		26.56	246.9	80.9	78.9
SIM Window 13						
Endrin	d_4 Endosulfan II		27.03	345.9	347.9	379.9
PBDE 17	$^{13}C_{12}$ PBDE 28		27.15	246.9	80.9	78.9
PBDE 25	$^{13}C_{12}$ PBDE 28		27.20	246.9	80.9	78.9
SIM Window 14						
d_4 Endosulfan II		$^{13}C_{12}$ PCB 138	27.51	411.9	413.9	409.9
PCB 118	$^{13}C_{12}$ PCB 101		27.55	325.9	327.9	323.9
Endosulfan II	d_4 Endosulfan II		27.56	405.9	407.9	371.9

Analytes, & Surrogates	Surrogate for Quantitation	Internal Standard for Quantitation	Retention Time (min)	Quantiation Ion m/z	Confirmation Ion m/z	2nd Confirmation Ion m/z
SIM Window 15						
Nonachlor, cis	d$_4$ Endosulfan II		27.79	443.8	445.8	441.8
$^{13}C_{12}$ PBDE 28		$^{13}C_{12}$ PCB 138	27.90	338.8	78.9	80.9
PBDE 28	$^{13}C_{12}$ PBDE 28		27.90	326.9	78.9	80.9
SIM Window 16						
Endrin aldehyde	d$_4$ Endosulfan II		28.24	379.9	381.9	345.9
PBDE 35	$^{13}C_{12}$ PBDE #28		28.42	326.9	78.9	80.9
PCB 153	$^{13}C_{12}$ PCB 180		28.48	359.9	361.9	357.9
PBDE 37	$^{13}C_{12}$ PBDE 28		29.02	326.9	78.9	80.9
SIM Window 17						
Endosulfan sulfate	d$_4$ Endosulfan II		29.33	385.9	387.9	421.8
PCB 138	$^{13}C_{12}$ PCB 180		29.65	360.0	362.0	358.0
$^{13}C_{12}$ PCB 138		Internal Standard	29.65	371.9	369.9	373.9
SIM Window 18						
PCB 187	$^{13}C_{12}$ PCB 180		30.29	393.9	359.9	397.9
PCB 183	$^{13}C_{12}$ PCB 180		30.54	393.9	359.9	397.9
PBDE 75	$^{13}C_{12}$ PBDE 47		31.72	324.9	78.9	80.9
SIM Window 19						
PBDE 49	$^{13}C_{12}$ PBDE 47		32.33	324.9	78.9	80.9
$^{13}C_{12}$ PCB 180		$^{13}C_{12}$ PCB 138	32.60	405.9	407.9	409.9
PBDE 47	$^{13}C_{12}$ PBDE 47		32.95	324.9	78.9	80.9
$^{13}C_{12}$ PBDE 47		$^{13}C_{12}$ PCB 138	32.95	336.7	78.9	80.9
SIM Window 20						
PBDE 66	$^{13}C_{12}$ PBDE 47		33.76	404.8	78.9	80.9
Mirex	$^{13}C_{12}$ PCB 180		34.10	367.8	369.8	403.8
PBDE 66	$^{13}C_{12}$ PBDE 47		35.10	325.9	78.9	80.9
SIM Window 21						
PBDE 100 L	$^{13}C_{12}$ PBDE 100		36.61	404.8	78.9	80.9
$^{13}C_{12}$ PBDE 100		$^{13}C_{12}$ PCB 138	36.61	416.7	78.9	80.9
PBDE 119			37.10	404.8	78.9	80.9
PBDE 99 L	$^{13}C_{12}$ PBDE 99		37.78	404.8	78.9	80.9
$^{13}C_{12}$ PBDE 99		$^{13}C_{12}$ PCB 138	37.79	416.7	78.9	80.9
PBDE 116	$^{13}C_{12}$ PBDE 99		38.21	404.8	78.9	80.9
SIM Window 22						
PBDE 118 L	$^{13}C_{12}$ PBDE 118		38.78	405.8	78.9	80.9
$^{13}C_{12}$ PBDE 118		$^{13}C_{12}$ PCB 138	38.78	417.7	78.9	80.9
SIM Window 23						
PBDE 85/155	$^{13}C_{12}$ PBDE 99		39.79	403.8	78.9	80.9
PBDE 155	$^{13}C_{12}$ PBDE 153		39.80	643.5	78.9	80.9
PBDE 126	$^{13}C_{12}$ PBDE 153		40.21	403.8	78.9	80.9
SIM Window 24						
PBDE 154	$^{13}C_{12}$ PBDE 153		40.63	482.7	78.9	80.9
PBDE 153 L	$^{13}C_{12}$ PBDE 153		42.08	403.8	78.9	80.9
$^{13}C_{12}$ PBDE 153		$^{13}C_{12}$ PCB 138	42.08	415.6	78.9	80.9
PBDE 138	$^{13}C_{12}$ PBDE 153		43.77	401.8	78.9	80.9
PBDE 166	$^{13}C_{12}$ PBDE 153		43.93	401.8	78.9	80.9
SIM Window 25						
PBDE 183 L	$^{13}C_{12}$ PBDE 183		45.51	481.7	78.9	80.9
$^{13}C_{12}$ PBDE 183		$^{13}C_{12}$ PCB 138	45.51	493.6	78.9	80.9
PBDE 181	$^{13}C_{12}$ PBDE 183		47.20	481.7	78.9	80.9

Table 3.2 Sampling Site Characteristics

Lake	US National Park	Latitude (dd)	Longitude (dd)	Elevation (m)	Fish Species	Date Sampled	n
Emerald	Sequoia-Kings Canyon	36.58	118.67	2810	brooktrout	08/24/03	10
Pear	Sequoia-Kings Canyon	36.60	118.67	2908	brooktrout	08/25/03	10
LonePine	Rocky Mountain	40.22	105.73	3018	brooktrout	09/13/03	10
Mills	Rocky Mountain	40.29	105.64	3030	rainbow trout	09/08/03	10
LP19	Mt. Rainier	46.82	121.89	1372	brooktrout	08/08/05	10
Golden	Mt. Rainier	46.89	121.90	1369	brooktrout	08/13/05	10
Hoh	Olympic	47.90	123.79	1379	brooktrout	09/08/05	10
PJ	Olympic	47.95	123.42	1384	brooktrout	09/13/05	10
Oldman	Glacier	48.50	113.46	2026	cutthroat trout	08/19/05	10
Snyder	Glacier	48.62	113.79	1597	cutthroat trout	08/23/05	10
McLeod	Denali	63.38	151.07	564	burbot, whitefish	08/10/04	4,2
Wonder	Denali	63.48	150.88	605	lake trout	08/12/04	10
Matcharak	Gates of the Arctic	67.75	156.21	502	lake trout	08/01/04	10
Burial	Noatak National Preserve	68.43	159.18	430	lake trout	08/02/04	10
						Total	136

Figure 3.1 – Map of National Parks Sampled

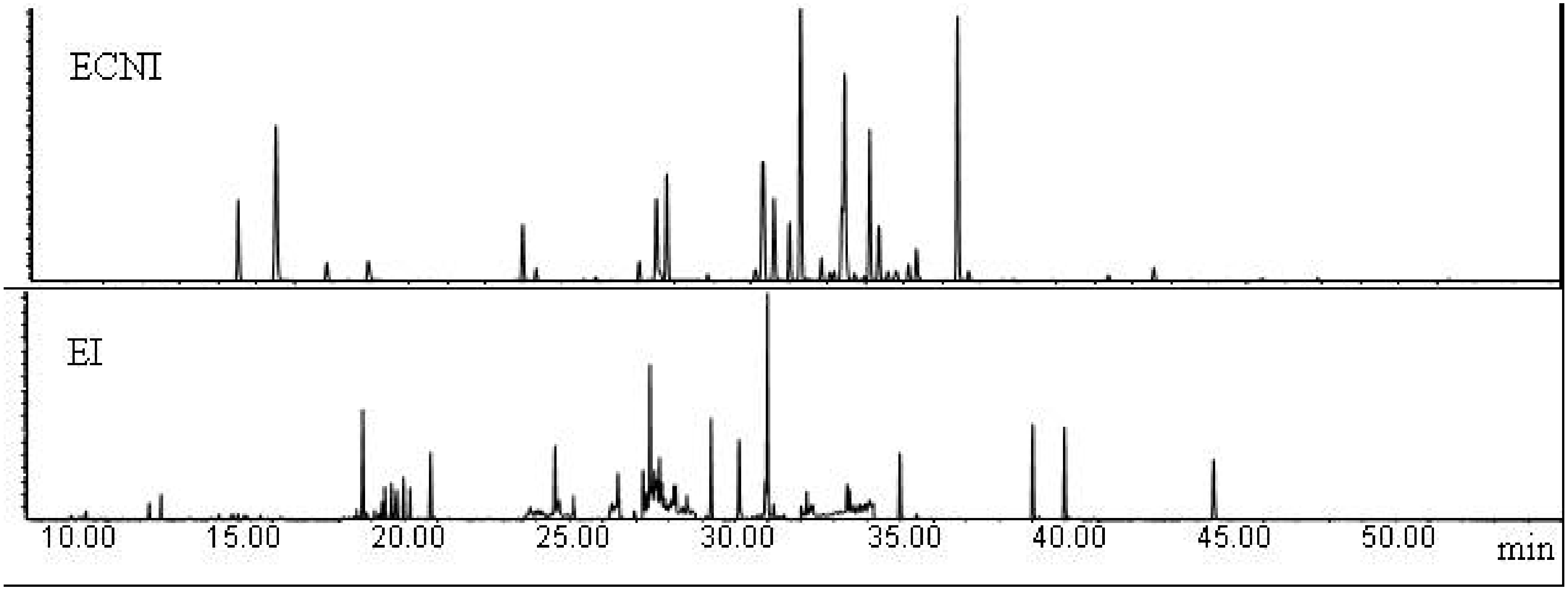

Figure 3.2 - Representative Final Fish Extract Selected Ion Chromatograms

Table 3.3 Fish analytical method recovery, estimated method detection limits, accuracy, and precision

Compounds	Log K_{ow}	Method Recovery[1] (%)		Estimated Method Detection Limit[2] (pg/g ww)		Determined Values for NIST SRM 1946 (ng/g ww)		Deviation from Certified Values[3] (%)
		Avg.	SD	Avg.	RSD %	Avg.	RSD %	% Diff
Organochlorines Pesticides & Metabolites								
HCH[4], gamma	3.8	38.2	1.6	17	7.5	1.0	46	0
HCH[4], alpha	3.8	37.6	1.6	0.2	8.1	5.4	6.5	0
HCH4, beta	4.0	44.3	1.7	7.8	1.7	0.46	34	
HCH4, delta	4.1	42.2	1.7	0.6	3.0			
Methoxychlor	4.5	62.1	1.8	99	73			
Heptachlor epoxide	4.6	33.6	2.0	14	2.2	5.3	1.1	0
Endrin	5.2	89.1	2.2	170	26	4.7	0.22	
Heptachlor	5.2	48.5	1.3	1.6	1.42	0.38	37	
Hexachlorobenzene	5.5	37.8	1.9	5.0	1.9	6.6	2.7	0
o,p'-DDE[5]	5.5	53.8	2.1	58	23	0.91	15	0
Chlordane, oxy	5.5	35.1	1.9	5.5	1.9	16	7.9	15
Dieldrin	5.5	95.3	3.6	8.4	21	34	4.8	0
Chlordane, cis	5.9	32.6	1.0	16	6.8	31	8.9	0
p,p'-DDD[6]	5.9	67.8	1.0	99	39	12	9.0	30
Nonachlor, trans	6.1	32.0	1.0	2.9	1.3	90	7.1	9.5
o,p'-DDD6	6.1	55.2	2.1	68	16	1.8	25	17
Chlordane, trans	6.1	31.4	1.0	1.6	0.96	9.7	66	16
Nonachlor, cis	6.4	40.3	1.5	5.0	1.0	49	5.9	16
Aldrin	6.5	39.4	1.6	21	3.5			
o,p'-DDT[7]	6.8	61.1	4.8	97	63	16	20	28
p,p'-DDE[5]	6.9	63.7	4.7	98	12	350	9.3	0
Mirex	6.9	54.0	3.3	6.8	1.5	6.1	3.2	0
p,p'-DDT[7]	6.9	68.1	2.1	94	50	34	6.1	0
Organochlorine Sulfide Pesticides & Metabolites								
Endosulfan sulfate	3.7	46.4	4.0	3.7	0.83	0.44	12	
Endosulfan I	4.7	36.0	3.2	4.9	2.46	0.10	10	
Endosulfan II	4.8	49.0	3.5	8.9	5.8			
Phosphorothioate Pesticides								
Parathion	3.8	44.4	9.6	9.1	1.0			
Ethion	5.1	48.8	10.5	1.9	2.59			
Chlorpyrifos	5.1	45.5	8.9	5.5	0.88			
Miscellaneous Pesticides								
Etridiazole	2.6	34.8	1.8	15	2.2			
Dacthal	4.3	62.2	2.2	2.6	1.6	4.6	11	
Triallate	4.6	88.0	2.3	11	1.80			
Trifluralin	5.3	42.9	3.4	7.2	0.89			
PolyChlorinated Biphenyls								
PCB 74	6.3	78.9	1.2	48	15	4.1	20	15
PCB 101	6.4	66.5	4.5	1.1	2.6	28	29	20
PCB 138	6.7	77.3	5.7	2.6	2.9	134	33	21
PCB 153	6.9	65.0	4.6	2.2	0.87	110	30	0
PCB 118	7.0	74.5	6.1	2.2	0.96	51	6.2	0
PCB 183	8.3	75.9	5.3	0.84	3.7	23	8.6	0
PCB 187	7.2	77.3	5.0	1.4	2.2	54	13	0
Method Averages								
Average	6.1	62	4.1	79	11	30	15	7.1
Min	2.6	32	0.3	0.2	0.83	0.10	0.22	0
Max	9.4	98	12	920	86	350	66	30

Compounds	Log K_{ow}	Method Recovery[1] (%)		Estimated Method Detection Limit[2] pg/g ww		Determined Values for NIST SRM 1946 (ng/g ww)		Deviation from Certified Values[3] (%)
		Avg.	SD	Avg.	RSD %	Avg.	SD %	% Diff
Polycyclic Aromatic Hydrocarbons								
Acenaphthylene	3.9	36.0	2.5	38	4.1			
Acenaphthene	4.0	54.4	5.5	50	2.5			
Fluorene	4.2	41.7	1.6	16	1.7			
Anthracene	4.5	51.8	5.4	59	6.8			
Phenanthrene	4.5	56.3	3.8	56	10			
Pyrene	5.1	63.7	5.4	6.7	3.5			
Fluoranthene	5.2	58.4	4.0	7.6	1.8			
Chrysene /Triphenylene	5.7	59.3	0.9	20	12			
Benzo(a)anthracene	5.9	59.4	2.3	26	0.96			
Retene	6.4	55.3	5.8	44	14			
Benzo(k)fluoranthene	6.5	64.6	0.3	23	0.9			
Benzo(a)pyrene	6.5	43.4	5.2	17	1.7			
Benzo(b)fluoranthene	6.6	64.4	0.9	20	1.6			
Indeno(1,,3-cd)pyrene	6.7	60.5	0.3	18	3.33			
Dibenz(a,h)anthracene	6.8	58.0	1.6	19	8.9			
Benzo(e)pyrene	6.9	57.8	0.7	100	34			
Benzo(ghi)perylene	7.0	60.1	0.7	6.3	1.3			
PolyBrominated Diphenyl Ethers[8]								
BDE 10	5.0	64.2	6.4	920	26			
BDE 7	5.0	49.7	2.4	120	43			
BDE 8	5.0	52.0	5.3	710	23			
BDE 12	5.8	45.2	2.3	880	18			
BDE 13	5.8	50.4	2.7	910	21			
BDE 15	5.8	82.2	6.3	860	15			
BDE 30	5.9	47.2	6.6	240	37			
BDE 32	5.9	46.9	2.2	38	7.6			
BDE 17	5.8	55.7	2.4	32	8.4			
BDE 25	5.9	55.9	2.3	43	7.1			
BDE 28	5.9	51.1	2.1	23	2.8	0.94	1.9	26
BDE 35	6.7	52.6	2.0	57	3.8			
BDE 37	6.7	52.3	2.1	40	8.1			
BDE 75	6.8	86.9	6.7	24	5.3			
BDE 49	6.8	94.1	7.1	30	3.6			
BDE 71	6.8	84.8	5.2	22	1.9			
BDE 47	6.8	91.1	7.5	14	1.1	29	10	0
BDE 66	6.8	83.6	8.5	120	26			n/a[9]
BDE 77	7.6	93.6	8.0	83	24			
BDE 100	7.7	79.0	8.4	6.7	1.1	8.4	2.7	0
BDE 119	7.7	78.9	7.2	19	14			
BDE 99	7.7	85.7	6.3	23	1.95	18	5.4	0
BDE 116	7.7	75.6	7.9	91	48			
BDE 85/155	7.7 / 8.6	91.8	8.3	37	10			
BDE 126	8.5	88.6	9.2	36	9.2			
BDE 118	7.7	75.0	11.9	200	86			
BDE 155	8.6	80.8	7.0	2.3	1.0	0.68	11	
BDE 154	8.6	79.7	7.4	8.3	2.7	6.2	18	0
BDE 153	8.6	78.6	6.7	6.5	3.1	2.9	9.3	0
BDE 138	8.6	81.6	7.1	1.1	1.1			
BDE 166	8.6	98.3	7.8	1.9	1.7			
BDE 183	9.4	81.5	5.8	1.6	0.95	0.23	14	
BDE 181	9.4	76.8	4.1	3.5	3.14			
BDE 190	9.4	72.4	5.0	5.0	2.5			

[1] Triplicate recoveries across entire method of ~8 ng/g ww tissue spikes. Blank and sample background corrected.

[2] 3:1 S:N of IS normalized response factors in three separate fish from Denali, Sequoia, and Rocky Mountain National Parks according to EPA Method 8280A

[3] Percentage difference between this method and NIST certified values for SRM # 1946 LakeTrout, 0% difference when method average is within certified confidence interval, n=5

[4] HexachloroCycloHexane

[5] DichloroDiphenyldichloroEthylene

[6] DichloroDiphenylDichloroethane

[7] DichloroDiphenylTrichloroethane

[8] Log K_{ow} Estimated by EPI Suite

[9] Interferant prohibited quantitation

Blank Cells indicate no certified, or refernce value for the SRM, and/or not detected here.

Table 3.4 Comparison of Contaminant Concentrations in Fish from Remote Areas (ng/g ww)

Location	tissue	Σ DDTs	Σ PBDEs	Σ PCBs	Σ HCHs	HCB	dieldrin	Σ chlordanes	n	year	ref
		average	average	average	average	average	average	average			
		range	range	range	range	range	range	range			
Tibetan Plateau	muscle	6.3	n/a	n/a	0.91	1	n/a	n/a	20	2005	31
		0.78 - 23			0.13 - 2.6	0.31 - 3.2					
Canadian mountains	muscle	4.4	n/a	7.7	n/a	n/a	n/a	n/a	91	1997,2001, 2003	29
US arctic	muscle	2.69	n/a	3.7	0.56	0.46	n/a	1.0	91	1993	12
US mountains, arctic	whole fish	6.4	1.6	1.6[a]	0.092	0.38	1	0.086	136	2003-2005	this study
		0.23 - 50	0.014 - 8.4	0.14 - 6.8	0.002 - 0.76	0.014 - 1.9	0.02 - 14	0.007 - 5.1			
European mountains	muscle	19	0.38	6.3	0.54	0.42	n/a	n/a	163	2000-2001	2,3
		0.25 - 65	0.07 - 1.1	0.68 - 17	0.10 - 1.6	0.14 - 1.0					
Pacific Ocean Salmon	muscle	~2	~0.2	~2.5	~0.75	~0.8	~0.3	~1	47	2002	42,43
		~0.8 ~ 10	~0.04 ~ 5	~1.1 ~ 10	~0.4 ~ 11	~0.3 ~ 3	~0.1 ~ 1	~0.4 ~ 2.75			

a – Sum of PCB 74,101,118, 138, 153, 183, 187 only, n/a – not available

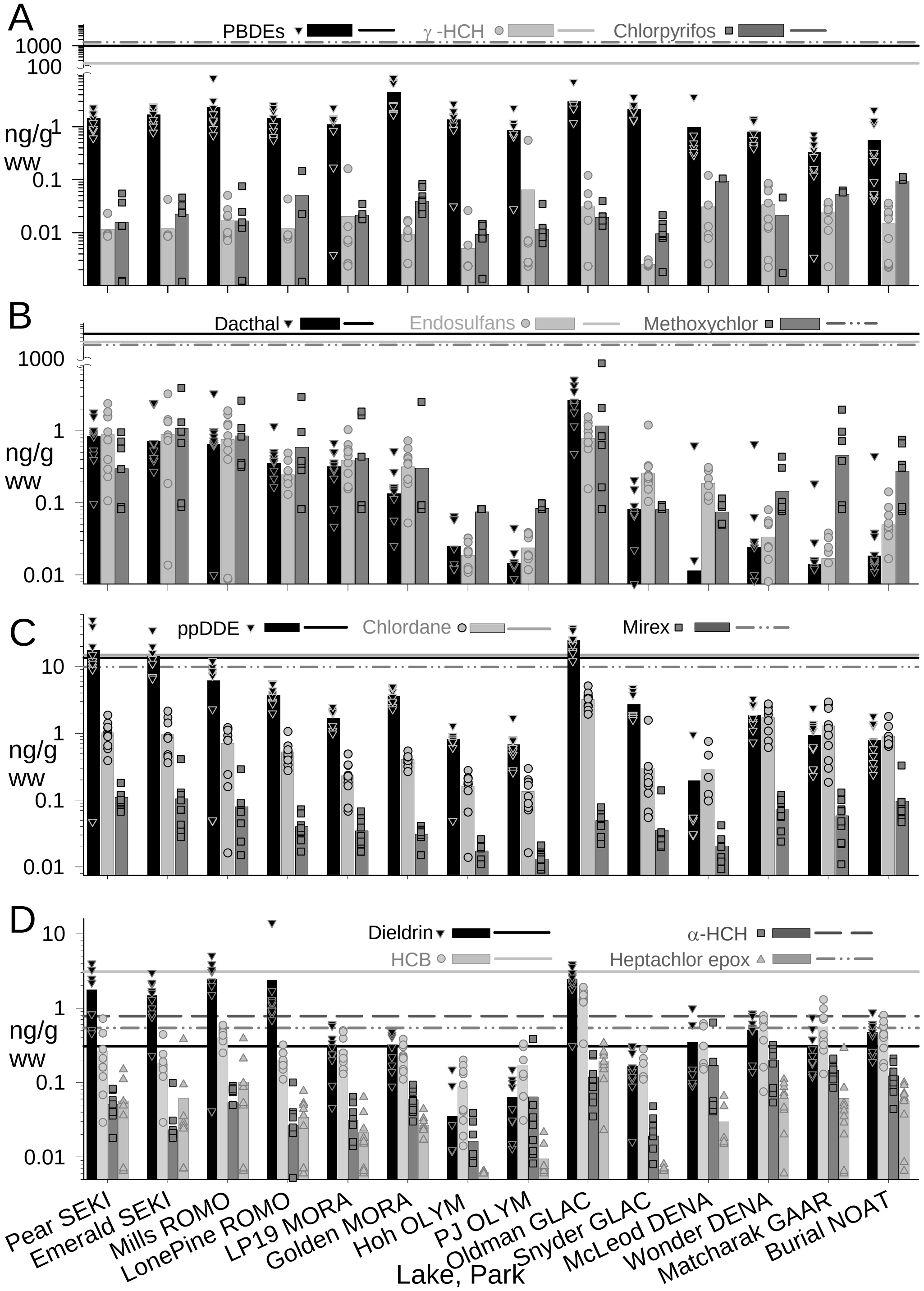

Figure 3.3 - Concentrations of select current (A,B) and historic use contaminants (C,D) in fish from western US national parks compared to estimated non-cancer (A,B) and cancer (C,D) screening values for subsistence fishers. SEKI – Sequoia, ROMO – Rocky Mountain, MORA – Mnt. Rainer, OLYM – Olympic, GLAC – Glacier, DENA - Denali, GAAR – Gates of the Arctic National Parks, and NOAT – Noatak National Wildlife Refuge

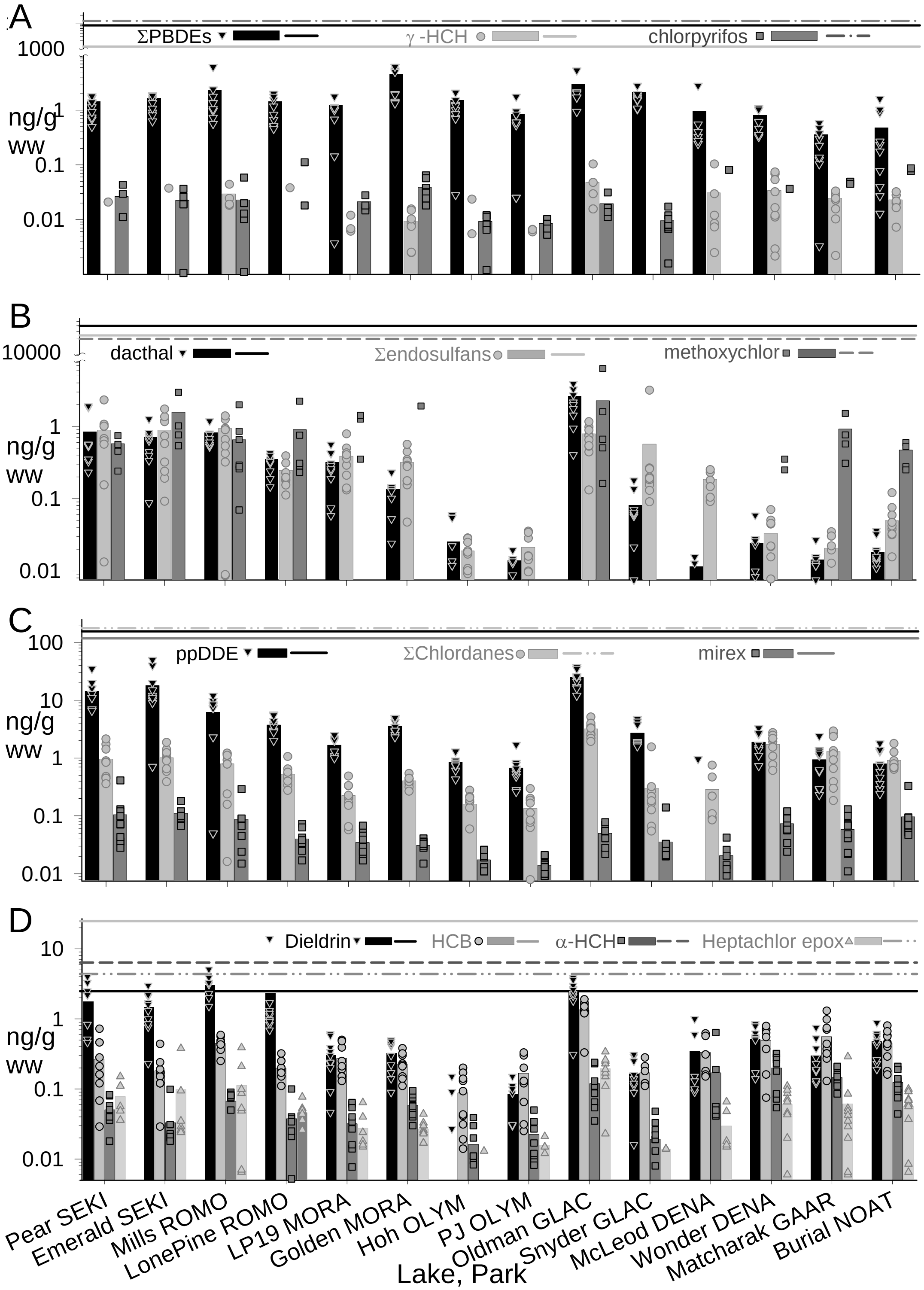

Figure 3.4 - Concentrations of select current (A,B) and historic use contaminants (C,D) in fish from western US national parks compared to estimated non-cancer (A,B) and cancer (C,D) screening values for recreational fishers.

Factors Affecting Accumulation of PBDEs, PCBs, and Current and Historic Use Pesticides in Western US National Park Fish

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4.1 Abstract

The effects of 7 fish and 9 ecosystem characteristics' on fish contaminant concentrations were tested for 28 SOCs in samples from lakes across Western US National Parks. Lipid, followed by age, were the most reliable fish characteristics explaining organic contaminant concentrations in fish tissues from cold North American lakes. Lipid was most significant and explanatory for most pesticide concentrations. Fish age better explained p,p'-DDE, mirex, PCB, and PBDE concentrations. After adjusting for lipid or age, mean daily air temperature (-8.8 to 6.9 °C) was the most significant and explanatory ecosystem characteristic for most of the historic use pesticides concentrations in fish. Contaminant deposition to the ecosystem from snow was the most predictive ecosystem characteristic for fish concentrations of the lipid adjusted current use pesticides. Elevation was the most significant ecosystem factor explaining concentrations of p,p'-DDE, mirex, PCBs, and PBDEs after adjusting for age of the fish. Proximity to sources (agricultural intensity or population density also explained a significant amount of several pesticides' and PBDEs' fish concentrations. Some evidence was observed for interactions between ecosystem temperature and fish growth rate effects as well as lake productivity and lipid effects on contaminant concentrations in fish.

4.2 Introduction

Semi-volatile organic compounds evaporate and condense with changing temperatures and undergo long range transport to locations remote from their known sources(*1*). More persistent and toxic SOCs are known to accumulate within food webs(*2*) and can reach body burdens that can negatively impact the health of even remote wildlife(*3*). The most significant source of these persistent organic pollutants to many humans as wildlife (such as birds) is fish.

Measured concentrations of SOCs in fish tissues have shown that concentrations can often vary up to three orders magnitude between individual fish within a given population(*4*). Since fish are an important part of human and wildlife diets, and since contaminant concentrations are so variable, it is important to develop a strong mechanistic understanding of the variation in fish contaminant concentrations.

Many previous studies and experiments have attempted to explain this variation in terms of a few key parameters(*4-7*).

Because many persistent contaminants are hydrophobic, fish lipid concentrations have been shown to explain significant portions of variability in fish SOC concentrations(*8*). In addition, fish age, sex, mass, length, condition characteristic, growth rate, trophic status, feeding location, and species are fish characteristics shown to affect SOC concentrations(*9*). Recently some studies have suggested that the degree of saturation in the fats of a fish might better predict contaminant concentrations in fish than total lipids(*10*). Non-fish characteristics, such as temperature, lake productivity, lake color, length of the food chain, and degree of ecosystem contamination have been shown to affect SOC concentrations in fish(*11*). Many previous studies were observational in nature, measured one or two key variables to explain certain fish SOC concentrations and did not test for effects of other characteristics, particularly competing and covariate characteristics. Understanding covariance and relative importance of different parameters can lead to new understandings of the relationships between fish SOC concentrations and fish and ecosystem characteristics. This is needed to improve the robustness of explanations of fish SOC concentrations.

Because SOCs tend to condense at colder temperatures, and because temperatures tend to decrease and higher elevations, several previous studies of remote or high elevation fish have reported significant correlations between fish SOC concentrations and elevation(*5,9,12*). However, fish and ecosystem characteristics that can affect fish SOC concentrations can co-vary with elevation or temperature, such as age, lipid, size or trophic level of the fish, or proximity to sources, precipitation rates, lake productivity and color(*6,13*). The combination of several covariates may inflate or reduce the apparent strength and significance of elevation or temperature as explanatory characteristics, depending on the relationships. Interaction between factors controlling fish SOC concentrations, such as temperature and SOC volatility(*12*), can complicate analysis of these factors, especially when not all significant controlling factors are measured. To fully understand observations of fish

SOC concentrations it is important that all major explanatory characteristics be measured and tested equally for their potential effects.

The objective of this research was to determine which ecosystem and individual fish characteristics best explain fish SOC concentrations in western US fish, to determine if temperature and elevation are significant explanatory characteristics in the presence of other factors (such as proximity to sources), and to determine what interactions (if any) might affect the robustness of these characteristics in explaining fish SOC concentrations in remote ecosystems.

4.3 Experimental

4.3.1 Sample Collection and Contaminant Analysis

All fish and lake samples were collected during the same 6 week period (7/28-9/13) of 2003, 2004, and 2005 using hook and line. Mass and length were measured and in field dissections were conducted along with a 100 uL blood draw for histopathological analyses. Sex was determined visually and confirmed through steroid and hormone measurements in the serum. Otoliths were removed, cross-sectioned and annuli counted to determine age. Gut contents were evacuated and stored and the carcass wrapped in clean foil or metalized polyester bags and frozen until laboratory storage at -25 C. Whole fish carcass was homogenized with liquid N_2 in a stainless steel blender until a frozen N_2 powder was obtained. Aliquots of ~20 g wet weight (ww) were ground with sodium sulfate until dry and free flowing, spiked with isotope labeled recovery surrogates and solvent extracted under temperature and pressure. Extracts were dried with sodium sulfate, an aliquot evaporated and gravimetrically measured for lipid content, and the remaining aliquot fractionated by silica and gel permeation chromatography to remove interfering molecules prior to gas-chromatographic mass spectrometric analysis.

4.3.2 Explanatory Characteristic Measurements

Ecosystem explanatory characteristics were directly measured where possible and estimated using appropriate techniques when not measured. Elevation, latitude and longitude of lakes were gathered from National Park Service documents.

Temperatures and precipitation were estimated for the last 30 years from existing nearby meteorological data and extrapolation techniques in the PRISIM model(*14,15*). Lake water chemistry and productivity parameters were measured with a YISI probe and 1 m grab samples of specific conductivity, dissolved organic carbon (DOC), total nitrogen, total phosphorus, and Chlorophyll A concentrations. Lake surface area was estimated from USGS digital raster graphics and for most of the lakes, when an accurate bathymetric maps were not available, sonographic bathymetric mapping was performed. Lake volume was estimated from bathymetric maps when prior published data was not available. Estimates of hydraulic residence times were calculated from annual precipitation estimates, and modeled catchment, lake, and vegetative evaporation as well as vegetative conductive transport and evapo-transpiration rates, normalized to lake volumes. Cropland intensity values were calculated as described previously(*16*), and population densities similarly using 2002 Landscan 30 s grid data and ARC-GIS. Contaminant snow flux to the ecosystem was measured every year over the same 3 years as fish samples and as reported previously(*16*).

4.3.3 Statistical Analysis of Fish Characteristics

The effect of 7 individual fish characteristics on fish contaminant concentrations were tested for 28 current and historical use pesticides, PCBs, and PBDEs in 14 lakes. Simple linear regression analyses were performed with log transformed fish contaminant concentrations and fish age, mass, fork length, growth rate, and condition factor for each of the 14 lakes using S-Plus software. Analysis of each of the 14 lakes' correlations between the fish characteristics and contaminant concentrations generated 14 estimates of the relationship between these characteristics and contaminant concentrations, independent of potentially covariate ecosystem characteristics. The average regression (slope and intercept) between a fish characteristic and contaminants' concentrations in fish was calculated from the regressions within each of the 14 lakes, weighted by the proportion of the variation explained (R^2) by each regression. This average regression was applied to the full contaminant dataset for the most significant fish characteristics, and the residuals further analyzed as described below.

4.3.4 Statistical Analysis of Ecosystem Characteristics

The effect of ecosystem characteristics on the accumulation of 28 contaminants in fish tissues from 14 lakes was investigated using multiple linear regression of log transformed fish contaminant concentrations (after adjusting for the most significant fish characteristics), averaged by lake. Adjusted fish contaminant concentrations (in the form of residuals) were further adjusted to all positive values to permit further analysis. These fish characteristic adjusted fish SOC concentrations were averaged by lake because individual fish are replicates when analyzing lake characteristics. The ecosystem characteristics initially investigated included 18 parameters, many of which were somewhat redundant. After inspection of cross correlation matricies and initial multiple regression with all 18 parameters, 9 non-redundant characteristics were selected for further investigations (Table 4.3). Significance of effect and portion of fish SOC concentrations explained by these ecosystem characteristics were tested with stepwise multiple linear regression (α in/out 0.05). These parameters included elevation, temperature, lake productivity, hydraulic retention time, summer precipitation, lake surface area, proximity to agricultural sources, proximity to human population sources, and measured winter SOC deposition to the ecosystems through snow.

4.4 Results and Discussion

4.4.1 Lake and Fish Characteristics

The 14 lakes sampled were without major inlets, outlets, glaciers, or anadromous fish, and contained reproducing salmonid populations. Descriptions of the fish are summarized in Table 4.1. All lakes were located with National Park or Wildlife Refuge boundaries and public access to the lake access was limited as no road access exists. These small, oligotrophic lakes were characterized by small catchment sizes, broad temperature, elevation, and geo-spatial ranges (Table 4.2). The fish populations were generally of three main salmonid species, brook trout (Salvelinus fontinalis), lake trout (Salvelinus namaycush), and cutthroat trout (Oncorhynchus clarki). One lake contained rainbow trout (Oncorhynchus mykiss), and in another only six specimens of burbot (Lota lota), and round whitefish (Prosopium cylindraceum) could be retrieved. Most of the lakes were characterized by short, ice free periods with large changes in productivity, but were generally nutrient poor. Most of the brook trout populations represented the top of likely short aquatic food chains, while the lakes with lake trout generally contained one more predatory species above the trout, usually pike (Essox lucius). The brook trout populations were much younger than the lake trout populations (5 vs. 18.6 yrs), and much smaller (148 vs. 1073 g). The sex ratios were very even, and the lipid varied slightly between lakes but averaged less than 10% in all populations (Table 4.1).

4.4.2 Contaminant Concentrations

Average concentrations of historic use pesticides in whole fish tissues from western US National Parks covered a large range, from 2 pg/g ww of a-HCH to 50 ng/g ww of p,p'-DDE, with dieldrin concentrations the highest on average. Current use pesticides varied slightly less, from 10 pg/g ww dacthal to 7 ng/g ww of methoxychlor. Dacthal was the most concentrated current use pesticide in fish tissues (0.5 ng/g ww). Lake average PBDE concentrations in fish varied the least (0.33 -4.5 ng/g ww). Since only 6 major congeners of PCBs were measured, measured ΣPCB and ΣPBDE concentrations were roughly equal at 1.6 ng/g ww. However, since the PBDE congener profile was dominated by two or three congeners, and the PCB profile was more evenly distributed, the average concentration of PBDEs # 47 and 99 exceeded all PCB congeners.

4.4.3 Effects of Fish Characteristics

Lipid was the most frequently significant ($p<0.05$) explanatory fish characteristic within each lake, and was positively correlated with fish contaminant concentrations (Figure 4.1). For most compounds, lipid explained the largest portion of the variation in fish SOC concentration (average $R^2=0.29$ across 28 compounds), especially for the pesticides (average $R^2=0.36$). Also, lipid was largely independent of other fish characteristics, both across, (Table 4.3) and within lakes.

Age was the second most frequently significant characteristic, explained the second largest portion of the variation in fish contaminant concentrations for most compounds (average R^2=0.22), and the largest portion fish PCB and PBDE concentrations (average R^2=0.26). Age was slightly more covariate with other fish characteristics than lipid (both across and within lakes), and did co-vary with some ecosystem characteristics (Table 4.3). This covariance of fish age and ecosystem characteristics likely masked evidence of positive age-SOC concentration regressions across all lakes ($p>0.05$, and negative slopes for most SOCs). However, age-contaminant relationships within lakes were generally significant and positive. Since age-contaminant regressions within lakes are independent of variation in ecosystem characteristics (i.e. all fish in a lake experience the same elevation), it is likely that the average age-SOC concentration regression within each lake is the best estimate of the effect of age on SOC concentrations for the fish studied.

Unlike a previous study of high elevation fish(*9*), growth rate was only intermittently significant in the fish studied here. Fish growth rate explained less variation than lipid or age (average R^2=0.20), and its regressions with a contaminants concentration frequently varied between significantly positive and significant negative from one lake to the next. Growth rate was slightly more co-variate with other fish characteristics than lipid or age within each lake, but did not co-vary with any ecosystem or fish characteristic across the lakes studied (Table 4.3).

Regressions between fish contaminant concentrations and fish mass, condition characteristic, fork length were less frequently significant that lipid, age, or growth rate, and explained less of the variation (average R^2=0.19, 0.18, and 0.15 respectively). Fish condition factor had the lowest degree of co-variance with other fish characteristics and ecosystem characteristics across all lakes (Table 4.3), but tended to co-vary with lipid within each lake. Fish mass and fork length were the most co-variate fish characteristics, both within and across lakes (Table 4.3)

In order to investigate the relative importance of various ecosystem characteristics on fish contaminant concentrations, concentrations of contaminants were adjusted by lipid or age in order to reduce the biological variability, prevent covariance effects, and simplify analysis of the magnitude of the effects of ecosystem characteristics. The 14 relationships between age or lipid and a given compound in 14 lakes' were averaged, plotted against the concentrations in all the fish (Figure 4.1, 4.2), and the remaining variation, in the form of the residuals, was used in analysis of ecosystem characteristics.

Age or lipid adjustment was selected for a given contaminant according to frequency of significant regressions in the 14 lakes, the strength of those regressions, and the consistency of the slope of those regressions. The relationship between lipid or age and a contaminant's concentration in fish, independent of ecosystem characteristics and their covariance, was estimated by averaging the slopes and intercepts of the 14 lakes' regressions weighted by their R^2. Because concentrations of historic use pesticides and pesticides with higher vapor pressures was best explained by lipid in the fish, these compounds' concentrations were lipid adjusted. Contaminants with variable (and sometimes negative) correlations with lipid were typically best explained by fish age, and were therefore adjusted by age (PCBs, PBDEs, mirex, p,p'-DDE). The contaminants that more strongly correlated with age tended to be those compounds with the longest half-lives in fish, those known to accumulate slowly (mirex and highly chlorinated PCBs like those measured here), and/or compounds that are formed by the degradation of other contaminants (p,p'-DDE from DDT, and tetra-hepta brominated PBDEs from debromination of deca-octa PBDEs). There is some evidence of age based accumulation of debrominated PBDEs in these fish as the slopes of the average age regression decreased with a PBDE congeners increasing bromination level, a rough measure of PBDE debromination rate(*17*). Previous work has established the importance of fish debromination on the fate of PBDEs(*17*).

4.4.4 Ecosystem Characteristics Covariance

Significant co-variance of several ecosystem characteristics precluded some characteristics' inclusion in final regression models of fish contaminant concentrations (Table 4.3, Figure 4.3). There was a moderate, but statistically non-significant positive correlation between the elevation and mean annual daily air temperature of the lakes studied (Table 4.3, Figure 4.3). Several previous studies of SOCs in high elevation fish have observed negative correlation between elevation and temperature(*5,9,12,18*).

This difference is likely due to co-variance of elevation with latitude in the lakes of this study (Figure 4.3). Since the positive elevation-temperature trend was weak, and likely introduced opposing effects on SOC accumulations in fish, both elevation and temperature were investigated in the stepwise multiple regression models to see if they were significantly correlated with fish SOC concentrations. Not surprisingly, other ecosystem characteristics with the large degrees of co-variance (HRT, summer precipitation, and lake surface area) tended not to be present in final models (Table 4.3). Finally, elevation was significantly and positively correlated with regional cropland intensity and these two parameters tended not to be present together in final models.

4.4.5 Effects of Ecosystem Characteristics

Temperature was the most significant characteristic affecting lipid adjusted lake average fish concentrations of historic use pesticides (HUPs), explaining 19-77% of the remaining variation (Figure 4.4). The negative slopes of contaminant concentrations as a function of temperature are consistent with work elsewhere(*5,9,12*), and theories of cold condensation controlling the relative deposition of persistent, more volatile SOCs to lake ecosystems. These negative regressions between fish concentrations and temperature could also be consistent with previous hypotheses that lower fish metabolism and respiration rates at lower temperatures result in slower contaminant depuration(*12,18*).

Previous work has shown that lake productivity tends to decline with decreasing thermal energy(*19*), and that lower lake productivity yielded higher fish contaminant accumulations(*11*). It therefore seems likely that colder lakes would tend to amplify the bioaccumulation of contaminants in fish, in addition to possible mechanisms of slower excretion from the fish and increased cold condensation to the lake. This is supported by the significant correlations between one measure of lake productivity (chlorophyll A concentration) and lake average fish contaminant concentrations (not shown) for several of these temperature correlated contaminants (HUPs). Although not entirely quantifiable, temperature co-variates likely did not drive these regressions since temperature and chlorophyll A were weakly or not correlated with other characteristics (HRT, lake surface area, Table 4.3) and none of these characteristics were significantly correlated with contaminant concentrations in fish.

Snow contaminant deposition was the most significant characteristic for lipid adjusted, lake average fish concentrations of current use pesticides (CUPs), and explained 30- 80% of the remaining variation (Figure 4.5). This positive regression is consistent with atmospheric transport efficiency, and variable active source regions controlling the relative deposition of CUPs to different ecosystems. Since CUPs have relatively short atmospheric half-lives relative to HUPs, transport of CUPs to different ecosystems is likely limited by degradation, as well as source intensity and proximity(*16*). Measured snow deposition likely combines several of those characteristics into a single measure, and is plausibly correlated with summertime CUP deposition since source proximity likely remains, and summer and annual precipitation rates are related and co-vary.

Elevation was the most significant characteristic for age adjusted lake average fish PCB, mirex, and PBDE concentrations. Elevation's positive regressions explained 23-65% of the remaining variation in fish concentrations of these SOCs (Figure 4.6). Although fish concentrations of these SOCs were also positively related to temperature and source proximity, elevation explained more of the variation in lake average age adjusted concentrations and was more significant. Additionally, temperature was not significant when the effect of elevation and/or proximity to source (Figure 4.7, 4.8) was included in the model (not shown). This is consistent with previous studies showing that many PCBs are too hydrophobic and low-volatility to show significant temperature effects at temperature ranges as cold as those studied here(*12,20*).

Elevational gradients of SOC concentrations have also been suggested to form from diurnal and seasonal wind and temperature cycles, pumping gas phase SOCs upslope, and relative condensation and more effective scavenging taking over at night, during season cooling times, and during high elevation precipitation(*21,22*). Absolute temperature may not predict the strength of these diurnal and seasonal cycles, and their effects have been observed in much warmer mountain systems than those measured here(*22*). Thus elevational gradients in fish PCBs, mirex, and PBDEs might be a measure of larger scale diurnal and seasonal cycles of atmospheric concentration in areas with larger elevational relief (and thus larger local temperature gradients). Co-variance of elevation with proximity to sources can not be dismissed as a potential contributing factor to the fish contaminant elevation trends. However, the moderate covariance of population and elevation, the larger significance of, and variance explained by elevation, and the fact that elevation and proximity to sources often remained significant when both were included in fish contaminants models, suggests that proximity to sources was not driving PCB, mirex, and PBDE elevational gradients.

Proximity to source (cropland intensity) was the most significant characteristic explaining p,p'-DDE's age adjusted lake average fish concentrations, explaining 65% of the remaining variability. This regression with source proximity is consistent with previous work documenting a relationship between snow flux of pesticides and regional agricultural activity for these same locations(*16*). In the case of p,p'-DDE the regression could largely be a measure of a potentially large re-emission from historical agricultural soils adjacent to Sequoia and Glacier National Parks, where the highest lake average fish p,p'-DDE concentrations were measured. Thus, in the case of the heavily used and long lived pesticide, DDT, local emission of its degradation product (p,p'-DDE) might be masking temperature or food web effects on fish concentrations across the areas studied here. Co-variance of elevation and agricultural intensity likely contributed to some portion of this regression, because the explanatory power and significance of elevation decreased when agricultural intensity was added to the model of fish p,p-DDE concentrations.

4.4.6 Independence of Fish and Ecosystem Characteristics

Because temperature so strongly affected lipid adjusted concentrations of historic use pesticides in these fish, and because metabolism of these lipids and ingestion are temperature dependant in pokilotherms like fish, tests for interactions between fish characteristics effects on contaminants (slopes of their simple linear regressions) and ecosystem characteristic were conducted. For several compounds (HCB, HCHs and dieldrin) significant positive regressions were observed between the slope of fish growth rate-contaminant correlations within lakes and ecosystem air temperatures. Significant negative correlations were observed between the slope of lakes' fish lipid-contaminant regressions and lake productivity (for PCB 153 and dieldrin), such that more productive lakes had weaker relationships between fish lipid and these contaminants' concentrations. These interactions are consistent with temperature's negative effect on fish growth rate and lake productivity's negative effect on food and contaminant availability.

4.4.6 Implications for National Park Fish Concentrations

These results suggest that lipid and age remain some of the most reliable predictors of organic contaminant concentrations in fish tissue across large scales of cold, North American lakes. Fish lipid or age, as well as ecosystem temperature (for more volatile compounds) or elevation (for less volatile compounds) can explain ~35-81% of the variation in individual fish contaminant concentrations across western US National Parks. Measurements of contaminant deposition to the ecosystem in the form of snow were not the most significant predictor of fish SOC concentrations, except for the more labile current use pesticides. Proximity to sources, while often marginally significant, was not the most important ecosystem characteristic explaining most SOC concentrations. Finally, temperature may be interacting with fish growth rate and lake productivity and their effects on some fish SOC concentrations, providing evidence for cold temperature enhancement of toxicologically relevant fish SOC accumulations.

4.5 Acknowledgements

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from all of the project partners. Further information about WACAP can be found on the web at: http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.htm. This document has been subjected to appropriate institutional peer review and/or administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 4.1 Average Fish Characteristics

Lake	US National Park	Date Sampled	Fish Species	Sex[a]	Fork Length (mm)	mass (g)	Age (yr)	LIPID (%)	n
Emerald	Sequoia-Kings Canyon	08/24/03	brooktrout	1.4	199	72.9	5	2.9	10
Pear	Sequoia-Kings Canyon	08/25/03	brooktrout	1.2	201	75.4	5	2.8	10
LonePine	Rocky Mountain	09/13/03	brooktrout	1.4	244	141	5	2.5	10
Mills	Rocky Mountain	09/08/03	rainbow trout	1.6	231	153	4	6.3	10
LP19	Mt. Rainier	08/08/05	brooktrout	1.5	237	122	5	3.8	10
Golden	Mt. Rainier	08/13/05	brooktrout	1.3	225	110	4	3.2	10
Hoh	Olympic	09/08/05	brooktrout	1.5	206	81.6	8	1.6	10
PJ	Olympic	09/13/05	brooktrout	1.5	197	67.4	6	2.4	10
Oldman	Glacier	08/19/05	cutthroat trout	1.4	382	596	4	9.9	10
Snyder	Glacier	08/23/05	cutthroat trout	1.5	179	56.8	5	3.6	10
McLeod	Denali	08/10/04	burbot, whitefish	1.3	237	110	4	2.6	4,2
Wonder	Denali	08/12/04	lake trout	1.4	457	1040	19	4.9	10
Matcharak	Gates of the Arctic	08/01/04	lake trout	1.5	508	1410	20	3.6	10
Burial	Noatak National Preserve	08/02/04	lake trout	1.5	411	768	17	3.4	10

a - male =1, female =2

Table 4.2 Lake Catchment Physical Characteristics.

Site	Park, State	Latitude (dd)	Longitude (dd)	Elevation (m)	Lake Volume (m^3)	Lake Max Depth (m)	Mean Depth[a]	Watershed Area (m^2)[b]	Lake Surface Area (m^2)
Emerald	SEKI, CA	36.58	118.67	2800	1.6E+05	10.0	6.3	1.5E+06	2.5E+04
Pear	SEKI, CA	36.60	118.67	2904	5.8E+05	27.0	7.9	1.6E+06	7.3E+04
LonePine	ROMO, CO	40.22	105.73	3024	1.3E+05	9.7	2.6	2.1E+07	4.9E+04
Mills	ROMO, CO	40.29	105.64	3030	7.8E+04	9.0	1.3	1.5E+07	6.1E+04
LP19	MORA, WA	46.82	121.89	1372	1.0E+05	12.1	5.4	1.6E+06	1.8E+04
Golden	MORA, WA	46.89	121.9	1372	6.9E+05	23.9	10.4	4.0E+06	6.6E+04
Hoh	OLYM, WA	47.90	123.79	1384	4.0E+05	14.9	5.2	2.4E+06	7.7E+04
PJ	OLYM, WA	47.95	123.42	1433	1.9E+04	6.4	2.5	3.8E+06	7.6E+03
Oldman	GLAC, MT	48.50	113.46	2026	1.3E+06	17.0	7.0	2.8E+06	1.8E+05
Snyder	GLAC, MT	48.62	113.79	1600	3.8E+04	3.5	1.5	4.0E+06	2.6E+04
McLeod	DENA, AK	63.38	151.07	609	1.8E+06	13.5	5.2	2.1E+06	3.6E+05
Wonder	DENA, AK	63.48	150.88	610	7.8E+07	70.0	29.2	3.2E+07	2.7E+06
Matcharak	GAAR, AK	67.75	156.21	488	2.2E+07	20.4	7.3	2.4E+07	3.0E+06
Burial	NOAT, AK	68.43	159.18	427	5.3E+06	24.1	8.1	2.5E+06	6.5E+05

Site	Park, State	Ave Annual PPT[c] (m/y)	Annual HRT[d] (y)	Total N (mg/L)	Total P (µg/L)	Chl A (µg/L)[e]	DOC (mg/L)	pH Value	Conductivity (µS/cm)
Emerald	SEKI, CA	1.44	0.089	0.168	1.47	0.62	0.94	6.22	5.4
Pear	SEKI, CA	1.44	0.263	0.111	0.59	0.64	0.82	6.10	4.0
LonePine	ROMO, CO	0.92	0.012	0.171	2.70	1.95	1.74	6.67	14.0
Mills	ROMO, CO	0.92	0.009	0.375	3.33	3.02	1.55	6.61	12.0
LP19	MORA, WA	2.84	0.025	0.074	0.92	0.60	1.37	6.63	10.7
Golden	MORA, WA	2.84	0.068	0.069	0.60	0.35	1.88	6.47	10.1
Hoh	OLYM, WA	1.65	0.111	0.058	1.16	0.83	0.74	7.52	63.7
PJ	OLYM, WA	1.65	0.003	0.091	2.78	1.77	1.05	8.14	127.4
Oldman	GLAC, MT	2.03	0.252	0.065	0.55	0.77	0.70	8.24	159.1
Snyder	GLAC, MT	2.03	0.005	0.095	2.67	4.73	0.65	6.42	16.8
McLeod	DENA, AK	0.38	5.943	0.131	1.04	0.61	2.25	7.24	8.4
Wonder	DENA, AK	0.38	7.503	0.105	0.50	0.49	2.10	8.18	190.1
Matcharak	GAAR, AK	0.30	11.09	0.284	1.09	0.96	4.71	8.31	248.1
Burial	NOAT, AK	0.30	242.3	0.233	9.06	0.81	3.32	7.57	35.1

[a]Mean Depth (volume/surface area). [b]Watershed 3D Surface Area. [c]PPT = Precipitation. [d]HRT = Hydraulic Residence Time [e]ChlA = Chlorphyll A

Table 4.3 - Correlation Coefficients of Significantly Correlated Fish and Ecosystem Characteristics

	fork length	mass	age	growth rate	condition factor	lipid	elevation	air temp.	chlorophyll A	HRT^a	summer PPT^b	lake surface area	cropland intensity
fork length													
mass	0.98												
age	0.84	0.89											
growth rate	0.63	0.55											
condition factor													
lipid				0.89									
elevation													
air temp.													
chlorophyll A													
HRT^a	0.75	0.71	0.73				-0.64	-0.80	-0.54				
summer PPT^b	-0.65	-0.63	-0.53					0.86		-0.70			
lake surface area			0.79				-0.57	-0.80		0.86	-0.71		
cropland intensity			-0.59				0.82						
population density							0.54			-0.64		-0.59	

a - Hydraulic Residence Time, b - Precipitation

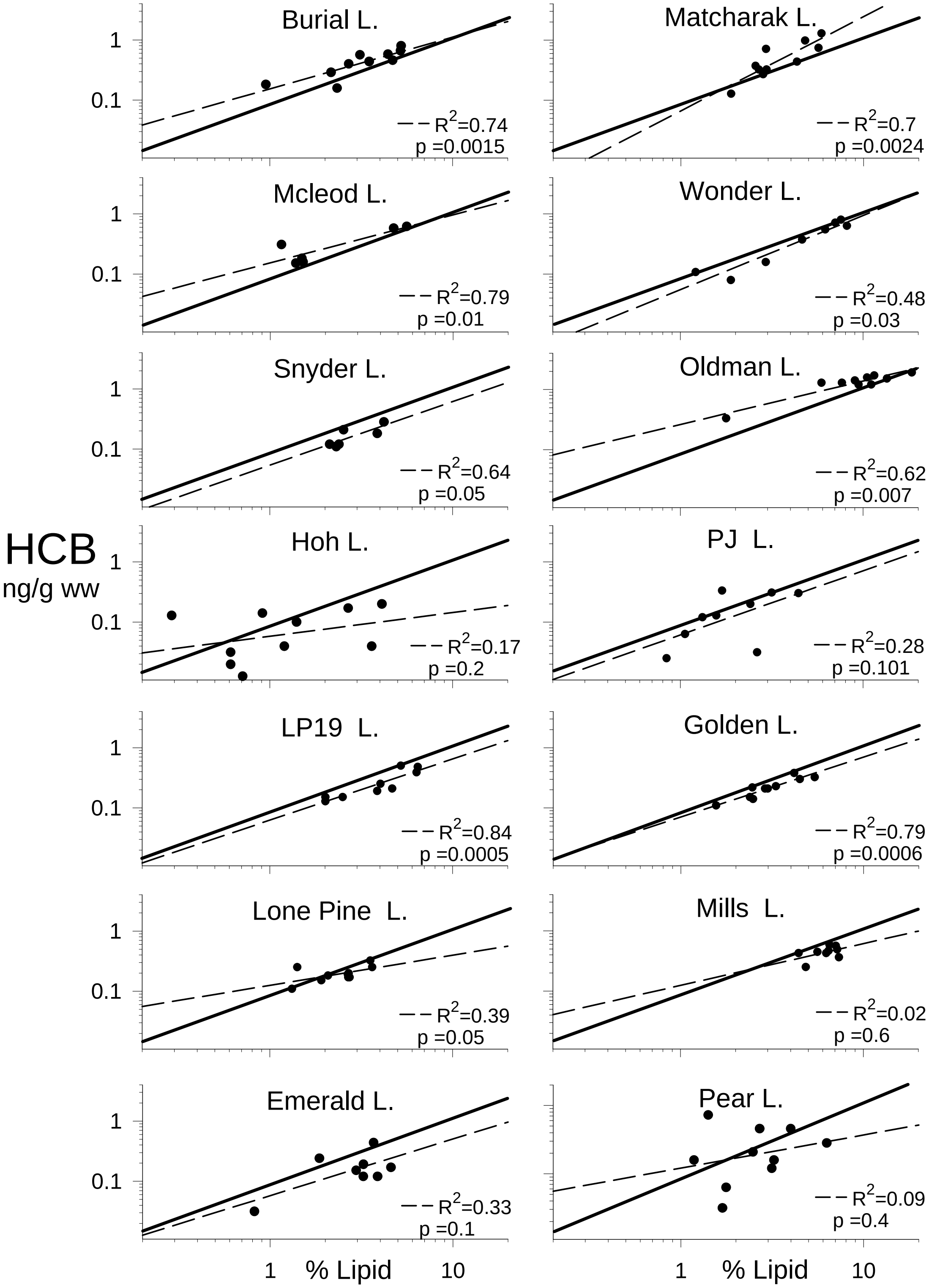

Figure 4.1 - Lipid – [HCB] correlations in fish from 14 western US National Park lakes (- - -), compared to the average correlation for all 14 lakes (—).

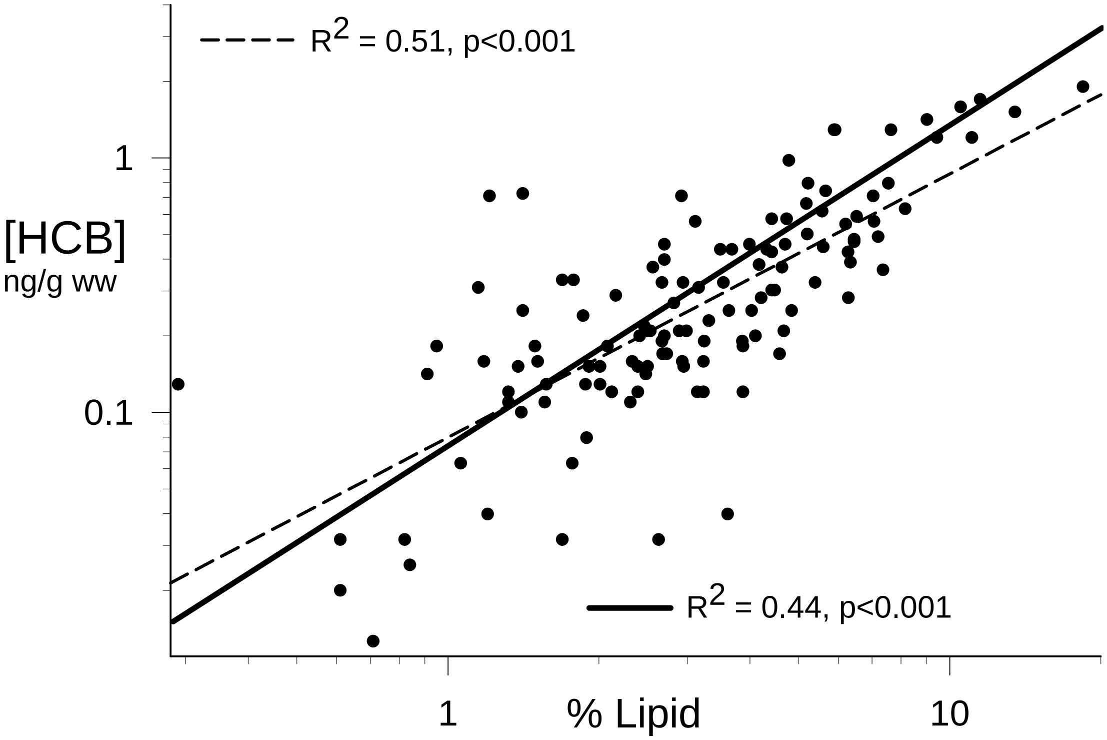

Figure 4.2 - Lipid – [HCB] correlation for 136 fish from 14 western US National Park lakes (- - -) (ie when lake characteristics co-vary), compared to the average correlation within each lake (—) (ie when lake characteristics are constant).

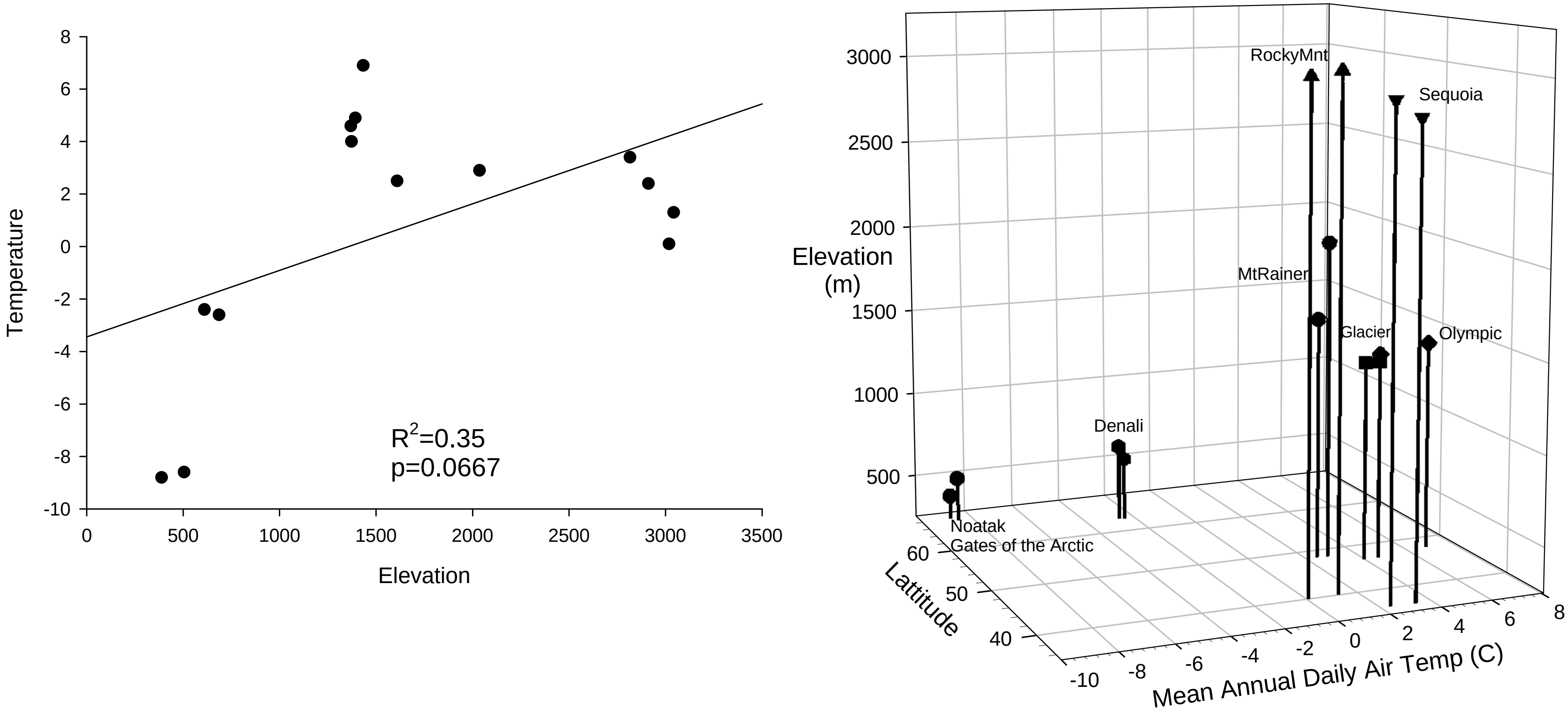

Figure 4.3 – Elevation, Mean Annual Daily Air Temperature, and Lattitude of lakes studied

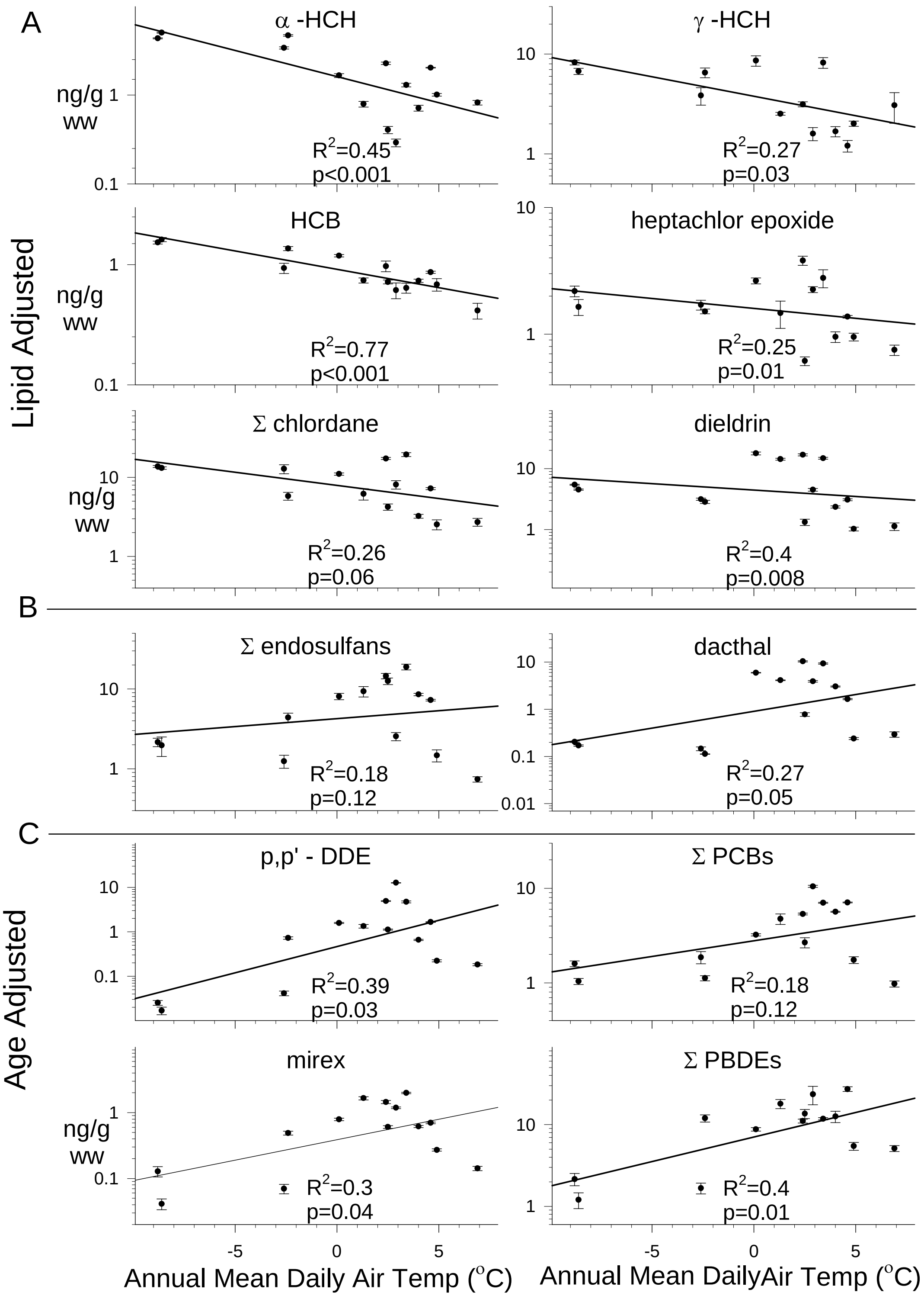

Figure 4.4 - Regression between lake air temperature and lake average fish concentrations of HUPs, CUPs, PCBs, and PBDEs adjusted for lipid (A & B) or age (C), in fish from western US National Parks.

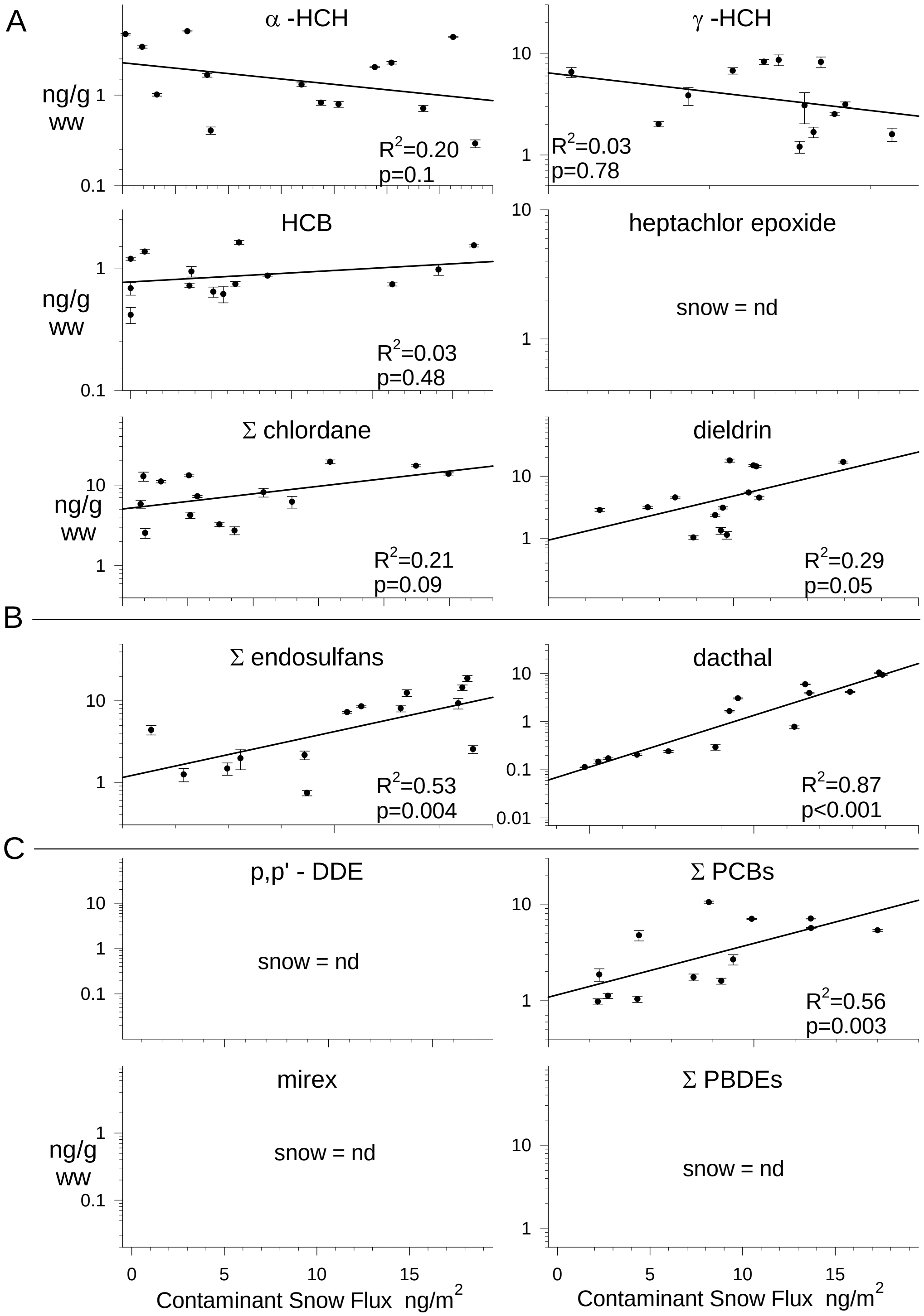

Figure 4.5 - Regressions between measured Contaminant Snow Flux the ecosystem and lake average fish concentrations of HUPs, CUPs, PCBs, and PBDEs adjusted for lipid (A & B) or age (C), in fish from western US National Parks.

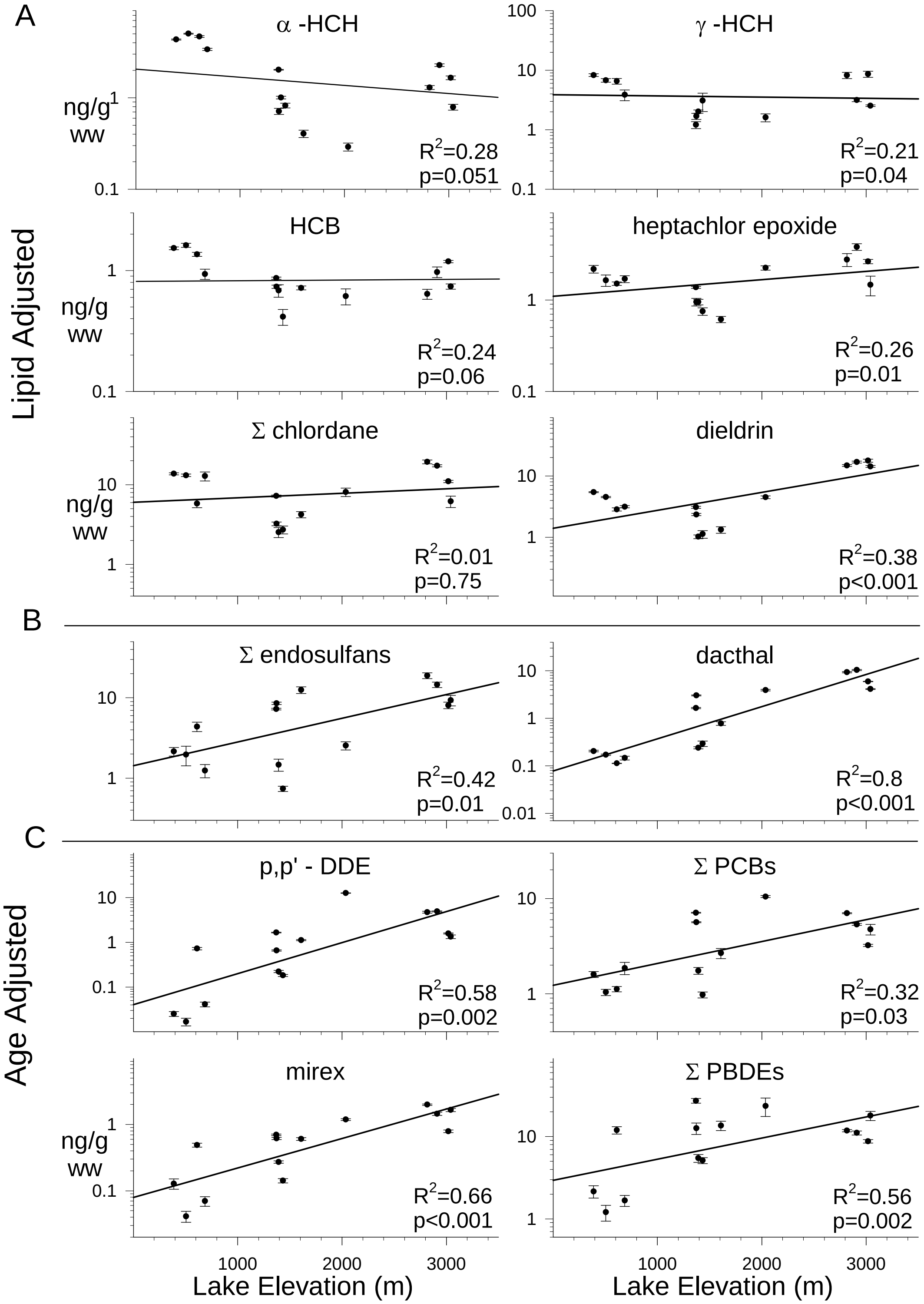

Figure 4.6 - Regressions between lake elevation and lake average fish concentrations of HUPs, CUPs, PCBs, and PBDEs adjusted for lipid (A , B) or age (C), in fish from from western US National Parks.

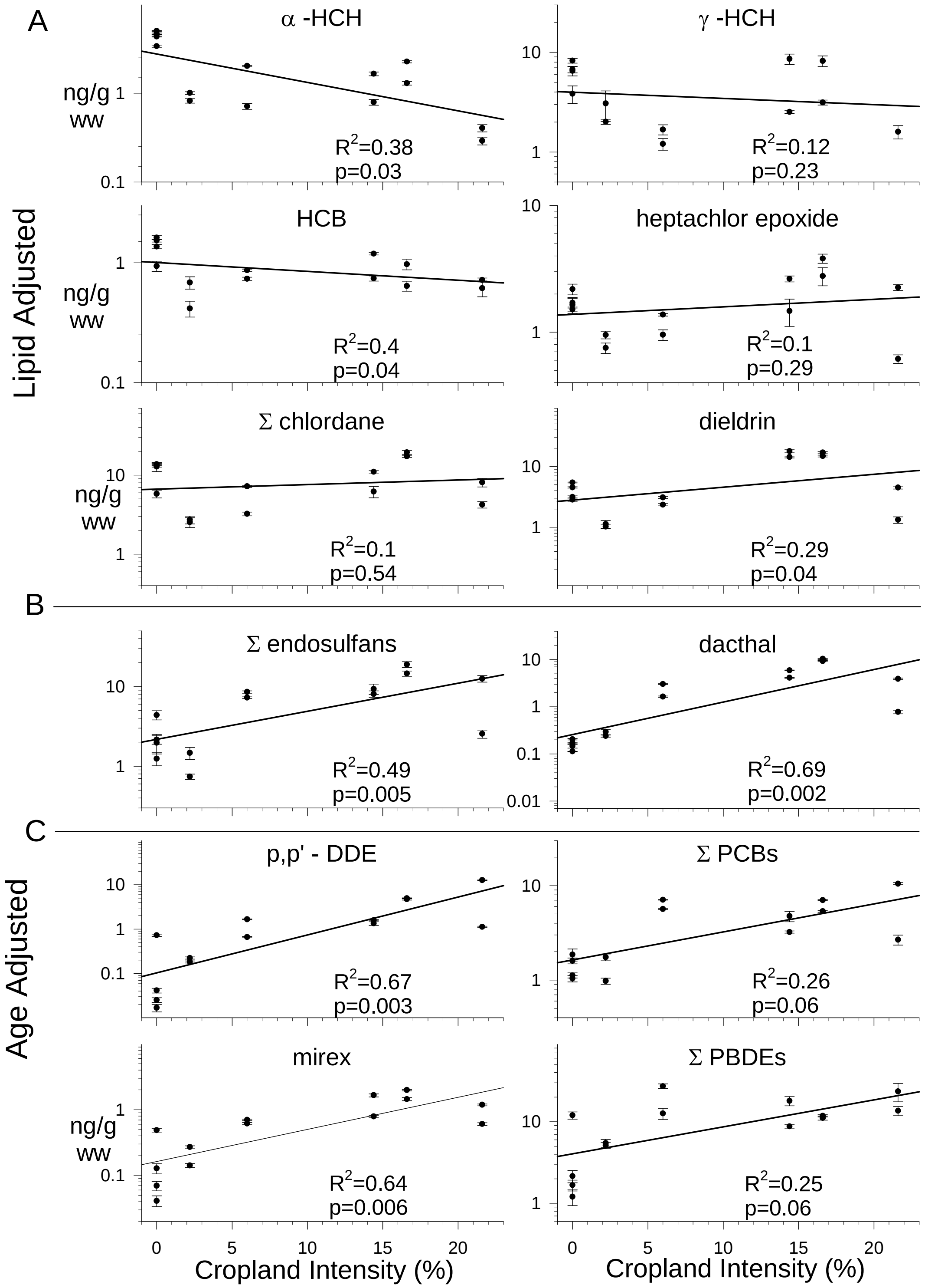

Figure 4.7 - Regressions between Regional Cropland Intensity and lake average fish concentrations of HUPs, CUPs, PCBs, and PBDEs adjusted for lipid (A & B) or age (C), in fish from western US National Parks.

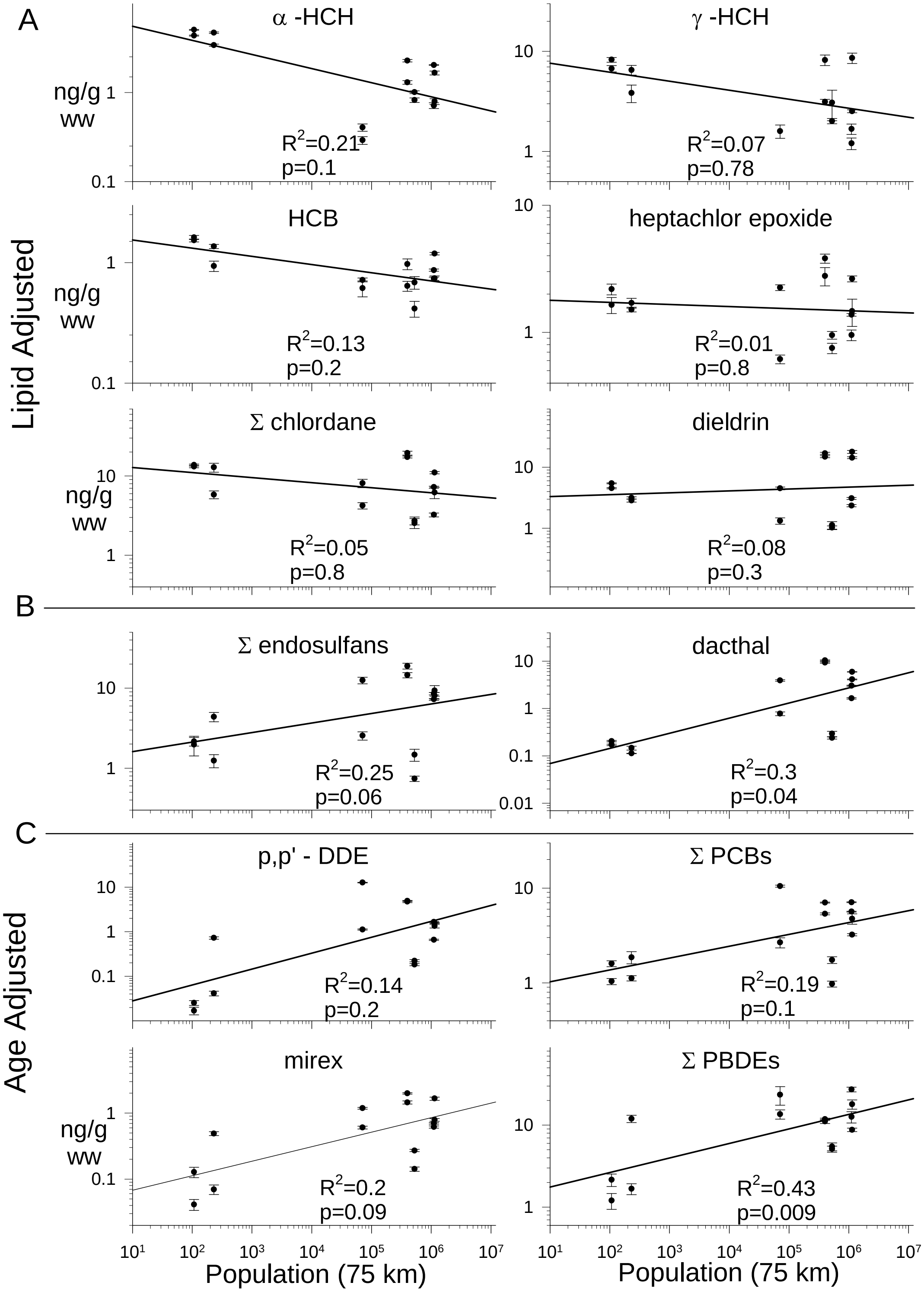

Figure 4.8 - Regressions between Regional Population (75 km) and lake average fish concentrations of HUPs, CUPs, PCBs, and PBDEs adjusted for lipid (A & B) or age (C), in fish from western US National Parks.

5. Conclusions

The concentrations of SOCs in cold ecosystems of the western US need to be measured, and the transport, deposition, and fate of the compounds needs to be assessed because of the toxicity of these compounds and because studies elsewhere have suggested that these types of ecosystems may be at particular risk for preferential accumulation of SOCs. These measurements require rigorous analytical techniques that are sensitive, specific, reproducible, and accurate. Since most analytical methods for complex biological matricies, such as fish, are not sufficiently sensitive to measure the ambient concentrations of SOCs expected in high elevation fish tissues, methods need to be adapted, especially to measure a broad range of chemicals with diverse physical-chemical properties. Measurements of chemicals with divergent properties are needed to test chemical accumulation and fate theories. In particular more selective methods are needed for recently identified SOCs, such as polybrominated diphenyl ethers, to permit analysis of their accumulation and fate.

A selective and sensitive gas chromatographic, isotope dilution, low resolution mass spectrometric technique for the measurement of polybrominated diphenyl ethers was developed. Ion source parameter optimizations determined that PBDE specific molecular and molecular fragment ion abundance was most sensitive to electron energy, followed by emission current, reagent gas pressure, and temperature in the electron capture negative ion source. Optimization of these source parameters yielded significant increases in PBDE specific molecular and molecular fragment ion production, likely due to stabilization of these fragment ions during electron capture processes and relative inhibition of excessive fragmentation to bromide ions. The optimized ECNI fragment ion production increased their sensitivity as quantitation ions and calculated instrumental detection limits (low pg to fg) were as low as previous methods monitoring the non-specific bromide ion for 2-7 brominated PBDEs. The quantitation of the more specific high mass molecular and molecular fragment ions permitted the use of isotope labeled recovery surrogates, which substantially increases the accuracy and precision of these measurements.

An analytical method was developed to quantify 91 SOCs in whole fish tissues at concentrations <1 part-per-billion (ppb). The method consisted of freeze fracture homogenization, sub-critical solvent extraction, silica adsorption and gel permeation chromatography to remove interferants, extract concentration and analysis by GC-MS with stable isotope labeled surrogate recovery correction. The developed GC-ECNI/MS method for PBDEs was integrated with GC/MS analyses of 58 other compounds by both EI and ECNI ion sources, to create a two injection analysis of a single extract for the isotope dilution internal standard quantitation of these 91 SOCs, including current and historic-use pesticides, PCBs, PAHs, and PBDEs. Analyte recovery was tested through low concentration (8 ppb ww) sample spike and recovery experiments, averaged 61±18% for the 91 analytes, and were reproducible (4.1 %RSD). Method detection limits (estimated at 3:1 signal to noise using response characteristics for analyte peak height, and signal noise from GC-MS analysis of three representative fish samples) ranged from 0.2 to 990 parts per trillion, with a median of 18. The method was found to be accurate and precise through the analysis of standard reference material (SRM, NIST #1946) during analyses made over the course of several months. 31 analytes with certified concentrations in the SRM were quantified, on average, to within 7 % of the certified values with 19 of the 31 measured within the certified confidence intervals provided by NIST.

The validated method was used to measure 91 SOCs in 136 fish from 7 western US National Parks, in order to determine contaminant levels across western national parks, test potential human and ecosystem health effects, and explore the mechanisms governing their distribution and accumulation. Contaminants were detected in greater than 60% of the samples for 28 of the analytes, 13 of which were compared to available EPA consumption fish consumption guidelines. Most of the measurements in fish were 1-6 orders of magnitude below screening values for recreational fishers, but in 8 of the 14 lakes from 5 parks, lake average fish concentrations of dieldrin and/or p,p’-DDE exceeded lifetime cancer screening values for subsistence fishers, and 5 of the lakes contained at least one fish with contaminant levels exceeding recreation fisher screening value. These results indicate that fish accumulation of atmospherically deposited contaminants in these high elevation ecosystems can result in concentrations relevant to human health.

Fish contaminant concentrations measured here were higher for PBDEs than fish in comparable lakes of Europe and pacific salmon, and higher for dieldrin as well. However, levels of DDTs and HCHs were lower in these high elevation North American fish than in Europe.

In Chapter 4 the concentrations of SOCs in these high elevation fish are compared to the fishs' biological, and the lakes' catchment characteristics, and a multiple linear regression model was developed to determine which fish and lake catchment characteristics best and most reliably explained the variability in fish SOC concentrations measured. Additionally, the role that physical chemical properties might play in governing the deposition and accumulation of SOCs in high elevation fish was discussed.

The effects of 7 fish and 9 ecosystem characteristics' on fish contaminant concentrations were tested for 28 SOCs in samples from lakes across Western US National Parks. Lipid, followed by age, were the most reliable fish characteristics explaining organic contaminant concentrations in fish tissues from cold North American lakes. Lipid was most significant and explanatory for most pesticide concentrations. Fish age better explained p,p'-DDE, mirex, PCB, and PBDE concentrations. After adjusting for lipid or age, mean daily air temperature (-8.8 to 6.9 °C) was the most significant and explanatory ecosystem characteristic for most of the historic use pesticides concentrations in fish, especially the more volatile. Contaminant deposition to the ecosystem from snow was the most predictive ecosystem characteristic for fish concentrations of the lipid adjusted current use pesticides dacthal and endosulfans. Elevation was the most significant ecosystem factor explaining concentrations of p,p'-DDE, mirex, PCBs, and PBDEs after adjusting for age of the fish. Proximity to sources (agricultural intensity or population density also explained a significant amount of several pesticides' and PBDEs' fish concentrations. Some evidence was observed for interactions between ecosystem temperature and fish growth rate effects as well as lake productivity and lipid effects on contaminant concentrations in fish.

Other less important characteristics that were significantly correlated with some contaminants' fish concentrations were growth rate (positive and negative), lake productivity(negative), and the age of the males and immature females (positive, and significant even when age of all fish was not significant). Slopes of several contaminants' concentration vs. growth rate regressions systematically and significantly decreased with decreasing ecosystem temperature, and several contaminants' concentration-lipid regression slopes decreased at lakes with increased lake productivity.

From the work here it is clear that instrumentation and methods exist to measure a wide range of SOCs at pg/g concentrations in fish tissues from remote high elevation ecosystems. However, it is also clear that for 63 of the compounds measured here, concentrations in fish are less than the low pg/g detection limits, likely much lower for compounds where frequency of non-detects was greater than 60% (PAHs, β, δ-HCH, heptachlor, aldrin, endrin, endrin aldehyde, triallate, chlorpyrifos, etridiazole, parathion, methyl parathion, ethion, and DDTs other than p,p'-DDE). This is a large analytical challenge that should be addressed if accurate environmental fate studies are needed for these compounds. Also, large quantities of solvent, and many hours of labor were required for the analytical measurements presented here. Reliable, affordable, low solvent use, and analyst friendly sample preparation techniques should be developed if accurate measurements of these compounds in fish are needed on a larger scale.

It is also clear from this work that the potential for human health effects from contaminants through fish consumption can be realized with-out point source contributions, but rather through contaminant redistribution and bioaccumulation, even in remote environments. Although altitudinal and temperature effects on contaminant accumulation have now been well documented, it has been shown that in locations other than altitudinal transects factors such as proximity to source regions, or precipitation patterns are important in describing relative levels of contaminants in remote lake ecosystems. Because few people interact with such remote ecosystems it may also be important to better understand the characteristics driving fish contaminant concentrations at slightly less remote locations, especially colder locations with older, larger fish. One question that arises is whether there are frequent scenarios where the characteristics identified here cease to explain fish contaminant concentrations. For example, does proximity to sources cease to explain variability in fish pesticide concentrations when all the fish studied are with 10 miles of major agricultural use, what if they are within 1 mile? If such is the case, the sites studied here would not permit this kind of an analysis. Also, the potential impacts on wildlife should be addressed as wildlife subsist on fish from these lakes to a much greater degree than most humans.

It is clear from this work that even with several characteristics combined we can often explain a little more than 50% of the variability in the fish contaminant concentrations. This suggests that if we were to apply our models to other locations and fish, even similar ones, we could likely only predict 50% of the variability. Since the concentrations in the fish varied over an order of magnitude within one lake and one species, it is important to be able to explain more than 50% of the variability to more accurately predict consumption risks.

It also appears that interactions may be occurring between different fish and ecosystem characteristics and their effects fish contaminant concentrations. This seems especially to be the case for temperature. However, lingering doubts remain because this was only observed for a few SOCs. This should be more rigorously tested. Controlled observation studies should be conducted on different temperature lakes with near identical atmospheric inputs to test for temperature interactions. These interactions are not easily modeled, can easily be missed in small datasets, and can have large impacts when the interaction is strong or the two factors are strongly related to the contaminant concentrations.

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Appendix A

Abbreviation	Full Name	Units	Description
Sample No			unique identifier
Fish #			2nd unique identifier
Park			4 letter Park code
Lake			Lake Name
extracted g		g	mass extracted
lipid %ww		%	solvent extractable lipid
moisture %ww		%	water in homogenate
TFNL	Trifluralin	ng/g ww	ww = wet weight
HCB	Hexachlorobenzene	ng/g ww	ww = wet weight
HCH	Hexachlorcyclohexane	ng/g ww	ww = wet weight
TRLTE	Triallate	ng/g ww	ww = wet weight
HCLR	Heptachlor	ng/g ww	ww = wet weight
DCPA	Dacthal	ng/g ww	ww = wet weight
Aldrin	Aldrin	ng/g ww	ww = wet weight
CLPYR O	Chlorpyrifos oxon	ng/g ww	ww = wet weight
CLPYR	Chlorpyrifos	ng/g ww	ww = wet weight
HCLR E	Heptachlor epoxide	ng/g ww	ww = wet weight
o-CLDN	Chlordane, oxy	ng/g ww	ww = wet weight
t-CLDN	Chlordane, trans	ng/g ww	ww = wet weight
ENDO I	Endosulfan I	ng/g ww	ww = wet weight
c-CLDN	Chlordane, cis	ng/g ww	ww = wet weight
t-NCLR	Nonachlor, trans	ng/g ww	ww = wet weight
Dieldrin	Dieldrin	ng/g ww	ww = wet weight
PCB	Polychlorinated biphenyl	ng/g ww	ww = wet weight
Endrin	Endrin	ng/g ww	ww = wet weight
ENDO II	Endosulfan II	ng/g ww	ww = wet weight
c-NCLR	Nonachlor, cis	ng/g ww	ww = wet weight
Endrin A	Endrin aldehyde	ng/g ww	ww = wet weight
ENDO S	Endosulfan Sulfate	ng/g ww	ww = wet weight
Mirex	Mirex	ng/g ww	ww = wet weight
ETDZL	Etridiazole	ng/g ww	ww = wet weight
ACY	Acenaphthylene	ng/g ww	ww = wet weight
ACE	Acenaphthene	ng/g ww	ww = wet weight
FLO	Fluorene	ng/g ww	ww = wet weight
PHE	Phenanthrene	ng/g ww	ww = wet weight
ANT	Anthracene	ng/g ww	ww = wet weight
PTHN	Parathion	ng/g ww	ww = wet weight
ETHN	Ethion	ng/g ww	ww = wet weight
FLA	Fluoranthene	ng/g ww	ww = wet weight
PYR	Pyrene	ng/g ww	ww = wet weight
Retene	Retene	ng/g ww	ww = wet weight
DDE	dichlorodiphenyldichloroethylene	ng/g ww	ww = wet weight
DDD	dichlorodiphenyldichloroethane	ng/g ww	ww = wet weight
DDT	dichlorodiphenyltrichloroethane	ng/g ww	ww = wet weight
MXCLR	Methoxychlor	ng/g ww	ww = wet weight
B[a]A	Benzo(a)anthracene	ng/g ww	ww = wet weight
CHR/TRI	Chrysene + Triphene	ng/g ww	ww = wet weight
B[b]F	Benzo(b)fluoranthene	ng/g ww	ww = wet weight
B[k]F	Benzo(k)fluoranthene	ng/g ww	ww = wet weight
B[e]P	Benzo(e)pyrene	ng/g ww	ww = wet weight
B[a]P	Benzo(a)pyrene	ng/g ww	ww = wet weight
I[1,2,3-cd]p	Indeno(1,2,3-cd)pyrene	ng/g ww	ww = wet weight
D[ah]A	Dibenz(a,h)anthracene	ng/g ww	ww = wet weight
B[ghi]P	Benzo(ghi)perylene	ng/g ww	ww = wet weight
BDE	polybrominated diphenyl ether	ng/g ww	ww = wet weight

Sample No	Fish #	Park	Lake	extracted g	lipid %ww	moisture %ww	TFLN ng/g ww	HCB ng/g ww	a-HCH ng/g ww
36102	EM2	SEKI	Emerald	22.2	3.87	73.89		0.12	0.031
36103	EM3	SEKI	Emerald	22.1	4.58	75.96		0.17	0.023
36104	EM4	SEKI	Emerald	22	0.82	74.4		0.029	0.02
36105	EM5	SEKI	Emerald	21	2.95	76.15		0.15	-0.00028
36106	EM6	SEKI	Emerald	22	3.24	74.03		0.19	0.02
36109	EM9	SEKI	Emerald	22.4	3.68	67.49		0.44	-0.00026
36111	EM11	SEKI	Emerald	22.2	1.32	71.54			-0.00026
36113	EM13	SEKI	Emerald	23.1	3.05	73.14			0.021
36115	EM15	SEKI	Emerald	22.1	3.23	74.45		0.12	0.018
36118	EM18	SEKI	Emerald	20.2	1.86	78.57	0.042	0.24	0.099
36161	P1	SEKI	Pear	22.4	2.48	74.45		0.21	0.058
36162	P2	SEKI	Pear	22.1	1.77	78.95	0.0063	0.068	0.036
36163	P3	SEKI	Pear	22.2	1.18	75.93	0.17	0.16	0.04
36164	P4	SEKI	Pear	21.4	1.41	76.78		0.72	0.08
36165	P5	SEKI	Pear	22.5	3.14	76.79		0.12	0.018
36167	P7	SEKI	Pear	22.2	3.23	74.17	0.17	0.16	0.04
36168	P8	SEKI	Pear	22.6	2.7	75.21		0.46	0.082
36169	P9	SEKI	Pear	21.7	1.69	75.96		0.029	0.018
36170	P10	SEKI	Pear	22.3	3.99	70.4		0.46	0.083
36171	P11	SEKI	Pear	22.2	6.28	68.65		0.28	0.051
36230	ML10	ROMO	Mills	22.4	7.07	71.88		0.56	0.09
36231	ML11	ROMO	Mills	24.6	7.2	72.28		0.49	0.08
36232	ML12	ROMO	Mills	22.5	4.84	74.66			
36233	ML13	ROMO	Mills	22.2	7.36	72.67		0.36	0.074
36236	ML16	ROMO	Mills	24	6.27	72.67		0.43	0.077
36238	ML18	ROMO	Mills	22.1	5.6	75.23		0.45	-0.00027
36239	ML19	ROMO	Mills	21.9	6.45	73.03	0.084	0.47	
36240	ML20	ROMO	Mills	23.5	6.52	74.76	0.017	0.59	0.084
36241	ML21	ROMO	Mills	20.9	7	73.73		0.25	0.081
36243	ML23	ROMO	Mills	24.7	4.42	78.39	0.017	0.43	0.05
36283	LP3	ROMO	LonePine	23.8	1.32	81.79	0.028	0.11	0.0052
36284	LP4	ROMO	LonePine	22.2	2.08	75.88		0.18	-0.00026
36285	LP5	ROMO	LonePine	22.4	2.67	75.23	0.17	0.19	0.04
36286	LP6	ROMO	LonePine	22	1.41	78.57	0.019	0.25	0.1
36287	LP7	ROMO	LonePine	23.1	3.54	75.43		0.32	0.038
36290	LP10	ROMO	LonePine	22.3	2.7	77.48		0.2	0.034
36291	LP11	ROMO	LonePine	22.2	2.68	75.35		0.17	0.021
36292	LP12	ROMO	LonePine	22	3.63	76.31		0.25	-0.00027
36293	LP13	ROMO	LonePine	22.4	1.91	76.83		0.15	0.025
36295	LP15	ROMO	LonePine	21.3	2.73	75.72		0.17	-0.00028
46100	MA1	GAAR	Matcharak	22.8	2.56	74.52		0.37	0.13
46101	MA2	GAAR	Matcharak	20.8	2.67	75.41		0.32	0.15
46102	MA3	GAAR	Matcharak	22.2	4.78	74.1		0.98	0.16
46103	MA4	GAAR	Matcharak	22.2	5.88	74.94		1.3	0.2
46105	MA6	GAAR	Matcharak	19.7	2.92	75.56		0.7	0.15
46109	MA10	GAAR	Matcharak	22.2	5.66	75.36		0.74	0.21
46110	MA11	GAAR	Matcharak	22.2	4.32	77.91		0.44	0.15
46111	MA12	GAAR	Matcharak	23.1	2.82	76.99		0.27	0.12
46113	MA14	GAAR	Matcharak	22.7	1.88	79.76		0.13	0.085
46114	MA15	GAAR	Matcharak	21	2.94	79.83		0.32	0.11
46160	B1	GAAR	Burial	16	0.95	76.04		0.18	0.044
46161	B2	GAAR	Burial	23.4	2.7	72.57		0.4	0.089
46162	B3	GAAR	Burial	22.5	2.33	74.94		0.16	0.075
46163	B4	GAAR	Burial	22.1	2.16	74.24	0.019	0.29	0.13
46165	B6	GAAR	Burial	19.2	4.7	70.45		0.46	0.1
46166	B7	GAAR	Burial	23.1	4.42	73.63		0.58	0.12
46168	B9	GAAR	Burial	20.5	3.11	72.46		0.56	0.14
46170	B11	GAAR	Burial	20	5.22	70.05		0.8	0.21
46171	B12	GAAR	Burial	22.1	5.18	74.03		0.66	0.19
46172	B13	GAAR	Burial	20.3	3.49	74.94		0.44	0.14
46220	MC1	DENA	McLeod	21.1	5.57			0.62	0.64
46221	MC2	DENA	McLeod	15.5	4.73			0.57	0.19
46222	MC3	DENA	McLeod	36.5	1.15	81.95		0.31	0.041
46223	MC4	DENA	McLeod	35.2	1.49	80.43		0.18	0.056
56371		DENA	McLeod	20	1.51	81.57	0.019	0.16	0.043
56372		DENA	McLeod	20	1.38	79.45		0.15	0.05
46281	W2	DENA	Wonder	24.6	2.93	74.55		0.16	0.072
46288	W9	DENA	Wonder	22.2	7.04	74.94		0.705	0.32

Sample No	Fish #	Park	Lake	extracted g	lipid %ww	moisture %ww	TFLN ng/g ww	HCB ng/g ww	a-HCH ng/g ww
46291	W12	DENA	Wonder	20.5	1.21	80.88	0.11	0.7	0.18
46292	W13	DENA	Wonder	23.4	1.89	81.1		0.075	0.054
46293	W14	DENA	Wonder	22	8.15	69.68		0.63	0.32
46294	W15	DENA	Wonder	22.2	2.76	78.07			
46295	W16	DENA	Wonder	17.3	7.55	72.89	0.014	0.79	0.28
46297	W18	DENA	Wonder	26.5	6.28	73.17			0.26
46298	W19	DENA	Wonder	23.4	6.2	76.69		0.55	0.23
46299	W20	DENA	Wonder	22	4.63	75.12		0.37	0.085
56101	L1	MORA	LP19	21.9	3.86	73.55		0.19	0.061
56102	L3	MORA	LP19	22.4	1.13	82.9			0.014
56104	L5	MORA	LP19	22.2	6.34	72.35		0.39	0.0077
56106	L7	MORA	LP19	19.9	5.2	76.53	0.017	0.5	0.064
56107	L8	MORA	LP19	19.9	6.45	71.25	0.011	0.48	-0.0037
56108	L9	MORA	LP19	20	2.5	77.17	0.013	0.15	0.034
56111	L12	MORA	LP19	20.3	2.01	76.42	0.014	0.15	0.027
56112	L13	MORA	LP19	20	4.03	77.89	0.011	0.25	0.054
56113	L14	MORA	LP19	22.1	4.67	80.72		0.21	0.04
56114	L15	MORA	LP19	22.1	2.01	79.86		0.13	0.016
56147	G2	MORA	Golden	22.3	4.17	76.99		0.38	0.075
56148	G3	MORA	Golden	20	4.48	77.98		0.3	0.083
56149	G4	MORA	Golden	20	3.31	77.81		0.23	0.059
56151	G6	MORA	Golden	20	2.39	77.56		0.15	0.04
56153	G8	MORA	Golden	20.1	2.46	81.43		0.22	0.058
56154	G9	MORA	Golden	20	2.89	77.12		0.21	0.049
56156	G11	MORA	Golden	22.6	2.48	80.38		0.14	0.043
56157	G12	MORA	Golden	22.6	1.56	77.65		0.11	0.03
56158	G13	MORA	Golden	22.2	5.39	74.26		0.32	0.094
56159	G14	MORA	Golden	19.9	2.99	77.38	0.0059	0.21	0.057
56191	OL1	GLAC	Oldman	22.2	5.91	72.12		1.3	0.065
56192	OL2	GLAC	Oldman	22.4	9.43	70.72		1.2	0.054
56193	OL3	GLAC	Oldman	22.2	7.64	71.02		1.3	0.11
56196	OL6	GLAC	Oldman	22.6	10.51	82.93		1.6	0.087
56197	OL7	GLAC	Oldman	22.7	9.01	66.16		1.4	
56198	OL8	GLAC	Oldman	22.4	11.5	66.52		1.7	
56199	OL9	GLAC	Oldman	22.4	18.43	55.98		1.9	0.23
56200	OL10	GLAC	Oldman	22.3	11.07	81.04		1.2	0.13
56201	OL11	GLAC	Oldman	22.2	13.49	64.59		1.5	0.24
56205	OL15	GLAC	Oldman	22	1.78	77.45		0.33	0.035
56236	SN1	GLAC	Snyder	20	2.12	76.82	0.0042	0.12	0.019
56238	SN3	GLAC	Snyder	20	2.53	82.1	0.0071	0.21	-0.0037
56240	SN5	GLAC	Snyder	20	2.39	78.06	0.0057	0.12	0.026
56241	SN6	GLAC	Snyder	22.2	2.31	79.66		0.11	0.013
56244	SN9	GLAC	Snyder	22.1	3.87	74.89		0.18	0.008
56245	SN10	GLAC	Snyder	20.9	4.21	76.09		0.28	0.048
56246	SN11	GLAC	Snyder	16.9	6.94	76.67	0.11		-0.0044
56248	SN13	GLAC	Snyder	21.1	4.2	76.22	0.0085		0.019
56249	SN14	GLAC	Snyder	20.3	4.42	76.14	0.0087		0.022
56250	SN15	GLAC	Snyder	19.9	2.62	78.47	0.0079		0.033
56281	H1	OLYM	Hoh	22.1	0.29	81.48	-0.0003	0.13	-0.0033
56282	H2	OLYM	Hoh	22.3	0.71	83.33		0.014	0.0094
56283	H3	OLYM	Hoh	22.1	4.1	77.18		0.2	0.039
56284	H4	OLYM	Hoh	22.6	1.2	80.49		0.041	0.011
56285	H5	OLYM	Hoh	22.3	3.61	74.91		0.043	-0.0033
56286	H6	OLYM	Hoh	22.1	0.61	83.67		0.031	0.011
56287	H7	OLYM	Hoh	22.4	2.68	78.4		0.17	0.03
56288	H8	OLYM	Hoh	22.3	1.4	81.54		0.093	0.02
56289	H9	OLYM	Hoh	22.5	0.91	79.84	0.0083	0.14	0.03
56290	H10	OLYM	Hoh	22.3	0.61	75.22		0.019	0.0083
56326	PJ30	OLYM	PJ	22.5	1.32	77.49		0.12	0.011
56327	PJ31	OLYM	PJ	22.1	0.84	78.54		0.025	0.0091
56328	PJ32	OLYM	PJ	22	3.16	75.6		0.31	0.027
56329	PJ33	OLYM	PJ	18.8	1.57	78.59		0.13	0.017
56330	PJ34	OLYM	PJ	18.7	1.06	81.01	0.0048	0.065	0.012
56331	PJ35	OLYM	PJ	19.4	4.42	75.62		0.3	0.034
56332	PJ36	OLYM	PJ	19.2	4.74	78.07			
56334	PJ38	OLYM	PJ	20.9	2.41	61.23	0.0055	0.2	0.034
56336	PJ40	OLYM	PJ	21.7	1.69	70.42	0.0052	0.33	0.05
56337	PJ41	OLYM	PJ	18.6	2.63	81.89		0.031	0.0082

Sample No	g-HCH ng/g ww	b-HCH ng/g ww	d-HCH ng/g ww	TRLTE ng/g ww	HCLR ng/g ww	DCPA ng/g ww	Aldrin ng/g ww	CLPYR O ng/g ww	CLPYR ng/g ww
36102	-0.017	-0.0077	-0.00056	0.014	0.04	0.51	-0.021	-0.043	0.022
36103	-0.017	-0.0078	-0.00056	-0.01	0.00	0.73	-0.02	-0.04	0.03
36104	-0.017	-0.0078	-0.00056	-0.01	0.04	0.10	-0.02	-0.04	
36105	-0.018	-0.0082	-0.00059	-0.012	-0.0017	0.84	-0.022	-0.046	0.021
36106	-0.017	-0.0078	-0.00056	-0.011	-0.0016	0.79	-0.02	-0.04	0.02
36109	-0.017	-0.0077	-0.00055	-0.011	-0.0016	0.89	0.17	-0.04	0.00
36111	-0.017	-0.0077	-0.00056	-0.011	-0.0016	0.45	-0.02	-0.04	
36113	-0.017	-0.0074	-0.00054	-0.011	-0.0015	0.96	-0.02	-0.04	0.04
36115	-0.017	-0.0078	-0.00056	-0.011	-0.0016	0.38	-0.02	-0.04	
36118	0.042	-0.0094	-0.00068	-0.013	0.051	1.5	-0.03	-0.05	
36161	-0.017	-0.0077	-0.00055	-0.011	-0.0016	2.2	-0.02	-0.04	0.03
36162	-0.017	-0.0078	-0.00056	-0.011	-0.0016	0.61	-0.02	-0.04	0.00
36163	-0.017	-0.0077	-0.00056	-0.011	-0.0016	0.4	-0.02	-0.04	0.00
36164	-0.019	-0.0083	-0.0006	-0.012	-0.0017	0.62	-0.02	-0.05	
36165	-0.017	-0.0076	-0.00055	-0.011	-0.0016	0.37	-0.02	-0.04	
36167	-0.017	-0.0077	-0.00056	-0.011	-0.0016	0.4	-0.02	-0.04	0.00
36168	0.023	-0.0076	-0.00055	-0.011	0.03	0.65	-0.02	-0.04	0.01
36169	-0.018	-0.0079	-0.00057	-0.011	-0.0016	0.26	-0.02	-0.04	
36170	0.023	-0.0077	-0.00056	-0.011	0.03	0.65	-0.02	-0.04	0.01
36171	-0.017	-0.0077	0.018	-0.011	0.034	2.3	-0.02	-0.04	0.05
36230	0.02	-0.0077	-0.00056	-0.011	-0.0016	0.94	-0.02	-0.04	0.02
36231	0.05	-0.007	-0.0005	-0.0099	-0.0015	1.4	0.62	-0.04	
36232									
36233	0.027	-0.0077	-0.00056	-0.011	-0.0016	0.6	-0.02	-0.04	
36236	0.021	-0.0071	-0.00052	-0.01	0.028	0.61	-0.02	-0.04	0.01
36238	-0.017	-0.0078	-0.00056	-0.011	-0.0016	0.9	0.17	-0.04	0.00
36239									
36240	-0.015	-0.0068	-0.00049	-0.0097	-0.0014	0.79	-0.02	-0.04	0.07
36241	-0.02	-0.0088	-0.00064	-0.012	-0.0018	0.64	-0.02	-0.05	0.01
36243	-0.014	-0.0063	-0.00045	-0.0089	-0.0013	0.7	-0.02	-0.04	
36283	-0.015	-0.0068	-0.00049	0.037	-0.0014	0.16	-0.02	-0.04	0.13
36284	-0.017	-0.0077	-0.00056	-0.011	-0.0016	0.38	-0.02	-0.04	
36285	-0.017	-0.0077	-0.00055	-0.011	-0.0016	0.4	-0.02	-0.04	0.00
36286	0.043	-0.0078	-0.00056	0.081	0.086	0.35	-0.02	-0.04	
36287	-0.017	-0.0074	-0.00054	-0.011	-0.0015	0.49	-0.02	-0.04	
36290	-0.017	-0.0077	-0.00056	-0.011	0.035	0.45	-0.02	-0.04	
36291	-0.017	-0.0077	-0.00056	-0.011	-0.0016	0.21	-0.02	-0.04	0.02
36292	-0.017	-0.0078	-0.00056	-0.011	-0.0016	0.45	-0.02	-0.04	
36293	-0.017	-0.0077	-0.00055	-0.011	-0.0016	0.27	-0.02	-0.04	
36295	-0.018	-0.008	-0.00058	-0.011	-0.0017	0.37	-0.02	-0.05	
46100	0.033	-0.006	-0.008	-0.0015	-0.018	0.012	-0.03	-0.51	
46101	0.017	-0.0065	-0.0087	-0.0016	-0.019	0.0075	-0.03	-0.56	0.06
46102	0.028	-0.0061	-0.0082	-0.0015	-0.018	0.016	-0.03	-0.52	0.05
46103	0.025	-0.0061	-0.0082	-0.0015	-0.018	0.028	-0.03	-0.52	
46105	0.033	-0.0069	-0.0092	-0.0017	-0.021	0.016	-0.03	-0.59	
46109	0.033	-0.0061	-0.0082	-0.0015	-0.018	0.012	-0.03	-0.52	
46110	0.037	-0.0061	-0.0082	-0.0015	-0.018	0.015	-0.03	-0.52	
46111	0.027	-0.0059	-0.0079	-0.0015	-0.018	0.012	-0.03	-0.50	
46113	-0.0045	-0.006	-0.008	-0.0015	-0.018	0.013	-0.03	-0.51	
46114	0.011	-0.0068	-0.0091	-0.0017	-0.02	0.012	-0.031	-0.58	
46160	0.0077	-0.0085	-0.011	-0.0021	-0.025	0.0038	-0.039	-0.73	
46161	-0.0044	-0.0058	-0.0078	-0.0015	-0.017	0.02	-0.027	-0.49	
46162	-0.0046	-0.0061	-0.0081	-0.0015	-0.018	0.014	-0.028	-0.52	
46163	0.031	-0.0062	-0.0082	-0.0016	-0.018	0.011	-0.028	-0.53	0.089
46165	0.022	-0.0071	-0.0095	0.037	-0.021	0.038	-0.033	-0.6	
46166	0.024	-0.0059	-0.0079	-0.0015	-0.018	0.013	-0.027	-0.5	
46168	-0.005	-0.0067	-0.0089	-0.0017	-0.02	0.015	0.14	-0.57	
46170	-0.0052	-0.0068	-0.0091	-0.0017	-0.02	0.034	-0.031	-0.58	
46171	0.036	-0.0062	-0.0082	-0.0016	-0.018	0.019	-0.028	-0.53	0.1
46172	0.018	-0.0067	-0.009	-0.0017	-0.02	0.016	-0.031	-0.57	
46220	0.12	-0.0065	-0.0086	-0.0016	-0.019	0.016	-0.03	-0.55	
46221	0.033	-0.0088	-0.012	-0.0022	-0.026	0.013	-0.04	-0.75	
46222	0.0091	-0.0037	-0.005	0.0041	-0.011		-0.017	-0.32	
46223	0.013	-0.0039	-0.0052	-0.00097	-0.012		-0.018	-0.33	
56371	0.0078	-0.0068	-0.0091	-0.0017	-0.02	0.0054	-0.031	-0.58	0.094
56372	-0.0051	-0.0068	-0.0091	-0.0017	-0.02		-0.031	-0.58	
46281	0.012	-0.0055	-0.0074	-0.0014	-0.016	0.0083	-0.025	-0.47	
46288	0.0775	-0.00615	-0.0082	-0.00155	0.002	0.028	-0.028	-0.525	

Sample No	g-HCH ng/g ww	b-HCH ng/g ww	d-HCH ng/g ww	TRLTE ng/g ww	HCLR ng/g ww	DCPA ng/g ww	Aldrin ng/g ww	CLPYR O ng/g ww	CLPYR ng/g ww
46291	0.036	-0.0066	-0.0088	-0.0017	-0.02	0.029	-0.03	-0.56	
46292	0.013	-0.0058	-0.0078	-0.0015	-0.017	0.0041	-0.027	-0.5	
46293	0.085	-0.0062	-0.0083	-0.0016	-0.018	0.024	-0.028	-0.53	
46294									
46295	-0.006	-0.0079	-0.011	-0.002	-0.023	0.063	-0.036	-0.67	-0.0031
46297	0.061	-0.0051	-0.0069	-0.0013	-0.015		-0.024	-0.44	
46298	-0.0044	-0.0058	-0.0078	-0.0015	-0.017	0.027	-0.027	-0.5	
46299	0.018	-0.0062	-0.0082	-0.0016	-0.018	0.01	-0.028	-0.53	0.041
56101	0.013	-0.0062	-0.0083	-0.0016	-0.018	0.35	-0.028	-0.53	
56102	-0.0046	-0.0061	-0.0081	-0.0015	-0.018	0.062	-0.028	-0.52	
56104	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.32	-0.028	-0.52	
56106	-0.0052	-0.0069	-0.0091	-0.0017	-0.02	0.65	-0.031	-0.58	0.031
56107	-0.0052	-0.0069	-0.0091	-0.0017	-0.02	0.48	-0.031	-0.58	0.018
56108	-0.0051	-0.0068	-0.0091	-0.0017	-0.02	0.21	-0.031	-0.58	
56111	-0.0051	-0.0067	-0.009	-0.0017	-0.02	0.27	-0.031	-0.57	0.016
56112	0.0065	-0.0068	-0.0091	-0.0017	-0.02	0.49	-0.031	-0.58	0.02
56113	0.0072	-0.0062	-0.0082	-0.0016	-0.018	0.29	-0.028	-0.53	
56114	-0.0047	-0.0062	-0.0082	-0.0016	-0.018	0.08	-0.028	-0.52	
56147	0.0098	-0.0061	-0.0081	0.0036	-0.018	0.26	-0.028	-0.52	0.043
56148	0.017	-0.0068	-0.0091	-0.0017	-0.02	0.15	-0.031	-0.58	0.074
56149	0.0095	-0.0068	-0.0091	-0.0017	-0.02	0.16	-0.031	-0.58	0.036
56151	0.0081	-0.0068	-0.0091	-0.0017	0.078	0.056	-0.031	-0.58	
56153	-0.0051	-0.0068	-0.0091	-0.0017	-0.02	0.15	-0.031	-0.58	0.024
56154	-0.0052	-0.0068	-0.0091	-0.0017	-0.02	0.16	-0.031	-0.58	0.028
56156	0.0096	-0.006	-0.008	-0.0015	-0.018	0.11	-0.028	-0.51	0.034
56157	0.008	-0.006	-0.0081	-0.0015	-0.018	0.025	-0.028	-0.51	0.02
56158	0.016	-0.0061	-0.0082	-0.0015	-0.018	0.15	-0.028	-0.52	0.065
56159	0.011	-0.0068	-0.0091	-0.0017	-0.02	0.14	-0.031	-0.58	0.027
56191	0.017	-0.0061	-0.0082	0.055	-0.018	1.1	-0.028	-0.52	0.012
56192	-0.0046	-0.0061	-0.0081	0.21	-0.018	2.6	-0.028	-0.52	0.018
56193	0.054	-0.0061	-0.0082	0.11	-0.018	1.7	-0.028	-0.52	0.018
56196	0.033	-0.006	-0.008	0.15	-0.018	2.4	-0.028	-0.51	0.015
56197		-0.006	-0.008	0.1	-0.018	2.1	-0.028	-0.51	
56198	-0.0046	-0.0061	-0.0081	0.11	-0.018	4	-0.028	-0.52	
56199		-0.0061	-0.0081	0.15	-0.018	4	-0.028	-0.52	
56200	-0.0046	-0.0061	-0.0082	0.13	-0.018	3.3	-0.028	-0.52	0.035
56201	0.12	-0.0061	-0.0082	0.34	-0.018	4.8	-0.028	-0.52	
56205	0.017	-0.0062	-0.0083	0.083	0.045	0.46	-0.028	-0.53	
56236	-0.0051	-0.0068	-0.0091	-0.0017	-0.02	0.076	-0.031	-0.58	0.0071
56238	-0.0052	-0.0068	-0.0091	-0.0017	-0.02	0.061	-0.031	-0.58	0.013
56240	-0.0051	-0.0068	-0.0091	-0.0017	-0.02	0.065	-0.031	-0.58	0.0077
56241	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.069	-0.028	-0.52	
56244	-0.0047	-0.0062	-0.0082	-0.0016	-0.018	0.15	-0.028	-0.53	
56245	-0.0049	-0.0065	-0.0087	-0.0016	-0.019	0.2	-0.03	-0.55	0.019
56246	-0.0061	-0.0081	-0.011	-0.002	-0.024		-0.037	-0.69	-0.0032
56248	-0.0049	-0.0065	-0.0086	-0.0016	-0.019	0.022	-0.03	-0.55	0.0084
56249	-0.0051	-0.0067	-0.009	-0.0017	-0.02	-0.015	-0.031	-0.57	0.0087
56250	-0.0052	-0.0069	-0.0092	-0.0017	-0.02		-0.031	-0.58	0.011
56281	-0.0047	-0.0062	-0.0082	-0.0015	-0.018	-0.00035	-0.028	-0.52	-0.0024
56282	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.0066	-0.028	-0.52	0.01
56283	0.0058	-0.0062	-0.0082	-0.0015	-0.018	0.064	-0.028	-0.52	0.013
56284	-0.0046	-0.006	-0.008	-0.0015	-0.018	0.012	-0.028	-0.51	0.008
56285	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.014	-0.028	-0.52	0.0071
56286	-0.0047	-0.0062	-0.0082	-0.0016	-0.018	0.012	-0.028	-0.52	0.013
56287	0.026	-0.0061	-0.0081	-0.0015	-0.018	0.059	-0.028	-0.52	0.0087
56288	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.023	-0.028	-0.52	0.013
56289	-0.0046	-0.0061	-0.0081	-0.0015	-0.018	0.058	-0.028	-0.52	0.012
56290	-0.0046	-0.0061	-0.0082	-0.0015	-0.018	0.0061	-0.028	-0.52	0.0069
56326	-0.0046	-0.006	-0.0081	-0.0015	-0.018		-0.028	-0.51	
56327	-0.0047	-0.0062	-0.0082	-0.0015	-0.018		-0.028	-0.52	
56328	0.0063	-0.0062	-0.0083	-0.0016	-0.018	0.013	-0.028	-0.53	
56329	-0.0055	-0.0072	-0.0097	-0.0018	-0.022	0.0088	-0.033	-0.62	0.0056
56330	-0.0055	-0.0073	-0.0097	-0.0018	-0.022	0.013	-0.033	-0.62	0.01
56331	-0.0053	-0.007	-0.0094	-0.0018	-0.021	0.015	-0.032	-0.6	0.0077
56332									
56334	0.007	-0.0065	-0.0087	-0.0016	-0.019	0.014	-0.03	-0.56	0.011
56336	0.0069	-0.0063	-0.0084	-0.0016	-0.019	0.02	-0.029	-0.53	0.009
56337	-0.0055	-0.0073	-0.0098	-0.0018	-0.022		-0.034	-0.62	0.0073

Sample No	HCLR E ng/g ww	o-CLDN ng/g ww	t-CLDN ng/g ww	c-CLDN ng/g ww	t-NCLR ng/g ww	c-NCLR ng/g ww	ENDO I ng/g ww	ENDO II ng/g ww	ENDO S ng/g ww
36102	0.029	0.11		0.076	0.4		0.087	0.024	1.3
36103	0.026	0.18	0.088	0.031	0.71	0.4	0.24	0.026	1.1
36104	-0.014	0.033	0.009	-0.016	0.28	0.058	0.021	0.011	0.18
36105	-0.014	0.077	0.041	0.053	0.28	0.2	0.064	0.024	0.18
36106	0.024	0.14	0.093	0.089	0.47	0.24	0.1		
36109	0.38	0.15	0.19	0.11	0.48	0.26	0.22	0.1	0.042
36111	-0.014	0.11	0.06	0.049	0.68	0.33	0.083	0.045	0.73
36113	0.035	0.35	0.14	0.041	0.98	0.35	0.29	0.021	1.3
36115	-0.014	0.11	0.063	0.04	0.48	0.23	0.078	0.017	0.57
36118	0.094	0.1	0.044	0.057	0.54	0.15	0.13	0.049	1.9
36161	0.056	0.26	0.094	0.055	1.3	0.008	-0.0048	-0.0087	0.0067
36162	-0.014	0.074	0.032	0.032	0.24	0.1	0.056	0.017	0.71
36163	0.036	0.059	0.029	0.016	0.25	0.091	0.04	0.011	0.12
36164	0.15	0.19	0.26	0.24	0.65	0.086	0.38	0.068	0.28
36165	-0.013	0.1	0.062	0.039	0.47	0.22	0.077	0.017	0.56
36167	0.036	0.059	0.029	0.016	0.25	0.091	0.04	0.011	0.12
36168	0.11	0.11	0.11	0.08	0.35	0.19	0.34	0.11	0.72
36169	-0.014	0.05	0.018	-0.016	0.19	0.094	0.035	0.024	1.2
36170	0.11	0.11	0.11	0.081	0.35	0.19	0.34	0.11	0.73
36171	0.049	0.24	0.17	0.14	0.99	0.6	0.4		2.4
36230	-0.013	0.092	0.11	0.12	0.3	0.3	0.26	0.13	0.093
36231	0.21	0.13	0.14	0.16	0.39	0.35	0.29	0.3	0.17
36232									
36233	0.087	0.091		0.067			0.18	0.095	1.2
36236	0.099	0.1	0.1	0.075	0.33	0.18	0.32	0.1	0.68
36238	0.39	0.15	0.2	0.11	0.49	0.26	0.22	0.1	0.043
36239									
36240	-0.014	0.15	0.11	0.15	0.25	0.12	0.43	0.13	1.1
36241	0.049	0.047	0.037	0.04	0.056	0.06	0.13	0.074	0.41
36243	0.053	0.11	0.1	0.12	0.44	0.34	0.13	0.056	0.86
36283	-0.012	0.026	0.055	0.051	0.14	0.065	0.023	-0.0077	0.17
36284	-0.014	0.079	0.026	0.18	0.17	0.069	0.053	0.022	0.13
36285	0.036	0.059	0.028	0.016	0.25	0.091	0.039	0.011	0.12
36286	0.077	0.11	0.028	0.28	0.35	0.29	0.033	0.042	0.047
36287	0.053	0.1	0.04	0.036	0.33	0.14	0.047	0.015	0.19
36290	0.05	0.073	0.031	0.021	0.32	0.11	0.044	0.029	0.37
36291	0.036	0.048	0.014	0.021	0.13	0.062	0.02	0.026	0.21
36292	0.044	0.067	0.025	0.056	0.25	0.08	0.051	0.011	0.29
36293	0.026	0.049	0.02	0.026	0.34	0.13	0.025	-0.0087	0.19
36295	-0.014	0.093	0.019	0.08	0.14	0.064			
46100	-0.012	0.032	0.011	0.085	0.15	0.11	0.0051	0.0095	0.0054
46101	-0.013	0.095	0.022	0.16	0.64	0.42	-0.0022	-0.0034	0.0042
46102	0.053	0.11	0.039	0.19	0.45	0.39	0.011	0.013	0.0076
46103	0.085	0.26	0.081	0.41	1	0.94	-0.0021	-0.0032	-0.00067
46105	0.048	0.17	0.045	0.46	1.3	0.95			-0.00076
46109	0.042	0.16	0.038	0.3	1	0.85			-0.073
46110	0.029	0.063	0.013	0.16	0.25	0.17			-0.00067
46111	0.29	0.061	0.018	0.13	0.37	0.35		0.023	-0.00065
46113	0.02	0.024	0.0056	0.026	0.076	0.052	-0.002	0.013	-0.00066
46114	0.035	0.04	0.012	0.06	0.11	0.077	0.0035	0.023	0.0053
46160	-0.017	0.033	0.0062	0.12	0.46	0.25	-0.0029	-0.0044	0.036
46161	0.1	0.11	0.017	0.12	0.24	0.15	0.011	0.033	-0.00064
46162	0.037	0.068	0.022	0.1	0.36	0.19	0.0073	0.0087	-0.00066
46163	-0.013	0.15	0.019	0.16	0.4	0.17	0.01	0.023	-0.00067
46165	0.063	0.093	0.018	0.17	0.3	0.19	0.0041		-0.00078
46166	0.061	0.14	0.037	0.24	0.8	0.56	0.02	0.02	0.092
46168	0.072	0.12	0.032	0.13	0.3	0.21	0.0097	0.013	0.011
46170	0.092	0.15	0.053	0.24	0.5	0.32	0.041	0.02	0.02
46171	0.069	0.074	0.026	0.11	0.24	0.23	0.02	-0.086	-0.00067
46172	0.056	0.068	0.031	0.11	0.3	0.18	0.024	0.0056	0.02
46220	0.066	0.057	0.022	0.099	0.12	0.17	0.051	0.006	0.2
46221	0.048	0.071	0.03	0.15	0.24	0.26	0.031	-0.0045	0.068
46222	0.015	0.035		0.023	0.075	0.086		-0.0019	0.2
46223	0.015	0.016		-0.014	0.036	0.039		0.0024	0.28
56371	0.018	0.02	0.0089	-0.024	0.034	0.046	0.016	0.015	0.13
56372	0.016	0.015	0.0039	-0.024	0.03	0.036	0.0037	-0.0035	0.11
46281	0.02	0.067	0.034	0.25	0.87	0.68	0.0045	0.0067	0.0048
46288	0.0865	0.12	0.035	0.195	0.68	0.51	0.012	0.009	0.0325

Sample No	HCLR E ng/g ww	o-CLDN ng/g ww	t-CLDN ng/g ww	c-CLDN ng/g ww	t-NCLR ng/g ww	c-NCLR ng/g ww	ENDO I ng/g ww	ENDO II ng/g ww	ENDO S ng/g ww
46291	0.046	0.13	0.025	0.33	1.3	0.95	-0.0035		0.074
46292	-0.012	0.022	0.0062	0.077	0.37	0.29	0.0027	0.005	-0.00064
46293	0.072	0.068	0.016	0.085	0.25	0.19	0.0063	-0.0032	0.016
46294									
46295	0.11	0.13	0.098	0.4	0.85	0.68	0.019	0.028	-0.00086
46297	0.097	0.12		0.21	0.35	0.4			0.0053
46298	0.066	0.14	0.053	0.35	1.1	0.83	0.0068	0.016	-0.00064
46299	0.043	0.12	0.03	0.32	1.2	0.51	0.013	-0.0032	0.035
56101	0.018	0.044	0.014	-0.022	0.13	0.035	0.15	0.038	0.73
56102	-0.012	0.013	0.0028	-0.021	0.034	0.0074	0.017	0.009	0.12
56104	0.015	0.044	0.022	0.048	0.15	0.066	0.049	0.024	0.072
56106	0.04	0.073	0.022	0.036	0.17	0.033	0.21	0.045	0.32
56107	0.064	0.13	0.032	0.04	0.22	0.066	0.086	0.039	0.11
56108	0.016	0.037	0.013	-0.024	0.12	0.03	0.064	0.023	0.24
56111	-0.014	0.041	0.011	-0.024	0.095	0.024	0.055	0.031	0.32
56112	0.024	0.057	0.016	0.032	0.097	0.025	0.12	0.051	0.32
56113	0.016	0.044	0.012	-0.022	0.076	0.02	0.1	0.041	0.32
56114	-0.013	0.019	0.0046	-0.022	0.033	0.0083	0.03	0.014	0.11
56147	0.03	0.11	0.033	0.031	0.27	0.096	0.048	0.024	0.32
56148	0.033	0.098	0.032	0.033	0.19	0.069	0.052	0.027	0.43
56149	0.024	0.075	0.021	0.025	0.18	0.061	0.063	0.028	0.28
56151	0.026	0.075	0.019	-0.024	0.16	0.048	0.02	0.011	0.019
56153	0.024	0.092	0.018	0.029	0.24	0.062	0.023	0.013	0.29
56154	0.03	0.092	0.018	0.027	0.24	0.06	0.025	0.016	0.13
56156	0.017	0.049	0.015	0.022	0.14	0.04	0.037	0.018	0.14
56157	0.017	0.057	0.011	-0.021	0.15	0.16	0.018	0.012	0.62
56158	0.044	0.12	0.035	0.042	0.18	0.063	0.054	0.029	0.23
56159	0.023	0.08	0.025	0.024	0.23	0.086	0.042	0.024	0.13
56191	0.11	0.23	0.53	0.64	1.3	0.78	0.25	0.054	0.2
56192	0.23	0.23	0.4	0.56	0.87	0.53	0.46	0.16	0.26
56193	0.15	0.28	0.76	0.96	1.9	1.2	0.38	0.14	0.34
56196	0.25	0.31	0.55	0.67	1.3	0.8	0.37	0.11	0.27
56197	0.17	0.19	0.38	0.41	0.95	0.57	0.28		0.33
56198	0.23	0.26	0.66	0.71	1.5	0.84	0.47	0.15	
56199	0.34	0.28	0.55	0.52	1.3	0.67	0.48	0.1	0.57
56200	0.19	0.19	0.28	0.36	0.88	0.49	0.51	0.074	0.45
56201	0.26	0.15	0.29	0.48	0.6	0.41	0.55	0.19	0.63
56205	0.023	0.14	0.35	0.55	1.3	0.93	0.043	0.023	0.079
56236	0.014	0.024	0.02	0.04	0.13	0.052	0.034	0.032	0.12
56238	-0.014	0.025	0.0096	0.032	0.11	0.04	0.02	0.031	0.17
56240	-0.014	0.027	0.0096	0.018	0.084	0.028	0.026	0.039	0.033
56241	-0.013	0.022	0.0074	0.017	0.059	0.021		0.04	0.13
56244	0.014	0.058	0.018	0.04	0.16	0.043	0.029	0.099	0.17
56245	0.014	0.033	0.01	0.017	0.086	0.035	0.047	0.062	0.18
56246	-0.016	0.086	0.03	0.4	0.29	0.75	0.16	1.4	2.3
56248	-0.013	0.025	0.013	0.018			0.022		0.18
56249	0.014	0.029	0.013	0.024			0.022		0.19
56250	-0.014	0.034	0.0076	0.013			0.013		0.13
56281	-0.013	-0.0092	-0.00028	-0.0049	-0.00048	-0.0019	-0.0021	-0.0032	-0.00067
56282	-0.012	-0.0091		-0.0048	0.0059	-0.0019	0.0039	-0.0031	0.0053
56283	-0.013	0.035	0.012	0.03	0.14	0.059	0.0058	-0.0032	0.024
56284	-0.012	0.013	0.0021	0.0089	0.11	0.04	0.0032	-0.0031	0.0077
56285	-0.012	0.0098	0.0027	0.017	0.099	0.043	0.0086	-0.0031	0.0089
56286	-0.013	0.011		0.009	0.09	0.027	0.0065	-0.0032	0.013
56287	0.013	0.035	0.0067	0.016	0.11	0.048	0.0074	-0.0031	0.022
56288	-0.012	0.015	0.002	0.014	0.12	0.035	0.0067	-0.0031	0.012
56289	-0.012	0.022	0.006	0.015	0.12	0.044	0.0048	-0.0031	0.021
56290	-0.012	-0.0091		-0.0048	0.041	0.018	0.004	-0.0031	0.0061
56326	0.012	0.029		0.014	0.22	0.032		-0.0031	0.01
56327	-0.013	-0.0092		-0.0049	0.0095	-0.0019		0.0039	0.0057
56328	0.021	0.042		0.019	0.11	0.029		0.0041	0.033
56329	-0.015	-0.011	0.0024	-0.0057	0.047	0.013	0.0035	-0.0037	0.011
56330	-0.015	0.012	0.0042	0.0059	0.043	0.012	0.0056	-0.0038	0.011
56331	0.015	0.06	0.0056	0.02	0.083	0.017	0.0036	-0.0036	0.026
56332									
56334	-0.013	-0.0097	0.0055	0.0091	0.055	0.014	0.0091	0.0056	0.021
56336	0.015	0.026	0.01	0.015	0.087	0.028	0.0043	-0.0032	0.012
56337	-0.015	-0.011	0.0011	-0.0058	0.0056	-0.0023	0.0044	-0.0038	0.0053

Sample No	Dieldrin ng/g ww	Endrin ng/g ww	Endrin A ng/g ww	PCB 74 ng/g ww	PCB 101 ng/g ww	PCB 118 ng/g ww	PCB 153 ng/g ww	PCB 138 ng/g ww	PCB 187 ng/g ww
36102	1	-0.17	-0.023	-0.048	0.23	0.28	0.74	0.79	0.36
36103	1.7	-0.17	-0.023	-0.05	0.00	0.15	0.48	0.47	0.30
36104	0.23	-0.17	-0.023	-0.05	0.10	0.12	0.45	0.45	0.29
36105	1.6	-0.18	-0.024	-0.051	0.016	0.1	0.55	0.47	0.3
36106	1.3	-0.17	-0.023	-0.048	0.21	0.18	0.55	0.44	0.32
36109	3	-0.17	-0.023	-0.048	0.077	0.27	0.58	0.59	0.22
36111	0.76	-0.17	-0.023	-0.048	0.19	0.21	1.40	1.20	0.72
36113	2.1	-0.16	-0.022	-0.046	0.071	0.16	0.51	0.50	0.28
36115	0.85	-0.17	-0.023	-0.048	0.052	0.22	0.65	0.61	0.44
36118	2.2	-0.21	-0.028	-0.059	0.23	0.33	0.73	0.68	0.30
36161	2.5	-0.17	-0.023	-0.048	0.17	0.26	0.74	0.70	0.34
36162	0.51	-0.17	-0.023	-0.048	0.069	0.16	1.00	0.96	0.59
36163	0.83	-0.17	-0.023	-0.048	-0.0011	0.076	0.29	0.28	0.13
36164	3.3	-0.18	-0.025	-0.052	0.051	0.083	0.75	0.71	0.30
36165	0.83	-0.17	-0.023	-0.047	0.052	0.21	0.64	0.60	0.43
36167	0.83	-0.17	-0.023	-0.048	-0.0011	0.076	0.29	0.28	0.13
36168	2.2	0.2	-0.023	-0.047	0.14	0.2	0.47	0.53	0.17
36169	0.46	-0.17	-0.024	-0.049	0.046	0.05	0.51	0.49	0.30
36170	2.2	0.2	-0.023	-0.048	0.14	0.2	0.48	0.54	0.17
36171	4	-0.17	-0.023	-0.048	0.13	0.024	0.47	0.46	0.23
36230	3.9	-0.17	-0.023	-0.048	0.14	0.26	0.69	0.70	0.24
36231	3.1	-0.15	-0.021	-0.043	0.16	0.17	0.57	0.57	0.20
36232									
36233	2.3	-0.17	-0.023	-0.048					
36236	2	0.19	-0.021	-0.044	0.13	0.19	0.44	0.50	0.16
36238	3.1	-0.17	-0.023	-0.048	0.078	0.28	0.58	0.59	0.23
36239							0.26	0.38	0.09
36240	3.3	0.32	-0.02	-0.042	0.037	0.17	0.12	0.14	0.05
36241	1.5	-0.19	-0.026	-0.055	-0.0011	0.049	0.11	0.11	0.04
36243	5.1	-0.14	-0.019	-0.039	0.035	0.26	0.43	0.36	0.16
36283	14	-0.15	-0.02	-0.042	0.075	0.3	0.20	0.21	0.08
36284	1.1	-0.17	-0.023	-0.048	0.031	0.079	0.23	0.20	0.09
36285	0.83	-0.17	-0.023	-0.048	-0.0011	0.076	0.31	0.32	0.13
36286	1.7	-0.17	-0.023	-0.048	0.078	0.2	0.63	0.63	0.22
36287	0.92	-0.16	-0.022	-0.046	0.073	0.075	0.19	0.19	0.07
36290	0.96	-0.17	-0.023	-0.048	0.062	0.1	0.31	0.28	0.12
36291	0.69	-0.17	-0.023	-0.048	0.06	0.13	0.36	0.29	0.13
36292	1.3	-0.17	-0.023	-0.048	0.052	0.07	0.16	0.15	0.06
36293	0.91	-0.17	-0.023	-0.048	0.12	0.2	0.57	0.51	0.20
36295	1.2	-0.18	-0.024	-0.05	0.046	0.062	0.41	0.41	0.14
46100	0.12	-0.064	-0.0092	-0.11	-0.044	0.12	0.32	0.27	0.08
46101	0.18	-0.07	-0.01	-0.12	0.39	0.4	0.95	0.81	0.33
46102	0.38	-0.065	-0.0094	-0.11	0.22	0.25	0.55	0.47	0.19
46103	0.53	-0.065	-0.0094	-0.11	0.39	0.4	0.85	0.71	0.29
46105	0.75	-0.074	-0.011	-0.13	0.69	0.65	1.60	1.40	0.56
46109	0.28	-0.065	-0.0094	-0.11	0.62	0.6	1.50	1.30	0.48
46110	0.23	-0.065	-0.0094	-0.11	0.16	0.26	0.97	0.77	0.34
46111	0.19	-0.063	-0.0091	-0.11	-0.043	0.25	0.67	0.54	0.24
46113	0.13	-0.064	-0.0092	-0.11	-0.044	0.033	0.14	0.11	0.04
46114	0.19	-0.072	-0.01	-0.13	-0.05	0.049	0.18	0.14	0.083
46160	0.23	-0.091	-0.013	-0.16	0.1	0.43	3	2.4	0.55
46161	0.43	-0.062	0.01	-0.11	-0.043	0.15	0.61	0.5	0.12
46162	0.26	-0.065	-0.0093	-0.11	-0.045	0.19	0.71	0.55	0.25
46163	0.19	-0.066	-0.0095	-0.11	0.21	0.26	0.69	0.57	0.11
46165	0.53	-0.076	-0.011	-0.13	-0.052	0.19	0.63	0.52	0.12
46166	0.58	-0.063	-0.0091	-0.11	0.25	0.37	1.2	1	0.36
46168	0.48	-0.071	-0.01	-0.12	-0.049	0.21	0.83	0.77	0.16
46170	0.88	-0.073	-0.01	-0.13	0.14	0.29	0.92	0.74	0.19
46171	0.62	-0.066	-0.0095	0.18	0.13	0.25	0.75	0.48	0.13
46172	0.58	-0.071	-0.01	-0.12	-0.049	0.18	0.56	0.44	0.14
46220	1	-0.069	-0.0099	-0.12	-0.048	0.043	0.12	0.13	0.033
46221	0.6	-0.093	-0.013	-0.16	0.094	0.09	0.3	0.28	0.11
46222	0.09	-0.04	-0.0057	-0.069	-0.027	0.044	0.17	0.17	0.014
46223	0.1	-0.041	-0.006	-0.071	-0.029	0.02	0.059	0.051	0.009
56371	0.15	-0.073	-0.01	-0.13	-0.05	0.031	0.09	0.09	0.0065
56372	0.13	-0.072	-0.01	-0.12	-0.05	0.018	0.078	0.077	0.0046
46281	0.17	-0.059	-0.0085	-0.1	0.049	0.43	1.6	1.4	0.56
46288	0.625	-0.0655	0.00275	-0.11	-0.0455	0.32	0.93	0.765	0.315

Sample No	Dieldrin ng/g ww	Endrin ng/g ww	Endrin A ng/g ww	PCB 74 ng/g ww	PCB 101 ng/g ww	PCB 118 ng/g ww	PCB 153 ng/g ww	PCB 138 ng/g ww	PCB 187 ng/g ww
46291	0.51	-0.071	-0.01	-0.12	-0.049	0.29	1.5	0.8	0.54
46292	0.14	-0.062	-0.009	-0.11	-0.043	0.22	0.98	0.78	0.5
46293	0.55	-0.066	-0.0095	-0.11	-0.046	0.14	0.37	0.31	0.11
46294									
46295	0.85	-0.084	-0.012	-0.14	-0.058	0.25	0.79	0.7	0.28
46297	0.79	-0.055	-0.0079	-0.095	-0.038				
46298	0.52	-0.062	-0.009	-0.11	0.054	0.43	1.4	1.3	0.53
46299	0.5	-0.066	-0.0095	-0.11	-0.045	0.34	0.98	1.4	0.34
56101	0.23	-0.066	-0.0095	-0.11	0.18	0.29	0.5	0.37	0.24
56102	0.046	-0.065	-0.0093	-0.11	0.1	0.17	0.67	0.47	0.31
56104	0.39	-0.065	-0.0094	-0.11	0.19	0.17	0.28	0.24	0.13
56106	0.61	-0.073	-0.011	-0.13	0.17	0.32	0.57	0.37	0.28
56107	0.58	-0.073	-0.011	-0.13	0.18	0.21	0.32	0.27	0.15
56108	0.24	-0.072	-0.01	-0.12	0.12	0.24	0.44	0.32	0.19
56111	0.2	-0.072	-0.01	-0.12	0.13	0.34	0.95	0.7	0.44
56112	0.34	-0.073	-0.01	-0.13	0.11	0.18	0.38	0.29	0.19
56113	0.3	-0.066	-0.0095	-0.11	0.095	0.21	0.56	0.33	0.28
56114	0.091	-0.066	-0.0095	-0.11	0.067	0.22	0.72	0.44	0.31
56147	0.48	-0.065	-0.0094	-0.11	0.16	0.32	0.68	0.55	0.35
56148	0.5	-0.073	-0.01	-0.13	0.19	0.3	0.49	0.41	0.23
56149	0.3	-0.073	-0.01	-0.13	0.19	0.24	0.49	0.4	0.22
56151	0.14	-0.073	-0.01	-0.13	0.13	0.25	0.6	0.49	0.29
56153	0.41	-0.072	-0.01	-0.12	0.18	0.31	0.67	0.54	0.32
56154	0.44	-0.073	-0.01	-0.13	0.18	0.31	0.67	0.52	0.32
56156	0.17	-0.064	-0.0093	-0.11	0.14	0.24	0.51	0.4	0.24
56157	0.089	-0.064	-0.0093	-0.11	0.15	0.22	0.57	0.47	0.28
56158	0.48	-0.065	-0.0094	-0.11	0.14	0.19	0.36	0.32	0.18
56159	0.22	-0.073	-0.011	-0.13	0.15	0.3	0.76	0.65	0.42
56191	1.8	-0.065	-0.0094	-0.11	0.3	0.45	0.9	0.82	0.44
56192	2.2	-0.065	-0.0093	-0.11	0.17	0.31	0.61	0.57	0.29
56193	2.1	-0.065	-0.0094	-0.11	0.42	0.62	1.3	1.2	0.64
56196	2.7	-0.064	-0.0093	-0.11	0.26	0.4	0.9	0.82	0.44
56197	2.3	-0.064	0.089	-0.11	0.19	0.28	0.53	0.5	0.24
56198	3.9	-0.065	-0.0094	-0.11	0.28		0.84	1	0.39
56199	3.6	0.074	-0.0093	-0.11	0.26	0.44	0.84	0.82	0.4
56200	3	-0.065	-0.0094	-0.11	0.24	0.1	0.53	0.5	0.24
56201	2.6	-0.065	-0.0094	-0.11	0.064	0.18	0.54	0.56	0.21
56205	0.31	-0.066	-0.0095	-0.11	0.37	0.46	1.5	1.4	0.6
56236	0.29	-0.073	-0.01	-0.13	-0.05	0.2	0.44	0.43	0.18
56238	0.089	-0.073	-0.01	-0.13	-0.05	0.086	0.26	0.26	0.1
56240	0.11	-0.073	-0.01	-0.13	-0.05	0.14	0.32	0.35	0.15
56241	0.16	-0.065	-0.0094	-0.11	-0.045	0.054	0.18	0.18	0.088
56244	0.31	-0.066	-0.0095	-0.11	-0.045	0.15	0.33	0.38	0.16
56245	0.25	-0.069	-0.01	-0.12	-0.048	0.049	0.13	0.13	0.055
56246	-0.032	-0.086	-0.012	-0.15	-0.059	-0.0046	0.27		
56248	0.14	-0.069	-0.0099	-0.12	-0.048	0.11	0.23		0.082
56249	0.16	-0.071	-0.01	-0.12	-0.049	0.11	0.22		0.084
56250	0.12	-0.073	-0.011	0.24	-0.05	0.088	0.23		
56281	-0.025	-0.066	-0.0095	-0.11	-0.045	-0.0035	-0.0012	-0.0021	-0.00036
56282	-0.025	-0.065	-0.0094	-0.11	-0.045	0.02	0.12	0.099	0.05
56283	0.15	-0.066	-0.0095	-0.11	-0.045	0.073	0.19	0.19	0.066
56284	-0.024	-0.064	-0.0093	-0.11	-0.044	0.11	0.33	0.36	0.12
56285	-0.025	-0.065	-0.0094	-0.11	-0.045	0.11	0.35	0.33	0.14
56286	-0.025	-0.066	-0.0095	-0.11	-0.045	0.1	0.3	0.3	0.096
56287	-0.024	-0.065	-0.0093	-0.11	-0.045	0.05	0.17	0.2	0.055
56288	-0.025	0.7	0.04	-0.11	-0.045	0.11	0.36	0.36	0.13
56289	0.091	-0.065	-0.0093	-0.11	0.056	0.12	0.34	0.36	0.1
56290	0.027	-0.065	-0.0094	-0.11	-0.045	0.074	0.32	0.3	0.11
56326	0.087	-0.064	-0.0093	-0.11	0.046	0.11	0.33	0.3	0.11
56327	-0.025	-0.066	-0.0095	-0.11	-0.045	0.03	0.11	0.1	0.056
56328	0.11	-0.066	-0.0095	-0.11	-0.046	0.062	0.19	0.15	0.064
56329	0.03	-0.077	-0.011	-0.13	-0.053	0.066	0.19	0.18	0.083
56330	0.031	-0.078	-0.011	-0.13	-0.054	0.068	0.28	0.23	0.12
56331	0.15	-0.075	-0.011	-0.13	-0.052	0.067	0.23	0.19	0.099
56332									
56334	-0.026	-0.069	-0.01	-0.12	-0.048	0.053	0.16	0.15	0.054
56336	0.1	-0.067	-0.0096	-0.11	-0.046	0.067	0.18	0.17	0.061
56337	-0.03	-0.078	-0.011	-0.13	-0.054	0.03	0.13	0.12	0.055

Sample No	PCB 183 ng/g ww	Mirex ng/g ww	ETDZL ng/g ww	ACY ng/g ww	ACE ng/g ww	FLO ng/g ww	PHE ng/g ww	ANT ng/g ww	PTHN ng/g ww
36102	0.13	0.12	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
36103	0.11	0.18	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
36104	0.096	0.12	-0.015	-0.038	-0.05	0.48		-0.059	-0.0091
36105	0.099	0.074	-0.016	-0.04	-0.052			-0.062	-0.0096
36106	0.1	0.084	-0.015	-0.038	-0.05			-0.059	-0.0091
36109	0.088	0.089	-0.015	-0.037	-0.049			-0.058	-0.009
36111	0.24	0.18	-0.015	-0.037	-0.049	0.76		-0.059	-0.009
36113	0.091	0.093	-0.014	-0.036	-0.047			-0.056	-0.0087
36115	0.14	0.1	-0.015	-0.038	-0.05		2.6	-0.059	-0.0091
36118	0.088	0.067	-0.018	-0.046	-0.06			-0.072	-0.011
36161	0.096	0.13	-0.015	-0.037	-0.049	0.5		-0.058	-0.009
36162	0.2	0.41	-0.015	-0.038	-0.05			-0.059	-0.0091
36163	0.037	0.036	-0.015	-0.037	-0.049			-0.059	-0.009
36164	0.12	0.12	-0.016	-0.04	-0.053	-0.017		-0.063	-0.0098
36165	0.14	0.099	-0.015	-0.037	-0.049	-0.016		-0.058	-0.0089
36167	0.037	0.036	-0.015	-0.037	-0.049			5.3	-0.009
36168	0.057	0.071	-0.015	-0.037	-0.049			-0.058	-0.0089
36169	0.093	0.043	-0.015	-0.038	-0.05			-0.06	-0.0092
36170	0.058	0.072	-0.015	-0.037	-0.049	9.9		-0.058	-0.009
36171	0.069	0.028	-0.015	-0.037	-0.049			-0.059	-0.009
36230	0.092	0.089	-0.015	-0.037	-0.049			-0.058	-0.009
36231	0.073	0.084	-0.013	-0.034	-0.045	0.65		-0.053	-0.0082
36232									
36233		0.086	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
36236	0.054	0.067	-0.014	-0.035	-0.046	-0.015		-0.054	-0.0083
36238	0.089	0.09	-0.015	-0.038	-0.05	0.26		-0.059	-0.0091
36239	0.034	0.024	-0.015	-0.038	-0.051	-0.016	-0.037	-0.06	-0.0093
36240	0.047	0.045	-0.013	-0.038	-0.05	-0.016	1.6	-0.059	-0.008
36241	0.016	0.015	-0.017	-0.043	-0.056	-0.018	4.4	-0.067	-0.01
36243	0.21	0.29	-0.012	-0.037	4.4	-0.016	7.8	-0.059	-0.009
36283	0.083	0.073	-0.013	-0.037	-0.043		3.3	-0.051	-0.009
36284	0.031	0.033	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
36285	0.042	0.036	-0.015	-0.037	-0.049	0.27	6.6	-0.058	-0.009
36286	0.069	0.063	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
36287	0.021	0.025	-0.014	-0.036	-0.047	-0.015		-0.056	-0.0087
36290	0.037	0.039	-0.015	-0.037	-0.049	0.81		-0.058	-0.009
36291	0.044	0.034	-0.015	-0.037	-0.049		3.2	-0.059	-0.009
36292	0.017	0.017	-0.015	-0.038	-0.05	0.28		-0.059	-0.0091
36293	0.06	0.042	-0.015	-0.037	-0.049			-0.058	-0.009
36295	0.045	0.038	-0.015	-0.039	-0.051	-0.016		-0.061	-0.0094
46100	0.03	0.022	-0.014	-0.036	-0.048	-0.015		-0.057	-0.0088
46101	0.1	0.073	-0.016	-0.04	-0.053	-0.017		-0.062	-0.0096
46102	0.055	0.041	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
46103	0.085	0.069	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
46105	0.17	0.13	-0.017	-0.042	-0.056	-0.018		-0.066	-0.01
46109	0.16	0.1	-0.015	-0.037	-0.049			-0.059	-0.009
46110	0.13	0.068	-0.015	-0.037	-0.049			-0.059	-0.009
46111	0.071	0.048	-0.014	-0.036	-0.047			-0.056	-0.0087
46113	0.017	0.011	-0.014	-0.037	-0.048	-0.016		-0.057	-0.0089
46114	0.027	0.023	-0.016	-0.042	-0.055	-0.018	0.87	-0.065	-0.01
46160	0.32	0.33	-0.021	-0.052	-0.069	-0.022		-0.082	-0.013
46161	0.054	0.062	-0.014	-0.035	-0.047	-0.015		-0.055	-0.0086
46162	0.075	0.072	-0.015	-0.037	-0.049	-0.016		-0.058	-0.0089
46163	0.074	0.052	-0.015	-0.038	-0.05			-0.059	-0.0091
46165	0.058	0.068	-0.017	-0.043	-0.057	0.0081		-0.068	-0.01
46166	0.13	0.094	-0.014	-0.036	-0.047			-0.056	-0.0087
46168	0.075	0.081	-0.016	-0.041	-0.053	-0.017		-0.064	-0.0098
46170	0.088	0.093	-0.016	-0.042	-0.055	-0.018		-0.065	-0.01
46171	0.071	0.069	-0.015	-0.038	-0.05			-0.059	-0.0091
46172	0.054	0.047	-0.016	-0.041	-0.054	-0.017	1.1	-0.064	-0.0099
46220	0.0097	0.026	-0.016	-0.039	-0.052	-0.017		-0.062	-0.0095
46221	0.033	0.042	-0.021	-0.053	-0.07	-0.023		-0.084	-0.013
46222	0.015	0.02	-0.009	-0.023	-0.03	-0.0096		-0.036	-0.0055
46223	0.0054	0.0093	-0.0093	-0.024	-0.031	-0.01		-0.037	-0.0057
56371	0.0095	0.014	-0.016	-0.042	-0.055	-0.018	0.81	-0.065	-0.01
56372	0.0078	0.012	-0.016	-0.041	-0.055	-0.018		-0.065	-0.01
46281	0.18	0.11	-0.013	-0.034	-0.045	0.3	1.3	-0.053	-0.0082
46288	0.115	0.069	-0.015	-0.0375	-0.0495	-0.016	1.7	1.3205	-0.00905

Sample No	PCB 183 ng/g ww	Mirex ng/g ww	ETDZL ng/g ww	ACY ng/g ww	ACE ng/g ww	FLO ng/g ww	PHE ng/g ww	ANT ng/g ww	PTHN ng/g ww
46291	0.082	0.1	-0.016	-0.04	-0.053	-0.088		-0.063	-0.0098
46292	0.16	0.12	-0.014	-0.036	-0.047			-0.056	-0.0086
46293	0.035	0.024	-0.015	-0.038	-0.05	0.42	2.8	-0.059	-0.0091
46294									
46295	0.088	0.056	-0.019	-0.048	-0.063	-0.02	1.7	-0.075	-0.012
46297		0.034							
46298	0.16	0.09	-0.014	-0.036	-0.047	0.48	2.9	-0.056	-0.0086
46299	0.19	0.058	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56101	0.081	0.023	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56102	0.13	0.048	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56104	0.045	0.017	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
56106	0.1	0.029	-0.017	-0.042	-0.055	-0.018	4.4	-0.065	-0.01
56107	0.054	0.017	-0.017	-0.042	-0.055	-0.018		-0.065	-0.01
56108	0.066	0.022	-0.016	-0.041	-0.055	-0.018		-0.065	-0.01
56111	0.18	0.06	-0.016	-0.041	-0.054	-0.017		-0.064	-0.0099
56112	0.061	0.024	-0.016	-0.042	-0.055	-0.018		-0.065	-0.01
56113	0.1	0.039	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56114	0.16	0.068	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56147	0.12	0.041	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56148	0.073	0.03	-0.016	-0.042	-0.055	-0.018	2.8	-0.065	-0.01
56149	0.07	0.03	-0.016	-0.042	-0.055	-0.018	6.3	-0.065	-0.01
56151	0.094	0.036	-0.016	-0.042	-0.055	-0.018	1.8	-0.065	-0.01
56153	0.1	0.035	-0.016	-0.041	-0.055	-0.018	2.2	-0.065	-0.01
56154	0.099	0.032	-0.016	-0.042	-0.055	-0.018	2.2	-0.065	-0.01
56156	0.075	0.028	-0.015	-0.037	-0.048	-0.016		-0.058	-0.0089
56157	0.089	0.03	-0.015	-0.037	-0.048	-0.016		-0.058	-0.0089
56158	0.059	0.015	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
56159	0.14	0.033	-0.017	-0.042	-0.055	-0.018		-0.065	-0.01
56191	0.13	0.054	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
56192	0.087	0.041	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56193	0.19	0.07	-0.015	-0.037	-0.049	-0.016	1.5	-0.059	-0.009
56196	0.13	0.055	-0.015	-0.037	-0.048	-0.016		-0.058	-0.0089
56197			-0.014	-0.037	-0.048	-0.015		-0.057	-0.0088
56198	0.091		-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56199	0.092		-0.015	-0.037	-0.049	-0.016	4.6	-0.058	-0.0089
56200	0.071	0.022	-0.015	-0.037	-0.049	-0.016	2.4	-0.058	-0.009
56201	0.06	0.028	-0.015	-0.037	-0.049	-0.016	4	-0.059	-0.009
56205	0.18	0.078	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56236	0.055	0.14	-0.016	-0.042	-0.055	-0.018		-0.065	-0.01
56238	0.031	0.03	-0.016	-0.042	-0.055	-0.018		-0.065	-0.01
56240	0.039	0.022	-0.016	-0.042	-0.055	-0.018		-0.065	-0.01
56241	0.026	0.024	-0.015	-0.037	-0.049	-0.016		-0.059	-0.009
56244	0.041	0.025	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56245	0.017	0.02	-0.016	-0.04	-0.052	-0.017		-0.062	-0.0096
56246		0.033							
56248		0.02	-0.016	-0.039	-0.052	-0.017		-0.062	-0.0095
56249		0.02	-0.016	-0.041	-0.054	-0.017		-0.064	-0.0099
56250		0.021							
56281	-0.00031	-0.0033	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56282	0.016	0.011	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56283	0.019	0.013	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56284	0.045	0.019	-0.015	-0.037	-0.048	-0.016		-0.058	-0.0089
56285	0.044	0.025	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56286	0.035	0.026	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56287	0.017	0.011	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56288	0.041	0.021	-0.015	-0.037	-0.049	-0.016		-0.058	-0.009
56289	0.039	0.02	-0.015	-0.037	-0.049	-0.016		-0.058	-0.0089
56290	0.038	0.026	-0.015	-0.037	-0.049	-0.016	1.2	-0.058	-0.009
56326	0.037	0.02	-0.015	-0.037	-0.049	-0.016		-0.058	-0.0089
56327	0.017	0.0092	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56328	0.02	0.015	-0.015	-0.038	-0.05	-0.016		-0.059	-0.0091
56329	0.019	0.0091	-0.017	-0.044	-0.058	-0.019	0.9	-0.069	-0.011
56330	0.042	0.021	-0.018	-0.044	-0.059	-0.019	1.2	-0.07	-0.011
56331	0.026	0.015	-0.017	-0.043	-0.057	-0.018		-0.067	-0.01
56332			-0.017	-0.043	-0.057	-0.018	2.8	-0.068	-0.01
56334	0.016	0.014	-0.016	-0.04	-0.052	-0.017	3.1	-0.062	-0.0096
56336	0.019	0.01	-0.015	-0.038	-0.05	-0.016	3.9	-0.06	-0.0092
56337	0.018	0.013	-0.018	-0.045	-0.059	-0.019	1.1	-0.07	-0.011

Sample No	ETHN ng/g ww	FLA ng/g ww	PYR ng/g ww	Retene ng/g ww	op-DDE ng/g ww	pp-DDE ng/g ww	op-DDD ng/g ww	pp-DDD ng/g ww	op-DDT ng/g ww
36102	-0.0019	-0.0075			-0.058	10	-0.068	-0.15	-0.13
36103	-0.0019	-0.0075	-0.0067	-0.04	-0.06	12.00	-0.07	-0.15	-0.13
36104	-0.0019	0.18	-0.0067	-0.04	-0.06	11.00	-0.07	-0.15	-0.13
36105	-0.002	-0.0079	-0.007	-0.046	-0.061	9	-0.072	-0.16	-0.13
36106	-0.0019	-0.0076	0.093	-0.044	0.078	20	-0.07	-0.16	-0.13
36109	-0.0019	-0.0074		-0.044	-0.057	15	-0.07	-0.15	-0.13
36111	-0.0019	-0.0075	-0.0067	-0.044	0.081	40	-0.07	-0.15	-0.13
36113	-0.0018	-0.0072	-0.0064		-0.055	0.71	-0.07	-0.15	-0.12
36115	-0.0019	-0.0075			-0.058	11	-0.07	-0.15	-0.13
36118	-0.0023	-0.0092	-0.0081	-0.054	0.091	50	-0.08	-0.19	-0.15
36161	-0.0019	-0.0074	-0.0066	-0.044	-0.057	13	-0.07	-0.15	-0.13
36162	-0.0019	-0.0075	-0.0067	-0.044	0.076	7	-0.07	-0.15	-0.13
36163	-0.0019	-0.0075	-0.0067	-0.044	0.082	16	-0.07	-0.15	-0.13
36164	-0.0021	-0.0081	-0.0072	0.34	-0.062	11	-0.07	-0.17	-0.14
36165	-0.0019	-0.0074	-0.0066	-0.043	-0.057	20	-0.07	-0.15	-0.12
36167	-0.0019	-0.0075	-0.0067	-0.044	0.096	35	-0.07	-0.15	-0.13
36168	-0.0019		0.19	1.3	-0.057	13	-0.07	-0.15	-0.12
36169	-0.0019				-0.059	6.6	-0.07	-0.16	-0.13
36170	-0.0019	-0.0075	-0.0066	-0.044	-0.057	11	-0.07	-0.15	-0.13
36171	-0.0019	-0.0075	0.051	-0.044	0.28	11	-0.07	-0.15	-0.13
36230	-0.0019	-0.0075	-0.0066	-0.044	-0.057	9.8	-0.07	-0.15	-0.13
36231	-0.0017	-0.0068	-0.006	-0.04	-0.052	7.5	-0.06	-0.14	-0.11
36232									
36233	-0.0019			0.2	-0.058	8.1	-0.07	-0.15	-0.13
36236	-0.0018	-0.0069	-0.0061	-0.041	-0.053	7.3	-0.06	-0.14	-0.12
36238	-0.0019	-0.0075	-0.0067	-0.044	-0.058	8.5	-0.07	-0.15	-0.13
36239	-0.002	-0.0077	-0.0068	-0.045	-0.059	-0.1	-0.07	-0.16	-0.13
36240	-0.0019	-0.0076	-0.0067	-0.044	-0.058	-0.1	-0.07	-0.16	-0.13
36241	-0.0022	-0.0086	-0.0076	1.2	-0.066	2.3	-0.08	-0.18	-0.14
36243	-0.0019	-0.0075	-0.0067	-0.044	-0.058	12	-0.07	-0.15	-0.13
36283	-0.0019	-0.0066	-0.0058	-0.039	-0.051	3	-0.06	-0.15	-0.11
36284	-0.0019	-0.0075			-0.058	2	-0.07	-0.15	-0.13
36285	-0.0019	-0.0074	-0.0066	-0.044	-0.057	3.9	-0.07	-0.15	-0.13
36286	-0.0019	0.2	-0.0067		0.065	5.7	-0.07	-0.16	-0.13
36287	-0.0018	-0.0072	-0.0064	-0.042	-0.055	2.9	-0.07	-0.15	-0.12
36290	-0.0019	-0.0075	-0.0066		-0.057	3.7	-0.07	-0.15	-0.13
36291	-0.0019	-0.0075	-0.0067	0.35	-0.058	3.5	-0.07	-0.15	-0.13
36292	-0.0019	-0.0076		-0.044	-0.058	4.4	-0.07	-0.16	-0.13
36293	-0.0019		-0.0066		-0.057	5.5	-0.07	-0.15	-0.13
36295	-0.002	-0.0078			-0.06	2.8	-0.07	-0.16	-0.13
46100	-0.0019		-0.0065		-0.056	0.28	-0.07	-0.15	-0.12
46101	-0.002	-0.008	-0.0071	1.3	-0.061	1.4	-0.07	-0.16	-0.13
46102	-0.0019	-0.0075	-0.0067		-0.058	0.59	-0.07	-0.15	-0.13
46103	-0.0019	-0.0075	-0.0067		-0.058	1.1	-0.07	-0.15	-0.13
46105	-0.0021	-0.0085	-0.0075		-0.065	2.4	-0.08	-0.17	-0.14
46109	-0.0019	-0.0075	-0.0067	0.38	-0.058	1.3	-0.07	-0.15	-0.13
46110	-0.0019	-0.0075	-0.0067	0.4	-0.058	0.62	-0.07	-0.15	-0.13
46111	-0.0018		-0.0064		-0.056	1.2	-0.07	-0.15	-0.12
46113	-0.0019	-0.0074	-0.0065	-0.043	-0.057	0.23	-0.07	-0.15	-0.12
46114	-0.0021	-0.0083	-0.0074	-0.049	-0.064	0.29	-0.075	-0.17	-0.14
46160	-0.0026	-0.01	-0.0093		-0.08	1.3	-0.094	-0.21	-0.18
46161	-0.0018	-0.0071	-0.0063		-0.055	0.29	-0.064	-0.15	-0.12
46162	-0.0019	-0.0074	-0.0066		-0.057	1.4	-0.067	-0.15	-0.12
46163	-0.0019		-0.0067		-0.058	0.24	-0.068	-0.15	-0.13
46165	-0.0022	-0.0087	-0.0077		-0.067	1.8	-0.078	-0.18	-0.15
46166	-0.0018	-0.0072	-0.0064		-0.056	0.36	-0.065	-0.15	-0.12
46168	-0.0021	-0.0081	-0.0072		-0.063	0.58	-0.073	-0.17	-0.14
46170	-0.0021	-0.0083	-0.0074		-0.064	0.78	-0.075	-0.17	-0.14
46171	-0.0019		-0.0067	0.46	-0.058	0.46	-0.068	-0.15	-0.13
46172	-0.0021	-0.0082	-0.0073		-0.063	0.74	-0.074	-0.17	-0.14
46220	-0.002	-0.0079	-0.007	-0.046	-0.061	-0.1	-0.071	-0.16	-0.13
46221	-0.0027	-0.011	-0.0095	0.6	-0.082	0.96	-0.097	-0.22	-0.18
46222	-0.0012	-0.0046	-0.0041	-0.027	-0.035	-0.06	-0.041	-0.094	-0.077
46223	-0.0012	-0.0047	-0.0042	0.31	-0.036	-0.062	-0.043	-0.097	-0.08
56371	-0.0021	-0.0083	-0.0074	-0.049	-0.064	-0.11	-0.075	-0.17	-0.14
56372	-0.0021	-0.0083	-0.0074	0.4	-0.064	-0.11	-0.075	-0.17	-0.14
46281	-0.0017	-0.0068	-0.006		-0.052	2.6	-0.061	-0.14	-0.11
46288	-0.0019	-0.0075	-0.00665		-0.0575	1.5	-0.0675	-0.155	-0.13

Sample No	ETHN ng/g ww	FLA ng/g ww	PYR ng/g ww	Retene ng/g ww	op-DDE ng/g ww	pp-DDE ng/g ww	op-DDD ng/g ww	pp-DDD ng/g ww	op-DDT ng/g ww
46291	-0.0021	-0.0081	-0.0072		-0.062	3.3	-0.073	-0.17	-0.14
46292	-0.0018		-0.0063		-0.055	1.4	-0.064	-0.15	-0.12
46293	-0.0019	-0.0076	-0.0067		-0.058	0.73	-0.068	-0.16	-0.13
46294									
46295	-0.0024	0.31	-0.0086		-0.074	1.1	-0.087	-0.2	-0.16
46297									
46298	-0.0018	-0.0071	-0.0063		-0.055	2.7	-0.064	-0.15	-0.12
46299	-0.0019	-0.0076	-0.0067	2.7	-0.058	1.7	-0.068	-0.15	-0.13
56101	-0.0019	-0.0076	-0.0067		-0.058	2	-0.069	-0.16	-0.13
56102	-0.0019	-0.0074	-0.0066		-0.057	1.1	-0.067	-0.15	-0.12
56104	-0.0019	-0.0075	-0.0067	9.3	-0.058	2.1	-0.068	-0.15	-0.13
56106	-0.0021	-0.0084	-0.0074	0.63	-0.064	1.1	-0.076	-0.17	-0.14
56107	-0.0021	-0.0084	-0.0074		-0.064	2.2	-0.076	-0.17	-0.14
56108	-0.0021	-0.0083	-0.0074	3	-0.064	2.1	-0.075	-0.17	-0.14
56111	-0.0021	-0.0082	-0.0073		-0.063	2.5	-0.074	-0.17	-0.14
56112	-0.0021	-0.0083	-0.0074		-0.064	1.3	-0.075	-0.17	-0.14
56113	-0.0019	0.044	-0.0067		-0.058	1.3	-0.068	-0.15	-0.13
56114	-0.0019	-0.0075	-0.0067		-0.058	1	-0.068	-0.15	-0.13
56147	-0.0019	-0.0075	-0.0066		-0.057	4.2	-0.067	-0.15	-0.13
56148	-0.0021	-0.0083	-0.0074		-0.064	3.5	-0.075	-0.17	-0.14
56149	-0.0021	-0.0083	-0.0074	0.56	-0.064	2.9	-0.075	-0.17	-0.14
56151	-0.0021	-0.0083	-0.0074	3	-0.064	2.9	-0.075	-0.17	-0.14
56153	-0.0021	-0.0083	-0.0074		-0.064	4.7	-0.075	-0.17	-0.14
56154	-0.0021	-0.0083	-0.0074		-0.064	4.9	-0.075	-0.17	-0.14
56156	-0.0019	-0.0074	-0.0065		-0.057	2.5	-0.067	-0.15	-0.12
56157	-0.0019	-0.0074	-0.0065	7.4	-0.057	3	-0.067	-0.15	-0.12
56158	-0.0019	-0.0075	-0.0067		-0.058	2.3	-0.068	-0.15	-0.13
56159	-0.0021	-0.0084	-0.0074		-0.064	5	-0.076	-0.17	-0.14
56191	-0.0019	-0.0075	-0.0067	-0.044	-0.058	23	-0.068	-0.15	-0.13
56192	-0.0019	-0.0074	-0.0066	-0.044	-0.057	17	-0.067	-0.15	-0.13
56193	-0.0019	-0.0075	-0.0067	-0.044	-0.058	35	-0.068	-0.15	-0.13
56196	-0.0019	-0.0074	-0.0065		-0.057	21	-0.067	-0.15	-0.12
56197	-0.0019	-0.0073	-0.0065	6.9	0.13	16	-0.066	-0.15	-0.12
56198	-0.0019	-0.0074	-0.0066		-0.057	25	-0.067	-0.15	-0.13
56199	-0.0019	-0.0074	-0.0066		-0.057	26	-0.067	-0.15	-0.12
56200	-0.0019	-0.0075	-0.0066		-0.057	38	-0.068	-0.15	-0.13
56201	-0.0019	-0.0075	-0.0066		0.17	12	-0.068	-0.15	-0.13
56205	-0.0019	-0.0076	-0.0067		-0.058	35	-0.068	2.4	0.73
56236	-0.0021	-0.0083	-0.0074		-0.064	1.9	-0.075	-0.17	-0.14
56238	-0.0021	-0.0083	-0.0074		-0.064	1.8	-0.075	-0.17	-0.14
56240	-0.0021	-0.0083	-0.0074		-0.064	4.8	-0.075	-0.17	-0.14
56241	-0.0019	-0.0075	-0.0067	0.11	-0.058	1.7	-0.068	-0.15	-0.13
56244	-0.0019	-0.0075	-0.0067		-0.058	4.3	-0.068	-0.15	-0.13
56245	-0.002	-0.008	-0.0071		-0.061	1.7	-0.072	-0.16	-0.13
56246									
56248	-0.002	-0.0079	-0.007		-0.061	3.8	-0.071	-0.16	-0.13
56249	-0.0021	-0.0082	-0.0073		-0.063	1.6	-0.074	-0.17	-0.14
56250									
56281	-0.0019	-0.0075	-0.0067		-0.058	0.61	-0.068	-0.15	-0.13
56282		-0.0075	-0.0066			0.43		-0.15	-0.13
56283	-0.0019	-0.0075	-0.0067		-0.058	0.91	-0.068	-0.15	-0.13
56284	-0.0019	-0.0074	-0.0065	0.53	-0.057	0.81	-0.067	-0.15	-0.12
56285	-0.0019	-0.0075	-0.0066		-0.057	1.3	-0.068	-0.15	-0.13
56286	-0.0019	-0.0075	-0.0067		-0.058	0.73	-0.068	-0.15	-0.13
56287	-0.0019	-0.0074	-0.0066		-0.057	0.84	-0.067	-0.15	-0.13
56288	-0.0019	-0.0075	-0.0066		-0.057	1.3	-0.067	-0.15	-0.13
56289	-0.0019	-0.0074	-0.0066		-0.057	0.81	-0.067	-0.15	-0.12
56290	-0.0019	-0.0075	-0.0066		-0.057	0.75	-0.067	-0.15	-0.13
56326	-0.0019	-0.0074	-0.0066		-0.057	1.7	-0.067	-0.15	-0.12
56327	-0.0019	-0.0075	-0.0067		-0.058	0.28	-0.068	-0.15	-0.13
56328	-0.0019	-0.0076	-0.0067		-0.058	0.83	-0.068	-0.16	-0.13
56329	-0.0022	-0.0089	-0.0079	1.6	-0.068	0.48	-0.08	-0.18	-0.15
56330	-0.0023	-0.0089	-0.0079	0.65	-0.069	0.59	-0.08	-0.18	-0.15
56331	-0.0022	-0.0086	-0.0076	2.1	-0.066	0.77	-0.078	-0.18	-0.14
56332	-0.0022	-0.0087	-0.0077	4.2	-0.067	0.54	-0.078	-0.18	-0.15
56334	-0.002	-0.008	-0.0071	4.6	-0.061	0.61	-0.072	-0.16	-0.13
56336	-0.0019	-0.0077	-0.0068	3.8	-0.059	0.66	-0.069	-0.16	-0.13
56337	-0.0023	-0.009	-0.008	2.8	-0.069	0.26	-0.081	-0.18	-0.15

Sample No	pp-DDT ng/g ww	MXCLR ng/g ww	B[a]A ng/g ww	CHR/TRI ng/g ww	B[b]F ng/g ww	B[k]F ng/g ww	B[e]P ng/g ww	B[a]P ng/g ww	I[1,2,3-cd]p ng/g ww
36102	-0.12		-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36103	-0.12	3.6	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36104	-0.12	1.2	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36105	-0.13	-0.16	-0.028	-0.021	-0.021	-0.025	-0.11	-0.018	-0.019
36106	-0.12	0.62	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36109	-0.12	0.89	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
36111	-0.12		-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36113	-0.12		-0.025	-0.019	-0.02	-0.022	-0.1	-0.016	-0.017
36115	-0.12		-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36118	-0.15	-0.18	-0.032	-0.024	-0.025	-0.028	-0.13	-0.02	-0.022
36161	-0.12	0.52	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
36162	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36163	-0.12	-0.15	0.2	0.04	-0.02	-0.023	-0.11	-0.017	-0.018
36164	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.11	-0.018	-0.019
36165	-0.12	0.65	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
36167	0.4	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36168	-0.12		-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
36169	-0.13	0.27	-0.027	-0.02	-0.021	-0.024	-0.11	-0.017	-0.018
36170	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36171	-0.12	0.87	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36230	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36231	-0.11	1	0.15	-0.018	-0.018	-0.021	-0.096	-0.015	-0.016
36232									
36233	-0.12	0.76	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36236	-0.11	2.4	-0.024	-0.018	-0.019	-0.021	-0.098	-0.015	-0.016
36238	-0.12		-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36239	-0.13	-0.15	-0.027	-0.02	-0.021	-0.024	-0.11	-0.017	-0.018
36240	-0.12	0.29	-0.026	-0.02	-0.021	-0.023	-0.11	-0.017	0.033
36241	-0.14	0.33	-0.03	-0.022	-0.023	-0.026	-0.12	-0.019	-0.02
36243	-0.12	0.31	-0.021	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36283	0.43	0.26	-0.023	-0.017	0.24	-0.02	-0.093	-0.015	-0.016
36284	-0.12	0.88	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36285	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
36286	-0.12	0.32	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
36287	-0.12		-0.025	-0.019	-0.02	-0.022	-0.1	-0.016	-0.017
36290	-0.12		-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36291	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
36292	-0.12	0.35	-0.026	-0.02	-0.021	-0.023	-0.11	-0.017	-0.018
36293	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
36295	-0.13	2.7	-0.027	-0.02	-0.021	-0.024	-0.11	-0.017	-0.019
46100	-0.12	-0.15	-0.025	-0.019	-0.02	-0.023	-0.1	-0.016	-0.017
46101	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.11	-0.018	-0.019
46102	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
46103	-0.12	0.89	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
46105	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.019	-0.02
46109	-0.12	0.66	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
46110	-0.12	0.35	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
46111	-0.12		-0.025	-0.019	-0.02	-0.022	-0.1	-0.016	-0.017
46113	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
46114	-0.14	1.8	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
46160	-0.17	0.31	-0.036	-0.027	-0.028	-0.032	-0.15	-0.023	-0.025
46161	-0.12	-0.14	-0.025	-0.018	-0.019	-0.022	-0.1	-0.016	-0.017
46162	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
46163	-0.12		-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
46165	-0.14	0.28	-0.03	-0.022	-0.023	-0.027	-0.12	-0.019	-0.021
46166	-0.12		-0.025	-0.019	-0.02	-0.022	-0.1	-0.016	-0.017
46168	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.12	-0.018	-0.019
46170	-0.14	0.69	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
46171	-0.12	0.61	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
46172	-0.13	-0.16	-0.029	-0.021	-0.022	-0.025	-0.12	-0.018	-0.02
46220	-0.13	-0.16	-0.028	-0.02	-0.021	-0.024	-0.11	-0.017	-0.019
46221	-0.18	-0.21	-0.037	-0.028	-0.029	-0.033	-0.15	-0.024	-0.026
46222	-0.075	-0.091	-0.016	-0.012	-0.012	-0.014	-0.065	-0.01	-0.011
46223	-0.078	-0.094	-0.016	-0.012	-0.013	-0.015	-0.067	-0.01	-0.011
56371	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56372	-0.14	-0.17	-0.029	-0.022	-0.022	-0.026	-0.12	-0.018	-0.02
46281	-0.11	0.4	-0.024	-0.018	-0.018	-0.021	-0.096	-0.015	-0.016
46288	-0.12	-0.15	-0.026	-0.0195	-0.02	-0.023	-0.11	-0.0165	-0.018

Sample No	pp-DDT ng/g ww	MXCLR ng/g ww	B[a]A ng/g ww	CHR/TRI ng/g ww	B[b]F ng/g ww	B[k]F ng/g ww	B[e]P ng/g ww	B[a]P ng/g ww	I[1,2,3-cd]p ng/g ww
46291	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.11	-0.018	-0.019
46292	-0.12	-0.14	-0.025	-0.018	-0.019	-0.022	-0.1	-0.016	-0.017
46293	-0.12	0.28	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
46294									
46295	-0.16	-0.19	-0.034	-0.025	-0.026	-0.03	-0.14	-0.021	-0.023
46297									
46298	-0.12	-0.14	-0.025	-0.018	-0.019	-0.022	-0.1	-0.016	-0.017
46299	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56101	-0.12	-0.15	-0.026	-0.02	-0.021	-0.023	-0.11	-0.017	-0.018
56102	-0.12	0.4	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56104	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56106	-0.14	1.5	-0.029	-0.022	-0.023	-0.026	-0.12	-0.019	-0.02
56107	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.019	-0.02
56108	-0.14	-0.17	-0.029	-0.022	-0.022	-0.026	-0.12	-0.018	-0.02
56111	-0.13	-0.16	-0.029	-0.021	-0.022	-0.025	-0.12	-0.018	-0.02
56112	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56113	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56114	-0.12	1.7	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56147	-0.12	2.3	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56148	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56149	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56151	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56153	-0.14	-0.16	-0.029	-0.021	-0.022	-0.026	-0.12	-0.018	-0.02
56154	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56156	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
56157	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
56158	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56159	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.019	-0.02
56191	-0.12	0.58	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56192	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56193	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56196	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
56197	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.017
56198	-0.12	0.77	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56199	-0.12	1.9	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56200	-0.12	7.9	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56201	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56205	1.1	0.18	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56236	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56238	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56240	-0.14	-0.17	-0.029	-0.022	-0.023	-0.026	-0.12	-0.018	-0.02
56241	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56244	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56245	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.11	-0.018	-0.019
56246									
56248	-0.13	-0.16	-0.028	-0.02	-0.021	-0.024	-0.11	-0.017	-0.019
56249	-0.13	-0.16	-0.029	-0.021	-0.022	-0.025	-0.12	-0.018	-0.02
56250									
56281	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56282									
56283	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56284	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
56285	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56286	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56287	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56288	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56289	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.016	-0.018
56290	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.11	-0.017	-0.018
56326	-0.12	-0.15	-0.026	-0.019	-0.02	-0.023	-0.1	-0.016	-0.018
56327	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56328	-0.12	-0.15	-0.026	-0.02	-0.02	-0.023	-0.11	-0.017	-0.018
56329	-0.15	-0.18	-0.031	-0.023	-0.024	-0.027	-0.13	-0.02	-0.021
56330	-0.15	-0.18	-0.031	-0.023	-0.024	-0.028	-0.13	-0.02	-0.021
56331	-0.14	-0.17	-0.03	-0.022	-0.023	-0.027	-0.12	-0.019	-0.02
56332	-0.14	-0.17	-0.03	-0.022	-0.023	-0.027	-0.12	-0.019	-0.021
56334	-0.13	-0.16	-0.028	-0.021	-0.022	-0.025	-0.11	-0.018	-0.019
56336	-0.13	-0.15	-0.027	-0.02	-0.021	-0.024	-0.11	-0.017	-0.018
56337	-0.15	-0.18	-0.031	-0.023	-0.024	-0.028	-0.13	-0.02	-0.021

Sample No	D[ah]A ng/g ww	B[ghi]P ng/g ww	BDE 10 ng/g ww	BDE 7 ng/g ww	BDE 8 ng/g ww	BDE 12 ng/g ww	BDE 13 ng/g ww	BDE 15 ng/g ww	BDE 30 ng/g ww
36102	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
36103	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.10	-0.93	-0.80
36104	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.10	-0.93	-0.81
36105	-0.02	-0.0066	-1	-0.14	-0.81	-1	-1.1	-0.97	-0.85
36106	-0.019	0.29	-1	-0.13	-0.77	-0.96	-1.10	-0.93	-0.81
36109	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.10	-0.91	-0.79
36111	-0.019		-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36113	-0.018	-0.006	-0.95	-0.13	-0.74	-0.91	-1.00	-0.89	-0.77
36115	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.10	-0.93	-0.80
36118	-0.023	-0.0076	-1.2	-0.16	-0.94	-1.2	-1.30	-1.10	-0.98
36161	-0.019		-0.98	-0.13	-0.76	-0.94	-1.10	-0.91	-0.79
36162	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.10	-0.93	-0.81
36163	-0.019	-0.0062	-0.99	-0.13	-0.76	-0.95	-1.10	-0.92	-0.80
36164	-0.02	-0.0067	-1.1	-0.14	-0.83	-1	-1.20	-1.00	-0.86
36165	-0.019		-0.97	-0.13	-0.76	-0.93	-1.10	-0.91	-0.79
36167	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36168	-0.019	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.10	-0.91	-0.79
36169	-0.019	-0.0063	-1	-0.14	-0.78	-0.96	-1.10	-0.94	-0.82
36170	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.10	-0.92	-0.80
36171	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36230	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.10	-0.92	-0.80
36231	-0.017		-0.89	-0.12	-0.69	-0.85	-0.98	-0.83	-0.72
36232									
36233	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36236	-0.017	0.028	-0.91	-0.12	-0.71	-0.87	-1.00	-0.85	-0.74
36238	-0.019	0.034	-0.99	-0.13	-0.77	-0.95	-1.10	-0.93	-0.81
36239	-0.019	-0.0064	-1	-0.14	-0.79	-0.97	-1.10	-0.95	-0.60
36240	-0.019		-0.87	-0.12	-0.68	-0.84	-0.96	-0.82	-0.71
36241	-0.021	-0.0071	-1.1	-0.15	-0.87	-1.1	-1.20	-1.10	-0.91
36243	-0.019	-0.0062	-0.8	-0.11	-0.62	-0.77	-0.88	-0.75	-0.65
36283	-0.019	-0.0062	-0.86	-0.12	-0.67	-0.83	-0.95	-0.81	-0.70
36284	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36285	-0.019	0.025	-0.98	-0.13	-0.76	-0.94	-1.10	-0.91	-0.79
36286	-0.019	-0.0063	-1	-0.13	-0.77	-0.95	-1.10	-0.93	-0.81
36287	-0.018	0.017		-0.13	-0.74	-0.91	-1.00	-0.89	-0.77
36290	-0.019		-0.98	-0.13	-0.76	-0.94	-1.10	-0.92	-0.80
36291	-0.019	0.032	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
36292	-0.019	-0.0063	-1	-0.13	-0.77	-0.96	-1.10	-0.93	-0.81
36293	-0.019	0.0063	-0.98	-0.13	-0.76	-0.94	-1.10	-0.91	-0.79
36295	-0.02	-0.0065	-1	-0.14	-0.8	-0.98	-1.10	-0.96	-0.83
46100	-0.018	0.17	-0.96	-0.13	-0.75	-0.92	-1.10	-0.90	-0.78
46101	-0.02	0.045	-1	-0.14	-0.81	-1	-1.20	-0.98	-0.85
46102	-0.019	0.031	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
46103	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
46105	-0.021		-1.1	-0.15	-0.86	-1.1	-1.20	-1.00	-0.90
46109	-0.019		-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
46110	-0.019		-0.99	-0.13	-0.77	-0.95	-1.10	-0.92	-0.80
46111	-0.018	0.025	-0.95	-0.13	-0.74	-0.91	-1.00	-0.89	-0.77
46113	-0.018	-0.0061	-0.97	-0.13	-0.75	-0.93		-0.90	-0.78
46114	-0.021	0.049	-1.1	-0.14	-0.81	-0.98	-1.2	-0.97	-0.85
46160	-0.026	-0.0087	-1.4	-0.18	-1.1	-1.3	-1.5	-1.3	-1.1
46161	-0.018	0.029	-0.93	-0.13	-0.72	-0.9	-1	-0.87	-0.76
46162	-0.019	-0.0061	-0.97	-0.13	-0.76	-0.93	-1.1	-0.91	-0.79
46163	-0.019	0.042	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
46165	-0.022	-0.0072	-1.1	-0.15	-0.89	-1.1	-1.3	-1.1	-0.93
46166	-0.018	0.029	-0.95	-0.13	-0.74	-0.91	-1	-0.89	-0.77
46168	-0.02	-0.0067	-1.1	-0.14	-0.83	-1	-1.2	-1	-0.87
46170	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
46171	-0.019	-0.015	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
46172	-0.021	-0.0068	-1.1	-0.14	-0.84	-1	-1.2	-1	-0.87
46220	-0.02	-0.0065	-1	-0.14	-0.81	-1	-1.1	-0.97	-0.84
46221	-0.027	-0.0089	-1.4	-0.19	-1.1	-1.4	-1.6	-1.3	-1.1
46222	-0.011		-0.6	-0.081	-0.47	-0.58	-0.66	-0.56	-0.49
46223	-0.012		-0.62	-0.083	-0.48	-0.6	-0.68	-0.58	-0.5
56371	-0.021	0.1	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56372	-0.021	0.065	-1.1	-0.15	-0.85	-1	-1.2	-1	-0.89
46281	-0.017	-0.0056	-0.89	-0.12	-0.69	-0.85	-0.98	-0.83	-0.72
46288	-0.019	-0.00625	-0.99	-0.13	-0.765	-0.95	-1.1	-0.92	-0.8

Sample No	D[ah]A ng/g ww	B[ghi]P ng/g ww	BDE 10 ng/g ww	BDE 7 ng/g ww	BDE 8 ng/g ww	BDE 12 ng/g ww	BDE 13 ng/g ww	BDE 15 ng/g ww	BDE 30 ng/g ww
46291	-0.02		-1.1	-0.14	-0.83	-1	-1.2	-1	-0.86
46292	-0.018	-0.0059	-0.94	-0.13	-0.73	-0.9	-1	-0.88	-0.76
46293	-0.019	-0.0063	-1	-0.13	-0.77	-0.96	-1.1	-0.93	-0.81
46294									
46295	-0.024	-0.008	-1.3	-0.17	-0.98	-1.2	-1.4	-1.2	-1
46297			-0.83	-0.11	-0.64	-0.79	-0.91	-0.77	-0.67
46298	-0.018	-0.0059	-0.94	-0.13	-0.73	-0.9	-1	-0.88	-0.76
46299	-0.019	0.016	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.81
56101	-0.019	-0.0063	-1	-0.13	-0.77	-0.96	-1.1	-0.93	-0.81
56102	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.91	-0.79
56104	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
56106	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56107	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56108	-0.021	-0.0069	-1.1	-0.15	-0.85	-1	-1.2	-1	-0.89
56111	-0.021	-0.0068	-1.1	-0.14	-0.84	-1	-1.2	-1	-0.88
56112	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56113	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56114	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56147	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56148	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56149	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56151	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56153	-0.021	-0.0069	-1.1	-0.15	-0.85	-1	-1.2	-1	-0.88
56154	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56156	-0.018	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.1	-0.91	-0.79
56157	-0.018	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.1	-0.91	-0.79
56158	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
56159	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56191	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
56192	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.91	-0.79
56193	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
56196	-0.018	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.1	-0.91	-0.79
56197	-0.018	-0.0061	-0.96	-0.13	-0.75	-0.92	-1.1	-0.9	-0.78
56198	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.91	-0.79
56199	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.91	-0.79
56200	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56201	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56205	-0.019	-0.0063	-1	-0.13	-0.77	-0.95	-1.1	-0.93	-0.81
56236	-0.021	-0.0069	-1.1	-0.15	-0.85	-1	-1.2	-1	-0.89
56238	-0.021	-0.0069	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56240	-0.021	0.076	-1.1	-0.15	-0.85	-1.1	-1.2	-1	-0.89
56241	-0.019	-0.0062	-0.99	-0.13	-0.77	-0.95	-1.1	-0.92	-0.8
56244	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56245	-0.02	-0.0066	-1	-0.14	-0.81	-1	-1.2	-0.98	-0.85
56246			-1.3	-0.17	-1	-1.2	-1.4	-1.2	-1.1
56248	-0.02	-0.0066	-1	-0.14	-0.81	-1	-1.1	-0.97	-0.84
56249	-0.021	-0.0068	-1.1	-0.14	-0.84	-1	-1.2	-1	-0.88
56250			-1.1	-0.15	-0.86	-1.1	-1.2	-1	-0.89
56281	-0.019	-0.0063							
56282			-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56283	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56284	-0.018	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.1	-0.9	-0.79
56285	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56286	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56287	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.91	-0.79
56288	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56289	-0.019	-0.0061	-0.97	-0.13	-0.76	-0.93	-1.1	-0.91	-0.79
56290	-0.019	-0.0062	-0.98	-0.13	-0.76	-0.94	-1.1	-0.92	-0.8
56326	-0.019	-0.0061	-0.97	-0.13	-0.75	-0.93	-1.1	-0.91	-0.79
56327	-0.019	-0.0063	-0.99	-0.13	-0.77	-0.95	-1.1	-0.93	-0.8
56328	-0.019	-0.0063	-1	-0.13	-0.77	-0.95	-1.1	-0.93	-0.81
56329	-0.022	-0.0074	-1.2	-0.16	-0.9	-1.1	-1.3	-1.1	-0.95
56330	-0.022	-0.0074	-1.2	-0.16	-0.91	-1.1	-1.3	-1.1	-0.95
56331	-0.022	-0.0071	-1.1	-0.15	-0.88	-1.1	-1.2	-1.1	-0.92
56332	-0.022	-0.0072							
56334	-0.02	-0.0066	-1	-0.14	-0.81	-1	-1.2	-0.98	-0.85
56336	-0.019	-0.0063	-1	-0.14	-0.78	-0.96	-1.1	-0.94	-0.82
56337	-0.022	-0.0074	-1.2	-0.16	-0.91	-1.1	-1.3	-1.1	-0.96

Sample No	BDE 32 ng/g ww	BDE 17 ng/g ww	BDE 25 ng/g ww	BDE 28 ng/g ww	BDE 35 ng/g ww	BDE 37 ng/g ww	BDE 75 ng/g ww	BDE 71 ng/g ww	BDE 66 ng/g ww
36102	-0.04	-0.034	-0.046	0.039	-0.061	-0.043	-0.026	-0.024	-0.13
36103	-0.04	-0.034	-0.046	0.043	-0.062	-0.043	-0.026	-0.024	-0.13
36104	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
36105	-0.043	-0.036	-0.049	-0.026	-0.065	-0.045	-0.028	-0.025	-0.14
36106	-0.041	-0.034	-0.047	0.033	-0.062	-0.043	-0.026	-0.024	-0.13
36109	-0.04	-0.034	-0.046	0.046	-0.061	-0.043	-0.026	-0.024	-0.13
36111	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
36113	-0.039	-0.033	-0.045	-0.024	-0.059	-0.041	-0.025	-0.023	-0.12
36115	-0.04	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
36118	-0.049		-0.057	0.031	-0.075	-0.052	-0.032	-0.029	-0.16
36161	-0.04	-0.034	-0.046	0.038	-0.061	-0.043	-0.026	0.24	-0.13
36162	-0.041	-0.034	-0.047	0.031	-0.062	-0.043	-0.026	-0.024	-0.13
36163	-0.04		-0.046	0.034	-0.061	-0.043	-0.026	-0.024	-0.13
36164	-0.043	-0.037	-0.05	0.029	-0.066	-0.046	-0.028	-0.026	-0.14
36165	-0.04	-0.034	-0.046	-0.024	-0.061	-0.042	-0.026	-0.024	0.13
36167	-0.04	-0.034	-0.046	0.051	-0.061	-0.043	-0.026	-0.024	-0.13
36168	-0.04		-0.046	0.034	-0.06	-0.042	-0.026	-0.023	-0.13
36169	-0.041	-0.035	-0.047	-0.025	-0.063	-0.044	-0.027	0.18	-0.13
36170	-0.04	-0.034	-0.046	0.059	-0.061	-0.043	-0.026	-0.024	-0.13
36171	-0.04	-0.034	-0.046	0.051	-0.061	-0.043	-0.026	-0.024	-0.13
36230	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
36231	-0.036	-0.031	-0.042	-0.022	-0.055	-0.039	-0.024	-0.022	-0.12
36232									
36233	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
36236	-0.037	-0.031	-0.043	0.026	-0.057	-0.04	-0.024	-0.022	-0.12
36238	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
36239	-0.041	-0.035	-0.048	-0.025	-0.063	-0.044	-0.027	-0.025	-0.13
36240	-0.036	-0.03	-0.041	-0.022	-0.054	-0.038	-0.023	-0.021	-0.11
36241	-0.046	-0.039	-0.053	-0.028	-0.07	-0.049	-0.03	-0.027	-0.15
36243	-0.033	-0.028	-0.038	-0.02	-0.05	-0.035	-0.021	-0.019	-0.1
36283	-0.035	-0.03	-0.041	-0.022	-0.054	-0.038	-0.023	-0.021	-0.11
36284	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
36285	-0.04	-0.034	-0.046	0.055	-0.061	-0.043	-0.026	-0.024	-0.13
36286	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
36287	-0.039	-0.033	0.059	-0.024	-0.059	-0.041	-0.025		-0.12
36290	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
36291	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
36292	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
36293	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
36295	-0.042	-0.035	-0.048	-0.026	-0.064	-0.045	-0.027	-0.025	-0.13
46100	-0.039	-0.033	-0.045	-0.024	-0.06	-0.042	-0.026	-0.023	-0.13
46101	-0.043	-0.036	-0.049	-0.026	-0.065	-0.046	-0.028	-0.025	-0.14
46102	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
46103	-0.04	-0.034	-0.046		-0.061	-0.043	-0.026	-0.024	-0.13
46105	-0.045		-0.052	-0.028	-0.069	-0.048	-0.03	-0.027	-0.15
46109	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
46110	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.026	-0.024	-0.13
46111	-0.039	-0.033	-0.045	-0.024	-0.059	-0.041	-0.025	-0.023	-0.12
46113	-0.039	-0.033	-0.045		-0.06	-0.042	-0.026	-0.023	-0.13
46114	-0.043	-0.036	-0.049	-0.026	-0.065	-0.046	-0.028	-0.025	-0.14
46160	-0.056	-0.047	-0.064	-0.034	-0.085	-0.06	-0.036	-0.033	-0.18
46161	-0.038	-0.032	-0.044		-0.058	-0.041	-0.025	-0.023	-0.12
46162	-0.04	-0.034	-0.046	0.051	-0.061	-0.042	-0.026	-0.024	-0.13
46163	-0.041	-0.034	-0.047	0.027	-0.062	-0.043	-0.026	-0.024	-0.13
46165	-0.047	-0.039	-0.054	-0.028	-0.071	-0.05	-0.03	-0.028	-0.15
46166	-0.039	-0.033	-0.045	-0.024	-0.059	-0.041	-0.025	-0.023	-0.12
46168	-0.044	-0.037	-0.05	-0.027	-0.067	-0.046	-0.028	-0.026	-0.14
46170	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.029	-0.027	-0.14
46171	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
46172	-0.044	-0.037	-0.051	-0.027	-0.067	-0.047	-0.029	-0.026	-0.14
46220	-0.042	-0.036	-0.049	-0.026	-0.065	-0.045	-0.028	-0.025	-0.14
46221	-0.058	-0.048	-0.066	-0.035	-0.088	-0.061	-0.037	-0.034	-0.18
46222	-0.025	-0.021	-0.028	-0.015	-0.037	-0.026	-0.016	-0.015	-0.078
46223	-0.025	-0.021	-0.029	-0.015	-0.039	-0.027	-0.017	-0.015	-0.081
56371	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.029	-0.027	-0.14
56372	-0.045	-0.038	-0.051	-0.027	-0.068	-0.047	-0.029	-0.026	-0.14
46281	-0.036	-0.031	-0.042	-0.022	-0.055	-0.039	-0.024	-0.022	-0.12
46288	-0.0405	-0.034	-0.0465	-0.0245	-0.0615	-0.043	-0.026	-0.024	-0.13

Sample No	BDE 32 ng/g ww	BDE 17 ng/g ww	BDE 25 ng/g ww	BDE 28 ng/g ww	BDE 35 ng/g ww	BDE 37 ng/g ww	BDE 75 ng/g ww	BDE 71 ng/g ww	BDE 66 ng/g ww
46291	-0.044	-0.037	-0.05	-0.027	-0.066	-0.046	-0.028	-0.026	-0.14
46292	-0.038	-0.032	-0.044	0.04	-0.058	-0.041	-0.025	-0.023	-0.12
46293	-0.041	-0.034	-0.047	-0.03	-0.06	-0.04	-0.03	-0.02	-0.13
46294									
46295	-0.052	-0.044	-0.06	-0.032	-0.079	-0.055	-0.034	-0.031	-0.17
46297	-0.034	-0.028	-0.039	-0.021	-0.051	-0.036	-0.02	-0.02	-0.11
46298	-0.038	-0.032	-0.044	-0.023	-0.058	-0.041	-0.03	-0.02	-0.12
46299	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.03	-0.02	-0.13
56101	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.03	-0.02	-0.13
56102	-0.04	-0.034	-0.046	-0.024	-0.061	-0.042	-0.03	-0.02	-0.13
56104	-0.04	-0.034	-0.046	0.031	-0.061	-0.043	-0.03	-0.02	-0.13
56106	-0.045	-0.038	-0.052	-0.027	-0.069	-0.048	-0.03	-0.03	-0.14
56107	-0.045	-0.038	-0.052	-0.027	-0.069	-0.048	-0.03	-0.03	-0.14
56108	-0.045	-0.038	-0.051	-0.027	-0.068	-0.047	-0.03	-0.03	-0.14
56111	-0.044	-0.037	-0.051	-0.027	-0.067	-0.047	-0.03	-0.03	-0.14
56112	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.03	-0.03	-0.14
56113	-0.041	-0.034	-0.047	0.044	-0.062	-0.043	-0.03	-0.02	-0.13
56114	-0.04	-0.034	-0.047	-0.025	-0.062	-0.043	-0.03	-0.02	-0.13
56147	-0.04	-0.034	-0.046	0.037	-0.061	-0.043	-0.03	-0.02	-0.13
56148	-0.045	-0.038			-0.068	-0.048		-0.03	
56149	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.03	-0.03	-0.14
56151	-0.045	-0.038	-0.051	0.028	-0.068	-0.048	-0.03	-0.03	-0.14
56153	-0.045	0.048	-0.051	-0.027	-0.068	-0.047	-0.03	-0.03	-0.14
56154	-0.045	0.11	-0.051	-0.027	-0.068	-0.048	-0.03	-0.03	-0.14
56156	-0.04	-0.033	-0.045	0.024	-0.06	-0.042	-0.03	-0.02	-0.13
56157	-0.04	-0.033	-0.046	-0.024	-0.06	-0.042	-0.03	-0.02	-0.13
56158	-0.04	-0.034	-0.046	-0.025	-0.061	-0.043	-0.03	-0.02	-0.13
56159	-0.045	-0.038	-0.052	-0.027	-0.068	-0.048	0.04	-0.03	-0.14
56191	-0.04	-0.034	0.071	0.067	-0.061	-0.043	-0.03	-0.02	-0.13
56192	-0.04	-0.034	-0.046	0.05	-0.061	-0.042	-0.03	-0.02	-0.13
56193	-0.04	-0.034	-0.046	0.037	-0.061	-0.043	-0.03	-0.02	-0.13
56196	-0.04	-0.033	-0.045	0.035	-0.06	-0.042	-0.03	-0.02	-0.13
56197	-0.039	-0.033	2.7	0.056	-0.06	-0.042	-0.03	-0.02	-0.13
56198	-0.04	-0.034	-0.046	0.072	-0.061	-0.043	-0.03	-0.02	-0.13
56199	-0.04	-0.034	-0.046	0.03	-0.061	-0.042	-0.03	-0.02	-0.13
56200	-0.04	-0.034	-0.046	0.045	-0.061	-0.043	-0.03	-0.02	-0.13
56201	-0.04	-0.034	-0.046	0.035	-0.061	-0.043	-0.03	-0.02	-0.13
56205	-0.041	-0.034	-0.047	0.049	-0.062	-0.043	-0.03	-0.02	-0.13
56236	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.029	-0.026	-0.14
56238	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.029	-0.027	-0.14
56240	-0.045	-0.038	-0.051	-0.027	-0.068	-0.048	-0.029	-0.027	-0.14
56241	-0.04	-0.034	-0.046		-0.061	-0.043	-0.026	-0.024	
56244	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
56245	-0.043	-0.036	-0.049		-0.065	-0.046		-0.025	
56246	-0.053	-0.045	-0.061	-0.032	-0.081	-0.056	-0.034	-0.031	-0.17
56248	-0.042	-0.036	-0.049	-0.026	-0.065	-0.045	-0.028	-0.025	-0.14
56249	-0.044	-0.037	-0.051	-0.027	-0.067	-0.047	-0.029	-0.026	-0.14
56250	-0.045	-0.038	-0.052	-0.027	-0.069	-0.048	-0.029	-0.027	-0.14
56281									
56282	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
56283	-0.04	-0.034	-0.047	0.025	-0.062	-0.043	-0.026	-0.024	-0.13
56284	-0.04	-0.033	-0.045	-0.024	-0.06	-0.042	-0.026	-0.023	-0.13
56285	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
56286	-0.04	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
56287	-0.04	-0.034	-0.046	-0.024	-0.061	-0.042	-0.026	-0.024	-0.13
56288	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
56289	-0.04	-0.034	-0.046	-0.024	-0.061	-0.042	-0.026	-0.024	-0.13
56290	-0.04	-0.034	-0.046	-0.024	-0.061	-0.043	-0.026	-0.024	-0.13
56326	-0.04	-0.033	-0.046	-0.024	-0.061	-0.042	-0.026	-0.024	-0.13
56327	-0.04	-0.034	-0.046	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
56328	-0.041	-0.034	-0.047	-0.025	-0.062	-0.043	-0.026	-0.024	-0.13
56329	-0.048	-0.04	-0.055	-0.029	-0.072	-0.051	-0.031	-0.028	-0.15
56330	-0.048	-0.04	-0.055	-0.029	-0.073	-0.051	-0.031	-0.028	-0.15
56331	-0.046	-0.039	-0.053	-0.028	-0.07	-0.049	-0.03	-0.027	-0.15
56332									
56334	-0.043	-0.036	-0.049	-0.026	-0.065	-0.046	-0.028	-0.025	-0.14
56336	-0.041	-0.035	-0.047	-0.025	-0.063	-0.044	-0.027	-0.024	-0.13
56337	-0.048	-0.041	-0.055	-0.029	-0.073	-0.051	-0.031	-0.028	-0.15

Sample No	BDE 77 ng/g ww	BDE 49 ng/g ww	BDE 47 ng/g ww	BDE 100 ng/g ww	BDE 99 ng/g ww	BDE 154 ng/g ww	BDE 153 ng/g ww	BDE 183 ng/g ww	BDE 119 ng/g ww
36102	-0.089	0.099	0.78	0.29	0.74	0.082	0.097	0.016	-0.02
36103	-0.089	0.081	0.98	0.23	0.68	0.11	0.14	0.01	-0.02
36104	-0.09	0.05	0.24	0.14	0.24	0.09	0.07	0.01	-0.02
36105	-0.094	0.12	0.92	0.23	0.65	0.11	0.085	0.02	-0.022
36106	-0.09	0.074	0.48	0.18	0.32	0.086	0.07	0.00	-0.02
36109	-0.088	0.058	0.9	0.34	0.93	0.15	0.12	0.03	-0.02
36111	-0.089	0.072	0.5	0.33	0.65	0.15	0.10	0.01	-0.02
36113	-0.086	0.079	0.43	0.18	0.27	0.069	0.06	0.01	-0.02
36115	-0.09	0.049	0.53	0.22	0.43	0.1	0.08	0.01	-0.02
36118	-0.11	0.1	0.89	0.36	0.88	0.14	0.10	0.02	-0.03
36161	-0.088	-0.032	0.75	0.22	0.54	0.1	0.07	0.01	-0.02
36162	-0.09	0.1	0.74	0.31	0.81	0.12	0.15	0.02	-0.02
36163	-0.089	0.048		0.23	0.4	0.13	0.08	0.01	-0.02
36164	-0.096	0.084	0.61					0.03	-0.02
36165	-0.088	0.1	0.64	0.24	0.71	0.067	0.07	0.02	-0.02
36167	-0.089	0.074	0.93	0.32	0.84	0.13	0.09	0.02	-0.02
36168	-0.088	0.068	0.6	0.2	0.44	0.095	0.10	0.00	-0.02
36169	-0.091	0.034	0.25	0.23	0.28	0.094	0.06	0.01	-0.02
36170	-0.089	-0.032	0.41	0.26	0.36	0.07	0.07	0.01	-0.02
36171	-0.089	0.097	0.96	0.25	0.48	0.058	0.04	0.01	-0.02
36230	0.16	0.07	0.61	0.19		0.062	0.05	0.03	-0.02
36231	-0.08	-0.029	0.57			0.058	0.07		-0.02
36232									
36233	-0.089	0.054	0.79	0.29	1	0.095	0.10	0.02	-0.02
36236	0.15	0.082	1.4	0.42	1.1	0.11	0.09	0.02	-0.02
36238	-0.09	-0.032	0.72	0.21	0.71	0.055	0.04	0.01	-0.02
36239	-0.092	-0.033	0.49	0.21	0.36	0.069	0.09	0.02	-0.02
36240	-0.079	0.085	0.86	0.19	0.55	0.062	0.06	0.04	-0.02
36241	-0.1	-0.037	0.52	0.13	0.56	0.062	0.05	0.03	-0.02
36243	-0.072	1.3	2.7	0.95	3.8	0.32	0.49	0.02	0.02
36283	-0.078	-0.028	1.1	0.24	1	0.063	0.14	0.02	-0.02
36284	-0.089	-0.032	0.37	0.12	0.3	0.033	-0.01	0.00	-0.02
36285	-0.088	0.12	1	0.4	0.88	0.15	0.16	0.05	-0.02
36286	-0.09	0.045	0.57	0.17	0.6	0.073	0.07	0.02	-0.02
36287	-0.086	-0.031	0.23	0.067	0.25	0.024	0.04	0.01	-0.02
36290	-0.089	-0.032	0.25	0.071	0.24	0.042	0.04	0.01	-0.02
36291	-0.089	0.04	0.46	0.14	0.33	0.057	0.05	0.03	-0.02
36292	0.12	0.038	1.1	0.16	0.61	0.052	0.05	0.04	-0.02
36293	-0.088	0.046	0.75	0.22	1.1	0.1	0.10	0.02	-0.02
36295	-0.093	0.039	0.25	0.093	0.15	0.032	0.04	0.02	-0.02
46100	-0.087	-0.031	0.13			0.014		0.01	-0.02
46101	-0.095	-0.034	0.28	0.071	0.25	0.041	0.07	0.01	-0.02
46102	-0.089	-0.032	0.12	0.038	0.1	0.012		0.07	-0.02
46103	-0.089	-0.032		0.12				1.20	-0.02
46105	-0.1	-0.036	0.2	0.075		0.038	0.05	0.02	-0.02
46109	-0.089	0.045	0.23	0.068	0.22	0.027	0.03	0.01	-0.02
46110	-0.089	-0.032	0.19	0.035	0.17	0.02	0.03	0.01	-0.02
46111	-0.086	-0.031	0.15			0.011		0.01	-0.02
46113	-0.087	-0.031					-0.01	0.00	-0.02
46114	-0.095	-0.034	0.14	0.045	0.17	0.033	0.072	0.16	-0.022
46160	-0.12	-0.045				0.04	0.05	0.025	-0.028
46161	-0.084	-0.03					-0.0066	0.025	-0.019
46162	-0.088	0.033	1.6	0.14	0.26	0.016	0.055	0.032	-0.02
46163	-0.09	-0.032	-0.015	-0.0072	-0.025	0.014	-0.007	0.0094	-0.021
46165	-0.1	-0.037	0.17	0.11			-0.008	-0.002	-0.024
46166	-0.086	-0.031	0.18	-0.0069	-0.024	0.029	-0.0067	-0.0017	-0.02
46168	-0.097	-0.035		0.033		0.012	-0.0075	-0.0019	-0.022
46170	-0.099	-0.036	0.2	0.052		0.027	0.044	0.0086	-0.023
46171	-0.09	-0.032	-0.015	-0.0072	-0.025	0.012	0.018	-0.0017	-0.021
46172	-0.097	-0.035	0.37	0.1	0.55	0.087	0.19	0.022	-0.022
46220	-0.094	-0.034	0.18	0.035	0.16	0.023	-0.0073	0.0098	-0.022
46221	-0.13	-0.046	0.3	0.088	0.25	0.04	-0.0099	-0.0025	0.033
46222	-0.054	-0.02	0.12	0.04	0.11	0.02	-0.0042	0.0081	-0.012
46223	-0.056	-0.02	0.15	0.029	0.14	0.014	-0.0044		-0.013
56371	-0.099	-0.036	1.2	0.38	1.5	0.24	0.33	0.066	-0.023
56372	-0.099	-0.036	0.33	0.07		0.025	0.061	-0.0019	0.028
46281	-0.08	-0.029	0.33	0.058			0.035		-0.018
46288	-0.089	-0.032	0.97	0.13	0.235	0.028	0.0305	0.0047	-0.0205

Sample No	BDE 77 ng/g ww	BDE 49 ng/g ww	BDE 47 ng/g ww	BDE 100 ng/g ww	BDE 99 ng/g ww	BDE 154 ng/g ww	BDE 153 ng/g ww	BDE 183 ng/g ww	BDE 119 ng/g ww
46291	-0.096	-0.035	0.24	0.057		0.037	0.058	-0.0019	-0.022
46292	-0.085	-0.031		0.12	0.36	0.043	0.043	0.005	-0.019
46293	-0.09	0.034	0.63	0.092	0.5		0.056		-0.021
46294									
46295	-0.11	-0.041	0.49	0.082	0.46	0.064	0.21	0.024	-0.026
46297	-0.075	-0.027	0.19	0.05	0.14	0.027	0.022		-0.017
46298	-0.085	-0.031	0.36	0.091	0.26		0.05	0.14	-0.019
46299	-0.09	-0.032	0.29	0.08	0.3	0.046	0.034	0.0059	-0.021
56101	-0.09	0.095	0.51	0.26	0.52	0.073	0.095	0.0062	-0.021
56102	-0.088	0.098	0.28	0.11	0.29	0.068	0.095	0.014	-0.02
56104	-0.089	0.072	0.81	0.24	0.96	0.071	0.2	0.17	-0.02
56106	-0.099	0.063						0.043	-0.023
56107	-0.099	-0.036						0.17	-0.023
56108	-0.099	0.044	0.45	0.2	0.45	0.049	0.11	-0.0019	-0.023
56111	-0.098	0.12					0.17	0.31	-0.022
56112	-0.099	-0.036					-0.0077	0.43	-0.023
56113	-0.09	0.13	1.4					0.013	-0.021
56114	-0.09	0.14	1.4					-0.0017	-0.021
56147	-0.089	0.26	2.9	0.68	3	0.23	0.28	0.027	0.04
56148	-0.099								
56149	-0.099	0.14	0.99	0.3	1	0.13	0.14	0.0087	-0.023
56151	-0.099	0.22	3.1	1.1	3.1	0.37	0.53	0.019	-0.023
56153	-0.098	0.21	2.6	0.75	2.6	0.34	0.36	0.013	0.04
56154	-0.099	0.28	3.2	0.95	3.3	0.43	0.46	0.027	0.076
56156	-0.087	0.13	0.79	0.21	0.65	0.11	0.078	0.0073	0.022
56157	-0.088	0.13	0.67	0.15	0.67	0.12	0.11	0.0047	-0.02
56158	-0.089	0.086	0.76	0.17	0.6	0.078	0.085	0.0096	-0.021
56159	-0.099	0.21	0.93	0.27	0.92	0.17	0.19	0.014	-0.023
56191	-0.089	0.14							-0.02
56192	-0.088	-0.032						-0.0017	-0.02
56193	-0.089	0.17						-0.0017	-0.02
56196	-0.088	-0.032						-0.0017	-0.02
56197	-0.087	-0.031	1.1	0.31	0.63	0.064	0.084	-0.0017	-0.02
56198	-0.088	-0.032	1.3	0.4	0.92	0.086	0.053	-0.0017	-0.02
56199	-0.088	-0.032	1.1	0.37	1	0.14	-0.0069	-0.0017	-0.02
56200	-0.089	-0.032				2.2	-0.0069	-0.0017	-0.02
56201	-0.089	-0.032	0.54	0.14	0.45	0.044	-0.0069	-0.0017	-0.02
56205	-0.09	0.21	3.1	0.65	2.8	0.27	0.27	0.0097	-0.021
56236	-0.099	0.057	0.91	0.24	0.8	0.078	0.086	0.0083	-0.023
56238	-0.099	-0.036	0.92	0.29	0.93	0.083	0.095	-0.0019	-0.023
56240	-0.099	-0.036	0.76	0.25	0.75	0.075	0.087	0.011	-0.023
56241	-0.089								0.023
56244	-0.09	0.033	0.99	0.21	0.8			0.051	-0.021
56245	-0.095								0.085
56246	-0.12	-0.042	1.8	0.34	1.2	0.13	0.18	0.013	-0.027
56248	-0.094	0.036	0.62	0.17	0.48	0.04		0.0036	-0.022
56249	-0.097	-0.035	0.68	0.15	0.44	0.043	0.052	0.014	-0.022
56250	-0.1	-0.036	0.71	0.18	1.4	0.11	0.15	0.012	-0.023
56281									
56282	-0.089	-0.032	0.39	0.075	0.35	0.031	0.048	0.0039	-0.02
56283	-0.09	-0.032	0.56	0.11	0.52	0.035	0.039	0.014	-0.021
56284	-0.087	0.12	0.73	0.25	0.82	0.072	0.062	0.0027	-0.02
56285	-0.089	0.16	0.69	0.19	0.6	0.07	0.053	-0.0017	-0.02
56286	-0.09	0.08	0.66	0.18	0.59	0.047	0.052	0.0027	0.064
56287	-0.088	0.045	0.48	0.1	0.43	0.024	0.029	0.0017	-0.02
56288	-0.089	0.12	0.81	0.22	0.79	0.07	0.061	0.0018	-0.02
56289	-0.088	0.071	1.2	0.26	1.1	0.085	0.079	0.0028	-0.02
56290	-0.089	0.056	0.38	0.13	0.3	0.038	0.023	-0.0017	0.027
56326	-0.088	0.084	1.1	0.17	0.87	0.072	0.061	-0.0017	-0.02
56327	-0.089	-0.032				0.012	0.016	-0.0017	-0.021
56328	-0.09	-0.032				0.014	0.014	0.0025	-0.021
56329	-0.11	0.05	0.28	0.058	0.26	0.023	0.031	0.0035	-0.024
56330	-0.11	-0.038	0.43	0.11	0.42	0.03	0.046	-0.002	-0.024
56331	-0.1	-0.037	0.35	0.07	0.28	0.019	0.022	0.0042	-0.023
56332									
56334	-0.095	-0.034	0.32	0.07	0.31	0.016	0.026	0.0032	-0.022
56336	-0.091	-0.033	0.56	0.087	0.48	0.031	0.043	0.0069	-0.021
56337	-0.11	-0.038	0.42	0.15	0.4	0.031	0.044	-0.0021	-0.024

Sample No	BDE 116 ng/g ww	BDE 85/155 ng/g ww	BDE 126 ng/g ww	BDE 118 ng/g ww	BDE 155 ng/g ww	BDE 138 ng/g ww	BDE 166 ng/g ww	BDE 181 ng/g ww	BDE 190 ng/g ww
36102	-0.12	0.041	-0.038	-0.24	0.011	-0.0012	-0.002	-0.0038	-0.0054
36103	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36104	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36105	-0.13	0.1	-0.04	-0.26	0.0094	-0.0013	-0.0021	-0.004	-0.0057
36106	-0.12	-0.04	-0.038	-0.25	0.011	-0.0012	-0.002	-0.0038	-0.0054
36109	-0.12	0.059	-0.038	-0.24	0.015	-0.0012	-0.002	-0.0037	-0.0053
36111	-0.12	-0.039	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36113	-0.12	-0.038	-0.037	-0.24	-0.0024	-0.0012	-0.0019	-0.0036	-0.0052
36115	-0.12	0.072	-0.038	-0.25	0.0092	-0.0012	-0.002	-0.0038	-0.0054
36118	-0.15	0.12	-0.047	-0.3	0.011	-0.0015	-0.0025	-0.0046	-0.0066
36161	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
36162	-0.12	-0.04	-0.038	-0.25	0.022	0.028	-0.002	-0.0038	-0.0054
36163	-0.12	0.043	-0.038	-0.24	0.014	-0.0012	-0.002	-0.0038	-0.0054
36164	-0.13	-0.043	-0.041	-0.26	-0.0027	-0.0013	-0.0022	-0.0041	-0.0058
36165	-0.12	-0.039	-0.038	-0.24	0.0057	-0.0012	-0.002	-0.0037	-0.0053
36167	-0.12	0.11	-0.038	-0.24	0.011	-0.0012	-0.002	-0.0038	-0.0054
36168	-0.12	-0.039	-0.037	-0.24	0.012	-0.0012	-0.002	-0.0037	-0.0053
36169	-0.12	-0.04	-0.039	-0.25	0.014	-0.0012	-0.0021	-0.0038	-0.0055
36170	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
36171	-0.12	0.081	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36230	-0.12	-0.039	-0.038	1.4	0.0047	-0.0012	-0.002	-0.0037	-0.0053
36231	-0.11	-0.036	-0.034	-0.22	-0.0022	-0.0011	-0.0018	-0.0034	-0.0048
36232									
36233	-0.12	-0.039	-0.038	-0.24	0.0099	-0.0012	-0.002	-0.0038	-0.0054
36236	0.16	0.053	-0.035	-0.23	0.0064	-0.0011	-0.0019	-0.0035	-0.005
36238	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36239	-0.12	-0.041	-0.039	-0.25	-0.0025	-0.0012	-0.0021	-0.0039	-0.0055
36240	-0.11	-0.035	-0.034	-0.22	-0.0022	-0.0011	-0.0018	-0.0033	-0.0048
36241	-0.14	-0.045	-0.043	-0.28	-0.0028	-0.0014	0.037	-0.0043	-0.0061
36243	-0.099	0.2	-0.031	-0.2	0.024	0.036	-0.0016	-0.0031	-0.0044
36283	-0.11	0.069	-0.033	-0.21	0.0071	-0.0011	-0.0018	-0.0033	-0.0047
36284	-0.12	-0.039	-0.038	-0.25	0.017	-0.0012	-0.002	-0.0038	-0.0054
36285	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
36286	-0.12	-0.04	-0.038	-0.25	0.0056	-0.0012	-0.002	-0.0038	-0.0054
36287	-0.12	-0.038	-0.037	-0.24	-0.0024	-0.0012	-0.0019	-0.0036	-0.0052
36290	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
36291	-0.12	0.26	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
36292	-0.12	0.37	-0.038	-0.25	0.01	-0.0012	-0.002	-0.0038	-0.0054
36293	-0.12	0.56	-0.038	-0.24	0.0074	0.021	-0.002	-0.0037	-0.0053
36295	-0.13	-0.041	-0.04	1.6	-0.0026	0.043	0.081	-0.0039	-0.0056
46100	-0.12	-0.038	-0.037	-0.24	-0.0024	-0.0012	-0.002	-0.0037	-0.0052
46101	-0.13	-0.042	-0.041	-0.26		0.025	-0.0022	-0.004	-0.0057
46102	-0.12	-0.039	-0.038	-0.25	0.0026	-0.0012	-0.002	0.027	0.027
46103	-0.12	-0.039	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
46105	-0.14	-0.044	-0.043	-0.28	0.0038	0.012	-0.0023	-0.0042	-0.0061
46109	-0.12	-0.039	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
46110	-0.12	-0.039	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
46111	-0.12	-0.038	-0.037	-0.24	-0.0024	-0.0012	-0.0019	-0.0036	-0.0052
46113	-0.12	-0.039	-0.037	-0.24	-0.0024	-0.0012	-0.002	-0.0037	-0.0053
46114	-0.13	-0.042	-0.04	-0.26	0.0006	0.025	-0.0021	-0.004	0.46
46160	-0.17	-0.055	-0.053	-0.34	-0.0034	0.017	-0.0028	-0.0052	-0.0075
46161	-0.12	-0.037	-0.036	-0.23	0.037	-0.0011	-0.0019	-0.0036	-0.0051
46162	-0.12	-0.039	-0.038	-0.24	-0.0024	-0.0012	-0.002	-0.0037	-0.0053
46163	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
46165	-0.14	-0.046	-0.044	-0.28	-0.0029	-0.0014	-0.0023	-0.0044	-0.0062
46166	-0.12	-0.038	-0.037	-0.24	0.0036	0.0072	-0.0019	-0.0036	-0.0052
46168	-0.13	-0.043	-0.041	-0.27	-0.0027	-0.0013	-0.0022	-0.0041	-0.0058
46170	-0.14	-0.044	-0.042	-0.27	-0.0027	-0.0013	-0.0022	-0.0042	-0.006
46171	-0.12	-0.04	-0.038	-0.25	0.0046	-0.0012	-0.002	-0.0038	-0.0054
46172	-0.13	-0.043	-0.042	-0.27	0.005	0.039	-0.0022	-0.0041	-0.0059
46220	-0.13	-0.042	-0.04	-0.26	-0.0026	-0.0013	-0.0021	-0.004	0.051
46221	-0.17	-0.056	-0.054	-0.35	-0.0035	-0.0017	-0.0029	-0.0054	-0.0077
46222	-0.074	-0.024	-0.023	-0.15	-0.0015	-0.00073	-0.0012	-0.0023	-0.0033
46223	-0.077	-0.025	-0.024	-0.15	-0.0016	-0.00076	-0.0013	-0.0024	-0.0034
56371	-0.14	0.2	-0.042	-0.27	0.018	0.074	0.052	-0.0042	-0.006
56372	-0.13	-0.044	-0.042	-0.27	-0.0027	-0.0013	-0.0022	-0.0042	-0.0059
46281	-0.11	-0.036	-0.034	-0.22	-0.0022	-0.0011	-0.0018	-0.0034	-0.0048
46288	0.275	-0.0395	-0.038	-0.25	0.00055	-0.0012	-0.002	-0.00375	-0.00535

Sample No	BDE 116 ng/g ww	BDE 85/155 ng/g ww	BDE 126 ng/g ww	BDE 118 ng/g ww	BDE 155 ng/g ww	BDE 138 ng/g ww	BDE 166 ng/g ww	BDE 181 ng/g ww	BDE 190 ng/g ww
46291	-0.13	-0.043	-0.041	-0.26	0.0077	-0.0013	-0.0022	-0.0041	-0.0058
46292	-0.12	-0.037	-0.036	-0.23	0.0042	0.0073	-0.0019	-0.0036	-0.0051
46293	-0.12	-0.04	-0.038	-0.25	-0.0025		-0.002	-0.0038	0.35
46294									
46295	-0.16	-0.051	-0.049	-0.31	0.0085	-0.0015	-0.0026	-0.0048	-0.0069
46297	-0.1	-0.033	-0.032	-0.21	0.0023	-0.001	-0.0017	-0.0032	-0.0045
46298	-0.12	-0.037	-0.036	-0.23	0.0051	-0.0011	-0.0019	0.31	0.31
46299	0.35	-0.04	-0.038	-0.25	0.0053	0.01	-0.002	-0.0038	-0.0054
56101	-0.12	-0.04	-0.039	-0.25	0.0083	-0.0012	-0.002	-0.0038	-0.0054
56102	-0.12	-0.039	-0.038	-0.24	0.0084	-0.0012	-0.002	-0.0037	0.12
56104	-0.12	-0.039	-0.038	-0.25	-0.0025	-0.0012	-0.002	0.25	0.25
56106	-0.14	-0.044	-0.043	-0.27		-0.0013	-0.0023	-0.0042	-0.006
56107	-0.14	-0.044	-0.043	-0.27		-0.0013	-0.0023	0.066	0.07
56108	-0.13	-0.044	-0.042	-0.27	0.0039	-0.0013	-0.0022	-0.0042	-0.0059
56111	-0.13	-0.043	-0.042	-0.27		-0.0013	-0.0022	-0.0041	-0.0059
56112	-0.13	-0.044	-0.042	-0.27		-0.0013	-0.0022	-0.0042	0.13
56113	-0.12		-0.038	-0.25	0.015	-0.0012	-0.002	-0.0038	-0.0054
56114	-0.12		-0.038	-0.25	0.017	-0.0012	-0.002	-0.0038	-0.0054
56147	-0.12	0.29	-0.038	-0.24	0.02	0.048	-0.002	-0.0037	-0.0053
56148	-0.14		-0.042				-0.0022	-0.0042	
56149	-0.14	0.11	-0.042	-0.27	0.0075	-0.0013	-0.0023	-0.0042	-0.006
56151	-0.14	0.39	-0.042	-0.27	0.021	0.058	-0.0023	-0.0042	-0.006
56153	-0.13	0.26	-0.042	-0.27	0.02	0.05	-0.0022	-0.0042	-0.0059
56154	-0.14	0.4	-0.042	-0.27	0.025	0.074	-0.0022	-0.0042	-0.006
56156	-0.12	0.071	-0.037	-0.24	0.0084	-0.0012	-0.002	-0.0037	-0.0053
56157	-0.12	0.094	-0.037	-0.24	0.008	-0.0012	-0.002	-0.0037	-0.0053
56158	-0.12	0.12	-0.038	-0.25	0.0064	-0.0012	-0.002	-0.0038	-0.0054
56159	-0.14	0.16	-0.042	-0.27	0.01	-0.0013	-0.0023	-0.0042	-0.006
56191	-0.12		-0.038	-0.25			-0.002	-0.0038	-0.0054
56192	-0.12	-0.039	-0.038	-0.24		-0.0012	-0.002	-0.0037	-0.0053
56193	-0.12	-0.039	-0.038	-0.24		-0.0012	-0.002	-0.0038	-0.0054
56196	-0.12	-0.039	-0.037	-0.24		-0.0012	-0.002	-0.0037	-0.0053
56197	-0.12	-0.039	-0.037	-0.24	-0.0024	-0.0012	-0.002	-0.0037	-0.0052
56198	-0.12	-0.039	-0.038	-0.24	0.019	-0.0012	-0.002	-0.0037	-0.0053
56199	-0.12	-0.039	-0.038	-0.24	-0.0024	-0.0012	-0.002	-0.0037	-0.0053
56200	-0.12	-0.039	-0.038	-0.24	0.16	-0.0012	-0.002	-0.0037	-0.0053
56201	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
56205	-0.12	0.22	-0.038	-0.25	0.024	-0.0012	-0.002	-0.0038	-0.0054
56236	-0.13	0.07	-0.042	-0.27	0.0074	0.0053	-0.0022	-0.0042	-0.006
56238	-0.14	0.067	-0.042	-0.27	0.011	-0.0013	-0.0022	-0.0042	-0.006
56240	-0.13	-0.044	-0.042	-0.27	0.0089	0.0039	-0.0022	-0.0042	-0.006
56241	-0.12		-0.038	-0.24			0.013		
56244	-0.12	0.15	-0.038	-0.25	0.019	0.019	-0.002	0.019	0.013
56245	-0.13		-0.04	-0.26			-0.0022		
56246	-0.16	0.16	-0.05	-0.32	-0.0032	0.037	-0.0027	-0.0049	-0.007
56248	-0.13	-0.042	-0.04	-0.26	-0.0026	-0.0013	-0.0021	-0.004	-0.0057
56249	-0.13	0.063	-0.042	-0.27	-0.0027	0.0077	-0.0022	-0.0041	-0.0059
56250	-0.14	0.073	-0.043	-0.27	0.0073	0.031	-0.0023	-0.0042	-0.006
56281									
56282	-0.12	-0.039	-0.038	-0.24	0.0067	-0.0012	-0.002	-0.0037	-0.0053
56283	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
56284	-0.12	-0.039	-0.037	-0.24	0.0081	-0.0012	-0.002	-0.0037	-0.0053
56285	-0.12	0.14	-0.038	-0.24	0.012	-0.0012	-0.002	-0.0037	-0.0053
56286	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
56287	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
56288	-0.12	-0.039	-0.038	-0.24	0.012	-0.0012	-0.002	-0.0037	-0.0053
56289	-0.12	-0.039	-0.038	-0.24	0.012	-0.0012	-0.002	-0.0037	-0.0053
56290	-0.12	-0.039	-0.038	-0.24	-0.0025	-0.0012	-0.002	-0.0037	-0.0053
56326	-0.12	-0.039	-0.038	-0.24	0.011	-0.0012	-0.002	-0.0037	-0.0053
56327	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
56328	-0.12	-0.04	-0.038	-0.25	-0.0025	-0.0012	-0.002	-0.0038	-0.0054
56329	-0.14	-0.047	-0.045	-0.29	-0.0029	-0.0014	-0.0024	-0.0044	-0.0063
56330	-0.14	-0.047	-0.045	-0.29	-0.0029	-0.0014	-0.0024	-0.0045	-0.0064
56331	-0.14	-0.045	-0.044	-0.28	-0.0028	-0.0014	-0.0023	-0.0043	-0.0061
56332									
56334	-0.13	-0.042	-0.04	-0.26	-0.0026	-0.0013	-0.0022	-0.004	-0.0057
56336	-0.12	-0.04	-0.039	-0.25	0.033	-0.0012	-0.0021	-0.0038	-0.0055
56337	-0.15	-0.047	-0.045	-0.29	0.006	-0.0014	-0.0024	-0.0045	-0.0064