Lessons learned from monitoring organic contaminants in three decades of marine samples from the Pacific basin archived at the USA's Marine Environmental Specimen Bank

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The USA's Marine Environmental Specimen Bank (ESB) has archived marine wildlife collections dating back to 1976. Numerous lessons have been learned including collecting the correct species and tissues for environmental contaminant monitoring, developing protocols for mitigating sample contamination, and ensuring that samples can be used for new analytes and techniques. Investigations of organochlorine contaminants in several collections from the Pacific basin for species, regional, and temporal trends revealed that α-hexachlorocyclohexane (HCH) declined for all species/regions and was lowest in samples from Hawaii while polybrominated diphenyl ether (PBDE) 47 significantly increased in Alaskan marine mammals with the highest levels in California sea lions and adult male cetaceans that stranded in Hawaii. Chlordanes and dichloro-diphenyl-trichloroethanes (DDTs) declined

except for beluga whales, and polychlorinated biphenyls (PCBs) significantly declined for only common and thick-billed murres from St. George Island, Alaska and common murres from St. Lazaria Island, Alaska. The Marine ESB is also in the process of ensuring easy access to sample information and previous analytical results for other researchers to use this invaluable resource.

Introduction

Trend monitoring studies are invaluable in describing historical and current contamination and modeling future trends by legacy persistent organic pollutants (POPs), e.g. polychlorinated biphenyls (PCBs) and past-use organochlorine pesticides, as well as contaminants of emerging concern.[1,2] Determining trends in environmental contaminants requires access to quality samples, and especially in the case of contaminants that were not historically monitored, environmental specimen banks (ESBs) are a logical choice for obtaining samples for this purpose. ESBs are facilities that participate in long-term preservation of environmental samples. There is an international network of ESBs (www.inter-esb.org) and several journal issues have been devoted to the description and role of ESBs in environmental monitoring [Science of the Total Environment 1993 Vol. 139–140, Chemosphere 1997 Vol. 34(9–10), Journal of Environmental Monitoring 2006 Vol. 8(8), Interdisciplinary Studies on Environmental Chemistry 2010 Vol. 4]. ESBs have thus been shown to be valuable resources of samples to investigate trends of contaminants as a function of sample type, species, location and time.

Monitoring contaminants in the marine environment is challenging due to the remoteness and the difficulty of obtaining samples. The USA's Marine ESB has sample collections dating back to 1976 for mussels and oysters, 1987 for marine mammals, 1999 for seabirds and since 2011 for sea turtles. However, many of these collections are opportunistic. Descriptions of the Marine ESB and these programs (except for the sea turtles) were previously reported by Pugh et al.[3] Currently the Marine ESB collection holds over 100,000 aliquots in liquid nitrogen vapor-phase freezers (-150 °C) from 12,000 animals. Figure 1 provides a general overview of the Marine ESB programmatic sampling locations. Lessons learned from monitoring organic contaminants from some of these marine samples banked at the Marine ESB are presented here.

Figure 1. Marine Environmental Specimen Bank (ESB) programs and generalized sampling locations.

The right species and tissue choice is important

In monitoring contaminant trends, careful choice of species and tissue is crucial to ensure the sample set accurately addresses study goals. For instance, if a researcher is interested in recent contaminant exposure, blood would be a better tissue than blubber/fat, which is more reflective of long-term contaminant exposure except in cases of re-mobilization due to starvation.[4,5] Likewise, if a researcher is interested in contaminants from a specific region, a non-migratory species should be chosen, or the migratory species should be sampled later in the season to ensure the majority of contaminants found in the sample are representative of the study region (e.g. Kucklick et al.[6]). Several guides to choosing species and tissues for biomonitoring have been published previously.[7-9] Provided below are examples from the Marine ESB on why the choice of

species and tissue can be extremely important when assessing environmental contaminant trends.

One component of the Marine ESB, the Seabird Tissue Archival and Monitoring Project (STAMP) began collecting eggs of murres (*Uria* spp.) and black-legged kittiwakes (*Rissa tridactyla*) in 1999. The rationale and protocols for these collections was described in detail by York et al.[10] Briefly, murres were chosen as deep diving with a clutch of only one large egg that that may be replaced if lost early in the season, so eggs were collected as early as possible. Kittiwakes were chosen to represent a different guild; surface-feeders that prey on small fish and euphausiids and lay up to three smaller eggs that were to be banked as a clutch. In 2004, glaucous gull (*Larus hyperboreus*) and glaucous-winged gull (*L. glaucescens*) eggs were added in partnership with the Bureau of Indian Affairs - Alaska Regional Subsistence Branch. Gulls are opportunistic predators and scavengers (including marine mammals and human refuse) and lay clutches of two or three eggs, which are an important food source for many Alaskan Natives. While contaminant information on gulls is important from a human health perspective and to establish baseline ranges of ecological values, using gull eggs for long-term biomonitoring is not advisable. The inability to always archive entire clutches (e.g. collection before the entire clutch was laid, after wild predation, or egg breakage in transport or processing) can lead to difficulty in accounting for laying order effects on contaminants.[11] The wide range of prey consumed by gulls also results in more variable contaminant concentrations, making the interpretation of spatial and temporal trends more challenging.

Life history is a major influence on contaminant burdens.[12,13] A priori knowledge of the questions that may be asked of a sample set is crucial for determining the correct species and tissue to sample as well as the metadata that needs to be recorded for future researchers to be able to properly choose samples from the specimen bank.

Elimination of all sample contamination is impossible, so protocols should be well documented and blanks created

Developing standardized protocols, Standard Operating Procedures (SOPs), or Standard Operating Guidelines (SOGs), is critical to the success of long-term ESB programs. The emphasis is to maintain, through optimal long-term preservation, collections of high-quality specimens that can be used for deferred analysis and evaluation.[14] To provide the highest quality specimens for continuous time-trend studies and spatial monitoring based on materials collected repeatedly over a long period of time (i.e., decades), all procedures

must follow standardized protocols. When developing SOPs many criteria should be considered, including the type of sample to collect, as previously discussed; how, if necessary, the sample should be processed; and how it should be stored (e.g. container type and storage condition). A pilot study for testing protocols should be conducted to determine if the protocol is feasible and if pre-analytical variables will have an effect on sample collection and processing. The success of the collection and storage protocols that are ultimately written depend on the success of the pilot study. All written protocols should also be updated on a regular basis (e.g. annually), made readily accessible for anyone providing samples to the ESB, and to ensure compliance by the contributor, a training program should be established. A well-planned and executed SOP or protocol can determine the success of an ESB by standardizing specimen handling procedures and ensuring uniformity and reproducibility of the processed specimens. In any long-term study, successful completion absolutely requires strict adherence to continuity of defined protocols.

Taking into consideration the field collection conditions as well as the possibility of extraneous sources of contamination, it is also recommended that a 'field blank' or 'reference blank' also be taken during the time of sample collection. Clean water from a water purification system can be collected in place of the tissue or fluid sample and should be handled in the exact same manner that the sample was collected, processed, and stored.

Polytetrafluoroethylene (PTFE)-based plastic containers (e.g., Teflon^{TM}) have been widely used as a storage container for archived samples as this material is inert and can withstand liquid nitrogen temperatures. PTFE-based plastics were also thought to be non-contaminating to the samples. However, since PTFE-based plastics were first widely used in ESBs, there have been numerous studies showing that PTFE-like compounds are pervasive in wildlife arising through food web exposure (see review by Reiner and Place[15]). This poses a challenge for the Marine ESB and other banks that have stored and processed samples using PTFE-based products. A thorough study was undertaken to estimate the amount of perfluorinated alkyl acids (PFAAs; historically the major component of PTFE-based plastics) that may have contaminated the samples. Negligible amounts of perfluorooctane sulfonate (PFOS) and perfluorononanoic acid (PFNA; approximately 0.2 ng/g and 0.1 ng/g, respectively) were found to leach from materials used during sample processing, but perfluorooctanoic acid (PFOA) was estimated to leach up to 1 ng/g.[16] While this PFAA contamination from sample processing and storage is minimal, in the Marine ESB, some samples are now being stored in both PTFE-based plastics and polypropylene containers to eliminate some of the PFAAs contamination concerns, but still

allow for organic analysis, especially of phthalates, for future temporal trend studies.

There will always be something new to study

An average of 4000 new chemicals are added to the Chemical Abstracts Service (CAS) REGISTRY (www.cas.org) every day.[17] While only a small percentage of these chemicals are expected to be produced in high enough volume and have the physical-chemical properties to become persistent, bioaccumulative, toxic compounds (PBTs),[18,19] this still leaves hundreds of new compounds each year that could be PBTs. Samples from the Marine ESB have been analyzed retrospectively for measuring several classes of contaminants of emerging concern and should also prove useful for future unknown PBTs as well.

PFAAs have over 200 industrial and commercial uses, the most well-known being stain-resistance,[20] and have been produced since the 1950s but were not known to be PBTs until the early 2000s. Reiner and Place[15] reviewed the studies of PFAAs in wildlife including retrospective studies of numerous species from international specimen banks. From the Marine ESB, beluga whales (*Delphinapterus leucas*),[21] northern fur seals (*Callorhinus ursinus*),[22] and five species of sea turtles[23,24] have had retrospective studies published. Seabird eggs have also been analyzed for PFAAs, but many were below the detection limit.[25]

Flame retardants have also been used for decades and were known to be PBTs in the 1980s.[26] Brominated flame retardants (BFRs) include polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Several reviews provide more in-depth information on flame retardants and in particular BFRs.[26-30] While others were reporting environmental concentrations of BFRs in the early 1990s, NIST did not begin to focus on BFRs until after assigning values to Standard Reference Materials (SRMs).[31] Since then, samples from various species in or associated with the Marine ESB have been analyzed for BFRs, including white-sided dolphins (*Lagenorhynchus acutus*),[32,33] California sea lions (*Zalophus californianus*),[34] beluga whales,[35] northern fur seals,[22] common and thick-billed murres (*Uria aalge* and *U. lomvia*),[36-40] glaucous and glaucous-winged gulls,[37,38,41] five species of sea turtles,[16,42-47] and 16 species of cetaceans that stranded in Hawaii.[48] In the near future, chlorinated and phosphorus flame retardants as reviewed by Marvin et al.[49] will also be examined.

Beyond chemical contaminants, measurement methods are continually being developed to detect disease agents and screen for far-reaching changes to

biological systems through omics techniques. Cryogenically stored tissue samples can be useful for these research topics and a sea turtle tissue bank has been developed with these uses in mind. The collection and banking of sea turtle tissues from the Pacific Basin began in 2011 under a project known as Biological and Environmental Monitoring and Archival of Sea Turtle Tissues (BEMAST).[50] Plasma samples archived by the BEMAST project were used to examine differences in the array of small molecule metabolites, using metabolomics, between green sea turtles (*Chelonia mydas*) with and without fibropapillomatosis (FP).[51] FP is a disease associated with a herpesvirus that causes the growth of debilitating tumors that can impede sight, foraging, and movement in threatened and endangered sea turtles. In the Hawaiian Islands, the disease prevalence peaked in the mid 1990's (≈50 % at one site) and has been declining since.[52] No significant differences were seen between the metabolome of turtles with or without tumors, but the methods developed from these preliminary samples[51] could be applied to a much larger sample size now available in the specimen bank. Currently, green sea turtle plasma samples archived by BEMAST from across the Pacific Ocean are being analyzed for gene expression through transcriptomics methods.[53] These results will be compared to FP prevalence and POPs measured previously in these same turtles[44] to determine if this disease or these contaminants influence the expression of certain genes.

Analytical methods improve over time

Analytical methods are constantly evolving as critically reviewed by Muir and Sverko.[54] Methods are changing so quickly that Analytical Chemistry now devotes the first issue of each year to new analytical methods and techniques.

While not specific to the Marine ESB, a classic example of analytical changes over time is that involving PCB analysis. PCBs are highly bioaccumulative and frequently monitored in ESB samples. One of the major changes in PCB analysis came as a result of the availability of individual PCB congeners[55] and the use of the congeners for developing methods using capillary column methods (e.g. Schulz et al.[56]). Once standards and methods became available, the newer congener analysis using capillary-column gas chromatography (GC) was soon favored over Aroclor standards for PCB analysis that relied on packed-column GC. However, values obtained from the newer PCB congener methods were less than half of those based on Aroclors derived using packed column GC.[57]

Using ESB samples, total PCB concentrations measured using older, non-capillary column GC have been adjusted to values generated using congener

specific analysis.[58] A set of common murre eggs archived in the ESB at the Swedish Museum of Natural History collected prior to 1988 that had total PCB values based on older methods were re-analyzed using congener-specific PCB methods. The observed relationship between total PCBs generated using both old and new methods allowed for the Swedish ESB to adjust older PCB data and construct a temporal record for total PCB concentrations in common murre eggs stretching back to the late 1960s. While the use of matrix-matched certified reference materials with each batch of samples does assist in accurately accounting for many analytical method changes, in this case, the ability to retrospectively compare values from different methods using banked samples was invaluable.

Properly collected and stored specimen bank samples allow researchers to retrospectively obtain baseline values and compare species and locations

One of the first retrospective studies from the Marine ESB examined PBDEs, HBCDs and the naturally occurring methoxylated polybrominated diphenyl ethers (MeO-BDEs) in blubber from California sea lions that stranded between 1993 and 2003.[34] Additional retrospective studies on blubber from Alaskan beluga whales subsistently harvested between 1989 and 2006 examined PFAAs, PBDEs, HBCDs, as well as PCBs and organochlorine pesticides.[21,35] The most recent study also examined these compounds in blubber from subadult male northern fur seals that were harvested on St. Paul Island, Alaska between 1987 and 2007 with paired livers being analyzed for PFAAs and vitamins A and E.[22] While no temporal trends were available, PCBs, organochlorine pesticides, PBDEs, and HBCDs baseline values were assigned for 16 species of cetaceans that stranded in the Main Hawaiian Islands from 1997 to 2011.[48] These studies demonstrated the usefulness of the Marine ESB to examine new compounds of interest as well as retrospective analysis with newer instrumentation.

The STAMP component has analyzed samples in batches throughout the collections with SRM 1946 Lake Superior Fish Tissue and an in-house murre egg homogenate.[59] Beginning with the 2001 collections, PBDEs were added to the list of routine analytes. PFAAs were retrospectively examined, but many were below the detection limit.[25] Black-footed albatross (*Phoebastria nigripes*) and Laysan albatross (*P. immutabilis*) egg collections from Hawaii began in 2010 to supplement the Alaskan egg data.

The BEMAST project has collected blood and scutes from live captures of green sea turtles, hawksbill sea turtles (*Eretmochelys imbricata*), and leatherback sea

turtles (*Dermochelys coriacea*). Fresh dead specimens of these species, as well as olive ridley sea turtles (*Lepidochelys olivacea*) and loggerhead sea turtles (*Caretta caretta*), are also sampled during necropsies for scutes, fat, muscle, bile, liver, blubber, GI tract and if available, follicles, shelled eggs, and fibropapilloma (FP) lesions, as well as skin from leatherbacks. Green and hawksbill sea turtle nests are also excavated after emergence and unhatched eggs collected.[50] Several BEMAST samples have been analyzed for POPs and heavy metals.[16,44,60,61] In one study, POPs and other halogenated phenolic compounds were found to not be responsible for initiating the disease FP in Hawaiian green sea turtles.[44]

For the purposes of further discussing organic contaminant temporal trends in the North Pacific basin, selected data from the studies on blubber from California sea lions (only males),[34] northern fur seals (juvenile males),[22] belugas (adult males),[35] and eggs from murres[25,36-40,62] archived by the Marine ESB were examined. Temporal trends data previously published for the marine mammals may differ slightly from the results shown here due to the selection of only certain samples to limit confounding factors, such as gender and age, and the use of a wet mass basis rather than lipid normalized basis as previously published for some of the data. Lipid content was not available for some samples, necessitating the use of wet mass basis, and the use of lipid normalization may cause additional bias as well, especially when contaminant and lipid levels are not correlated.[63] The recently collected albatross[25] and sea turtle[16,44] samples were excluded as these have fewer years available for temporal trends and the sea turtle data is from plasma further confounding the comparisons. In addition, the 16 species of cetaceans stranded in the Hawaiian Islands[48] were excluded due to lack of temporal comparisons within one species, gender, and age class. However, the data from the albatross and male cetacean samples are shown in Table 1 for spatial comparisons.

Summary statistics on ng/g wet mass basis followed methods recommended in Helsel.[64] Briefly, non-parametric Kaplan-Meier estimates were used for data sets with >50% detection, the robust maximum likelihood or robust regression on order statistic estimates were used for data sets with 20-50% detection, and for data sets with <20% detection only the proportions above or below the maximum reporting limit are provided. Data sets with 100% detection follow standard distribution-based statistics. Hypothesis testing for temporal trends in data sets with <100% detection were tested using the Akritas-Theil-Sen nonparametric estimate of slope with the Turnbull estimate of intercept, while generalized linear models fitting normal/lognormal distributions as appropriate (Kendall's tau regression in the case of nonparametric distribution) were used for data sets with 100% detection. Only compounds with near 100% detection rate were used for

this investigation. Of the PBDEs, only PBDE 47 was available for statistical testing because not all samples were analyzed for PBDEs or the other congeners were below detection for the majority of the samples. For the hexachlorocyclohexanes (HCHs), α-HCH was only used due to differences in pathways among the HCH isomers[65] and a lack of β-HCH data for some samples. The sum of dichloro-diphenyl-trichloroethanes (DDTs: 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT), chlordanes (oxychlordane, cis-chlordane, cis-nonachlor, trans-chlordane and trans-nonachlor) and 18 PCB congeners (28+31, 66, 99, 101, 105, 106+118, 132+153, 138+163, 146, 170, 180+193, 183, and 187) were also investigated (Table 1). Temporal trends were visualized (Figure 2) using a locally-weighted moving average for non-significant sets (broken lines) and the generalized linear model for significant sets (solid lines) with the 95% standard error (SE) slope as the shaded region. The data points for each species/location/year are limited due the mostly opportunistic collections of the Marine ESB necessitating care when comparing trends and attempting to make predications. However, exercises like this allow hypotheses to be formed and if feasible, a more targeted sampling program to be developed.

PBDE 47 levels were an order of magnitude greater in central California sea lions compared to other species collected from Alaska (Figure 2.). Other geographical comparisons for PBDEs showed greater levels in livers of sea otters (*Enhudra lutris*) from California compared with Washington, Alaska, or Russia,[66] and in blood plasma of bald eagle (*Haliaeetus lueucocephalus*) nestlings from California compared with British Columbia, Canada.[67] While a point source for PBDEs is not known in California, a law (TB117) requiring polyurethane foam and baby products sold in California to not ignite when exposed to an open flame for 12 seconds, may have resulted in high levels of these contaminants as a pentaBDE mixture (BDEs 47, 97, 99, 100, and 153) was the major chemical added to meet this flame-resistant requirement until its ban in 2003.[68] Northern fur seals from St. Paul Island, Alaska, and beluga whales from Cook Inlet and the Chukchi Sea showed a significant ($p < 0.05$) increasing temporal trend for PBDE 47 while other species did not (Table 1 and Figure 2).

Selected other compounds were examined for temporal changes (Table 1). α-HCH was the dominant isomers of technical HCH that was used as an insecticide from 1943 until being banned in the late 1970s to early 1990s and is one of the most abundant PBTs in arctic air and water.[69] All species and locations showed a decline in α-HCH, with only the trend for common murre eggs from Bluff, Alaska not significant ($p > 0.05$). However, this location only has samples from 2002, 2005 and 2008, so more years of collections may be needed to see significant trends.

Table 1. Summary statistics (ng/g wet mass) for selected contaminants with temporal trend slopes in male marine mammal and seabird egg samples organized geographically from the Marine Environmental Specimen Bank (ESB).

Species	Location	n	Age	$\sum_{18}$PCBs				∑DDTs				∑Chlordanes				α-HCH				PBDE 47			
				Mean	Median	SD	Slope	Mean	Median	SD	Slope	Mean	Median	SD	Slope	Mean	Median	SD	Slope	Mean	Median	SD	Slope
Blubber																							
9 species of cetaceans	Hawaii strandings	10	Juvenile	4460	2130	8100	NA	10600	3350	20000	NA	1040	508	1500	NA		<2.52		NA	242	34.2	50	NA
9 species of cetaceans	Hawaii strandings	10	Adult	3250	2800	1900	NA	6680	6500	3400	NA	770	746	430	NA		<2.40		NA	48.6	33.5	40	NA
California Sea Lion (*Zalophus californianus*)	Central CA Coast	26	Juvenile & Adult	Not Measured																876	794	380	→[c]
Beluga Whale (*Delphinapterus leucas*)	Cook Inlet, AK	14	Adult	985	877	400	→	1960	1810	890	→	494	439	170	→[b]	34.8	33.3	11	↘[***,c]	11.2	7.98	6.5	↗[***,a]
Northern Fur Seal (*Callorhinus ursinus*)	St. Paul I., AK	50	Juvenile	1040	1090	310	→	NA	910	1200	↘[*,d]	537	455	270	↘[***,b]	NA	34.3	29	↘[***,e]	16.2	11.3	14	↗[***,b]
Beluga Whale (*Delphinapterus leucas*)	Chukchi Sea, AK	23	Adult	2700	2570	920	→	3740	3910	1400	→	2240	2370	670	→	40.0	27.8	29	↘[*,b]	8.39	7.17	5.0	↗[***,b]
Eggs																							
Laysan Albatross (*Phoebastria immutabilis*)	Main Hawaiian Islands	43	Not Applicable (NA)	217	194	85	NA	223	174	150	NA	18.2	16.7	5.7	NA	0.362	0.362	0.035	NA		<0.143		NA
Common Murre (*Uria aalge*)	St. Lazaria I., AK	53		137	122	74	↘[*,b]	200	175	87	↘[***,b]	8.36	6.87	5.7	↘[***,b]	0.981	0.941	4.0	↘[**,c]	10.5	7.3	11	→[b]
Thick-billed Murre (*Uria lomvia*)	St. Lazaria I., AK	36		120	112	74	→[b]	196	192	83	↘[***,b]	7.49	6.18	6.3	→[*,b]	1.49	0.952	1.6	↘[*,a]	NA	6.74	10	→[d]
Thick-billed Murre (*Uria lomvia*)	Buldir I., AK	15		56.0	52.6	21	→	109	108	22	↘[*]	NA	5.98	1.9	↘[d]	1.06	0.939	0.43	↘[***,f]	0.419	0.464	0.27	→
Common Murre (*Uria aalge*)	St. George I., AK	31		45.2	34.9	27	↘[***, a]	63.0	39.9	30	↘[***,d]	7.87	5.52	6.2	↘[***,b]	1.12	1.07	0.48	↘[***]	0.271	0.300	0.12	→
Thick-billed Murre (*Uria lomvia*)	St. George I., AK	29		46.6	45.5	20	↘[***]	76.7	82.2	29	↘[**]	5.30	4.87	2.8	↘[***]	2.11	1.55	1.8	↘[*,a]	0.343	0.273	0.22	→
Common Murre (*Uria aalge*)	St. Lawrence I., AK	13		44.3	41.2	8.9	→	57.0	46.9	23	→[b]	5.22	5.80	2.8	↘[*,c]	0.783	0.754	0.25	↘[*]	0.264	0.281	0.10	→[g]
Thick-billed Murre (*Uria lomvia*)	St. Lawrence I., AK	21		45.1	46.5	15	→	NA	45.4	28	↘[*,e]	5.68	5.77	2.7	↘[**,c]	NA	0.724	4.0	↘[**,e]	0.351	0.279	0.23	→
Common Murre (*Uria aalge*)	Bluff, AK	15		45.4	46.8	16	→	43.6	44.1	13	↘[*]	7.04	4.88	5.0	↘[b]	NA	0.327	0.18	↘[d]	0.750	0.630	0.66	→[b]

[a] Log-normal dataset, non-parametric distribution; [b] Log-normal dataset and distribution; [c] Normal dataset, log-normal distribution; [d] Median/interquartile range (IQR) dataset, non-parametric distribution; [e] Median/IQR dataset, normal distribution; [f] Log-normal dataset, normal distribution; [g] 92 % detection frequency, non-parametric distribution;[*] $p < 0.05$;[**] $p < 0.01$;[***] $p < 0.005$

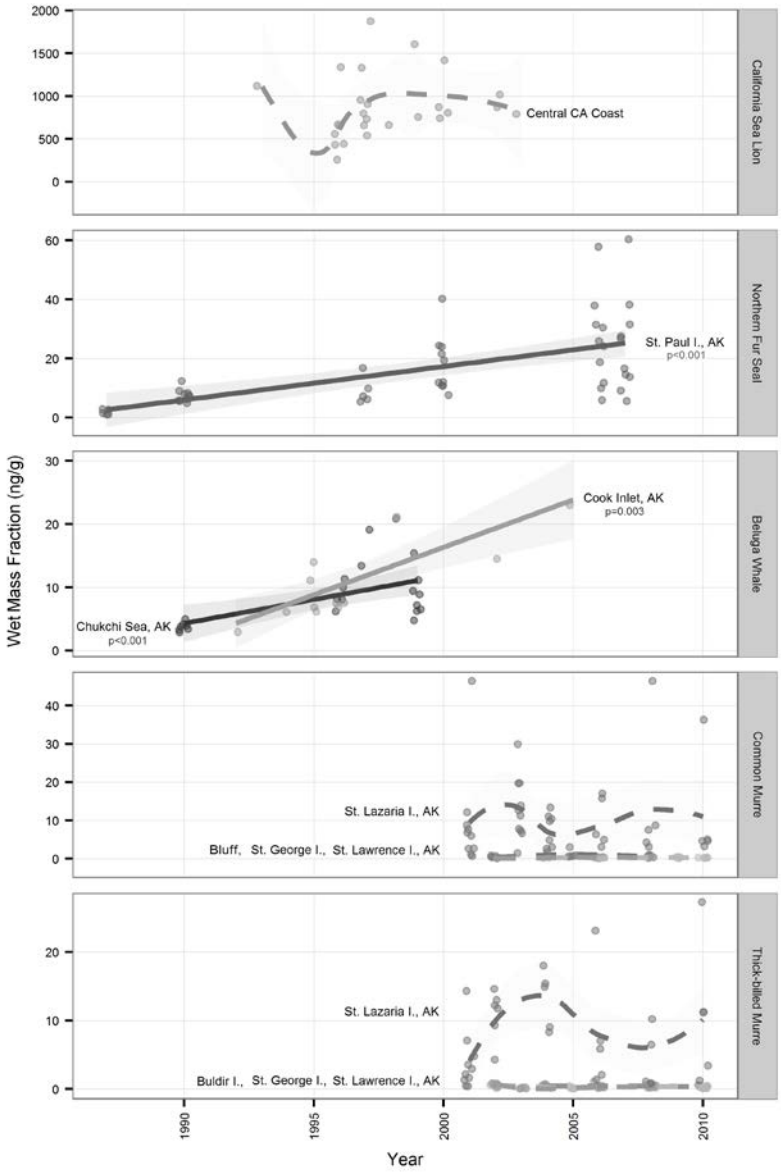

Figure 2. Levels of PBDE 47 in marine mammal blubber and seabird eggs from the North Pacific. Solid lines indicate significant ($p < 0.05$) temporal trends. Note: the scale changes for each species and the murre colonies overlap except St. Lazaria I., AK

Chlordanes, another insecticide used predominantly for termite control in the US from 1946 to 1988,[70] exhibited also mostly negative trends, with the exception of beluga whales from Cook Inlet, Alaska, which showed a 0.2 % increase but was not significant ($p > 0.05$). Beluga whales from the Chukchi Sea had a very large negative slope but this was also not significant along with the common murres from Bluff, Alaska. Results were similar for DDT and its metabolites. DDT was first synthesized in 1874 and used as an insecticide since 1939.[71] While production and use was limited by the Stockholm Convention beginning in 2004, DDT continues to be produced and used to treat malaria.[72] For DDTs, the Bluff common murre eggs showed a significant ($p < 0.05$) decline, but those from St. Lawrence Island, Alaska were not significant. PCBs were produced from 1930 until 1993 for use as coolants and lubricants in electrical equipment.[73] The sum of 18 major PCB congeners (out of a possible 209) showed significant ($p < 0.05$) negative declines for only common and thick-billed murres from St. George Island, Alaska and common murres from St. Lazaria Island, Alaska. Beluga whales from both Cook Inlet and the Chukchi Sea and common murre eggs from St. Lawrence, Island and Bluff showed positive, but non-significant ($p > 0.05$) trends.

Due to species and tissue differences, geographical differences are difficult to examine. However, with the exception of PBDE 47 discussed above, these selected contaminants were highest in beluga whales from the Chukchi Sea and the cetaceans stranded in Hawaii compared to all other species and locations shown in Table 1. Beluga whales from Cook Inlet were similar in concentration to Northern fur seals from St. Paul Island, Alaska. A more thorough comparison of the beluga populations is available in Hoguet et al.[35] Among the murre eggs, St. Lazaria Island in the Southeast Gulf of Alaska had the highest levels of PCBs, DDTs, and PBDE 47. The PBDE 47 levels in St. Lazaria murres were similar to beluga whales and northern fur seals (Table 1). Chlordanes and α-HCH were similar among all locations of murre eggs. The Laysan albatross eggs from Hawaii had lower levels of α-HCH and PBDE 47 compared to the murre eggs, but higher levels of PCBs, DDTs, and chlordanes. The cetaceans stranded in Hawaii also had very low levels of α-HCH, reflecting the trend discussed by Li and Macdonald for α-HCH to dominate at higher latitudes.[65] While PBDE 47 in the Hawaiian Laysan albatross eggs was generally below detection, the cetaceans stranded in Hawaii had higher levels than the Alaskan marine mammals. A manuscript detailing the temporal changes and geographical differences of contaminants in murre eggs is in preparation, but distinctive time point geographical differences are detailed in Vander Pol et al.[36-40, 62]

ESBs are for the common good, but researchers need easy access to sample information and previous contaminant results

The Marine ESB samples are available to other researchers via tissue access policies. One project is federally mandated by United States Law and is available at: https://mmhsrp.nmfs.noaa.gov/tissbk. Other projects have policies established within written protocols and procedures and are provided in publicly available reports.[50,74] These policies are similar to the data published by the Japanese Environmental Specimen Bank,[75] Antarctic Environmental Specimen Bank,[76] and German Environmental Specimen Bank (UPB).[77]

A new data platform that is currently being developed is the Marine Sample Tracking and Analytical Reporting (STAR). Marine STAR will make it easier for researchers to not only determine which samples are available in the Marine ESB, but also view the results of previous chemical analysis with links to publications via a web-based interface. Currently only the UPB has interactive contaminant data available to the public. Similar resources applied to all specimen banks would greatly enhance our understanding of global trends regarding environmental contaminants in biotic matrices.

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Disclaimer

Certain commercial equipment or instruments are identified in the paper to specify adequately the experimental procedures. Such identification does not imply recommendations or endorsement by the NIST nor does it imply that the equipment or instruments are the best available for the purpose.

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