Use of Catalogued Long-term Biological Collections and Samples for Determining Changes in Contaminant Exposure to Organisms

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Abstract For decades, biological materials have been collected and held in museum collections, natural history collections (NHC), herbaria and environmental specimen banks (ESB). Those biological materials and accompanying data represent a potentially important source of retrospective analyses of contaminants and other chemical tracers. In ideal situations, those can provide valuable insights into changes in contaminant accumulation and concentrations over time and space. This chapter explores the benefits of such curated and catalogued specimens for contaminant research, as well as limitations and key considerations which must be kept in mind when using such samples. Three case studies examining temporal trends in contaminants using long-term biological collections are also presented.

Keywords Museum · Contaminants · Mercury · Organochlorines · Birds · Fish · Retrospective analyses

Introduction

Museum and herbarium specimens of animals and plants stored worldwide in natural history collections (NHC), as well as catalogued samples from environmental specimen banks (ESB), can be valuable for documenting long-term changes in biotic accumulation of contaminants. Those sources of biological tissues often complement long-term contaminant monitoring programs, such as the long-running Sportfish Monitoring Program by the Ontario Ministry of Environment (Province of Ontario 2013), which typically analyzed organisms, such as fish, at the time of

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J. M. Blais et al. (eds.), *Environmental Contaminants*, Developments in Paleoenvironmental Research 18, DOI 10.1007/978-94-017-9541-8_15

sampling, but do not store samples because of logistical constraints. Monitoring programs can be used to carry out retrospective analyses of *data* (e.g., French et al. 2006; Gandhi et al. 2014); however, they do not allow for retrospective analyses of *samples* for other emerging contaminants or chemical tracers. Both monitoring programs and retrospective analyses of catalogued samples provide valuable insights and have their respective advantages and disadvantages (Gewurtz et al. 2011), although only catalogued archive samples make it possible to reassess emerging chemicals and legacy contaminants using improved analytical technology.

While typically not collected for chemical analyses, animal, plant and other biological specimens held in NHCs, ESBs, biological collections in museums and herbaria represent a valuable repository of catalogued samples collected during periods when scientists were not as aware about environmental contaminants (Table 1). Those specimens, which can date back to the mid-1800s or even earlier, can be useful indicators of environmental contamination during a period of increasing industrialization prior to the 1970s. As a result, those catalogued tissues provide baseline data on contaminant concentrations for comparing against those of modern organisms. NHC specimens are diverse, ranging from whole organisms to various types of tissues, all carefully preserved and catalogued as per standard curation practices for that type of collection. Analyses of NHC specimens are often highly appealing to environmental scientists, as inclusion of those samples in studies can make it possible to extend temporal analyses of tissue contaminant concentrations over decades (e.g. Frederick et al. 2004), even centuries in some cases (e.g., Outridge et al. 2009). However, the issues of contamination, preservation and chemical stability due to storage need to be taken into consideration. Museum and herbaria specimens were often not collected for the specific purpose of chemical analyses, so interpretations of such data are not always straightforward (e.g., Renauld et al. 1995; Hogstad et al. 2003).

In contrast, biological tissue archives and ESBs especially set up for the purpose of chemical monitoring and appropriate long-term storage of samples for chemical analyses have typically been established for only a few decades at most. Typically, selected tissues are isolated, processed in clean laboratories, and frozen with rigorous quality control. There are at least 23 ESB in 15 countries at the time of this writing, with more being developed (Day et al. 2014). Long-term specimen archives were established by many national and regional governments when society became concerned about increasing environmental contaminants and environmental health, usually around the 1970s (e.g., Kolossa-Gehring et al. 2012). Countries such as Germany, Sweden, Japan, United States of America, and Canada have established long-term archives typically centered around specific types of tissues such as marine mammals (Becker et al. 1997; Miyazaki 1994), aquatic organism tissues (McGoldrick et al. 2010), terrestrial and avian wildlife (Braune et al. 2010). A few countries also maintain multi-matrix (e.g. many types of samples from animal, plant and non-living material) ESB, including Germany (Kolossa-Gehring et al. 2012) and Sweden (Odsjö 2006), which produce useful information on the national state of environment.

Table 1 Typical tissue and sample type analysed for contaminants and chemical tracers from catalogued archives held in Natural History Collections and Environmental Specimen Banks

Birds	Fish	Mammals	Reptiles	Invertebrates	Plants
• Feathers • Egg contents • Egg shells • Toe pads	• Whole fish (preserved) • Whole fish (homogenized) • Muscle • Scales • Otoliths	• Fur, hair & baleen • Keratin structures (nails, claws) • Ossified tissues: Bone, teeth, tusks & other ossified tissues • Blubber • Organs	• Scales • Skin • Shell (Turtles) • Muscle	• Whole body • Shell-removed • Muscle (e.g. from legs or tails)	• Flowering parts. • Roots • Tree cores • Tree bark • Whole moss & lichen. • Seaweed and other algae.

Increasingly, researchers are recognizing the high value of museum and herbaria NHC to obtain data on biological tissue contaminant concentrations prior to the 1970s. This chapter will provide a critical examination of both museum and herbaria NHC and long-term monitoring specimen banks for contaminant research, and discuss the benefits of using those resources for such research. We will first detail the types of tissues and specimen collections that have been used for contaminant analyses. Then we will outline challenges and key limitations to keep in mind when interpreting data obtained from such collections. Finally, we provide three case studies that successfully used long-term specimen collections to extend analyses of contaminants beyond what was feasible for modern sampling. All specimen collections share one thing in common: specimens tend to be catalogued and indexed in a common institutional database for reference. Therefore, from here on, we will use "catalogued" as a key descriptor to refer to specimen and tissue samples from any kind of long-term collection.

The Uses of Catalogued Tissues and Specimens for Contaminant Research Museums and herbaria around the world contain biological specimens, often collected for taxonomic and systematic research, and maintained by professional curators over time using standard NHC protocols. Collections can include both local organisms acquired as part of most museums' and herbaria's mandates to increase knowledge of natural history in their region, and those from international locations associated with specific research projects undertaken by curatorial staff. Many museums and herbaria are long-established, with the oldest items in their catalogued collections dating back approximately to the same era as for their establishment—although many biological materials can date back centuries especially if collected as a part of anthropological or archeological research. Over the past few decades. As support for taxonomic and systematic research declined, but funding has increased for other areas of biological research (Pyke and Ehrlich 2010), thereby increasing attention in the value of museum and herbaria collections as repositories of biological tissues for analyses in the opening decades of the twentieth century (Suarez and Tsutsui 2004; Lavoie 2013).

The use of NHC specimens for contaminant analyses is not a recent phenomenon, with many pioneering studies taking place around the time of increased concern about environmental contaminants in the 1960s and the 1970s. Those studies tended to focus on birds and mammals whose external tissue structures (feathers, fur, teeth) were easily accessed and subsampled without extensive structural damage to the museum specimen. Many bird and mammal specimens are stored as skins, gently stuffed with cotton wool, so there are typically no internal organs available for analyses. Skins are typically treated with fungicides and pesticides to prevent insect and fungus loss, which are important considerations for any researcher wishing to undertake contaminant analyses of such specimens.

In the 1960s, the increasing use of DDT and its observed impacts on bird populations were becoming increasingly apparent. As a result, it was important to establish a baseline for comparison with modern bird samples. Several scientists undertook analyses of catalogued bird egg and bird feathers, as well as analyzing a database

of eggshell thicknesses going back to the 1880s. They were able to demonstrate significant and positive relationships between increasing DDT concentrations, the decline of bird populations and the thinning of eggshells over time (Ratcliffe 1967; Hickey and Anderson 1968; Peakall 1974). Likewise, a Swedish study of preserved bird specimens demonstrated a consistent pattern of increasing mercury over time between 1940 and 1950, likely associated with industrial development (Berg et al. 1966). Scientists in Japan attempted to use bat specimens from a museum Chiroptera collection in Tokyo to establish a pre-application baseline prior to the use of organomercuric fungicides for agriculture in the region (Miura et al. 1978). Such research has continued with a steady series of publications since that period, which have investigated specific concerns that can only be understood using catalogued biological collections. Those include spatiotemporal patterns of contaminants throughout a large region (e.g., marine mammals of the Arctic; Dietz et al. 2009; birds of Michigan; Head et al. 2011) or to undertake retrospective analyses of specific contaminants known to influence population health for a vulnerable species (e.g. endangered Florida panthers *Puma concolor coryi*; Newman et al. 2004).

Correspondingly, in line with the bird and mammal research, there was a similar movement towards analyses of chemically wet-preserved fish from museum ichthyological collections in the early 1970s (e.g., Miller et al. 1972; Evans et al. 1972; Barber et al. 1972). Whole fish are typically fixed in formalin for a short period before transferred to ethanol or another alcohol preparation for long-term storage in glass or metal for larger fish. However, serious doubt was cast upon the use of wet-preserved fish collections for retroactive contaminant analyses (Gibbs et al. 1974; Renauld et al. 1995). Around this time, long-term aquatic freshwater and marine specimen banks and monitoring programs were established in the 1970s and 1980s, ensuring a better quality of sample and analyses for fish contaminant research. Subsequently, very little was published on preserved fish until the early 2000s when there was a resurgence of interest and a better capacity to clean and identify specific compounds and congeners of interest separate from the total contaminant burden. Currently, most modern studies focus on mercury, specifically methylmercury, in preserved fish, with the theory that most methylmercury measured in fish tissues would be of biological origin via accumulation, not via external contamination which is assumed to be mostly inorganic mercury (e.g., Drevnick et al. 2007; Hill et al. 2010; Kraepiel et al. 2003; Poulopoulos 2013). Exploratory investigations have been carried out to assess the potential of using wet-preserved fish tissues analyses of other elements as well (Renauld et al. 1995; Poulopoulos 2013).

Plants, mosses, algae and other primary producer materials from any herbarium, museum or specimen bank appear to be less cited in the literature compared to animal tissue studies. Herbaria typically store pressed plant material with identifying diagnostic structures attached to a flat labelled whiteboard, while mosses, lichen and fungi are air-dried and stored in a labelled paper envelope or container. Mercury and arsenic contamination of herbaria from older preservation methods remain a major concern for many herbaria worldwide (Oyrazun et al. 2007), making for another complicating consideration for researchers. In ecological studies, moss and

lichen samples from herbaria are more frequently considered (e.g., Herpin et al. 1997; Minganti et al. 2014) relative to other types of primary producer specimens, likely due to their utility as atmospheric biomonitors of contaminants (Augusto et al. 2013; Foan et al. 2010; Wolterbeek 2002), and their storage method minimizing contamination. Tree ring cores for dendrochronological and dendrochemical research have been used increasingly for metal and contaminant analyses (Siwik et al. 2010; Watmough and Hutchinson 1996), which also brings in the potential for analyses of older wood material in museums and herbaria for multi-decadal and multi-century contaminant analyses (Padilla and Anderson 2002). All considerations and challenges associated with sampling animal specimens in catalogued collections at museums also apply to plant and primary producer materials in herbaria and archeological collections.

Specimen archives and ESBs, by their nature, are maintained for high quality samples and data. As a result, there is extensive standardized documentation of specimens (size, location of sampling, names of samplers, time of sampling, etc.), quality control used for sample processing and storage as well as quality control for analytical results (Day et al. 2014). Therefore, data obtained from ESBs tend to be of the highest quality, and are typically more consistent and more robust than those from NHC specimens. Furthermore, properly prepared and frozen or dried catalogued tissues tend to be the least altered (McFarland et al. 1995), so thus can be analysed for a wider range of contaminants such as organic compounds relative to wet-preserved museum samples. Those ESB samples also tend have larger volume, so larger number of subsamples can be analysed. As a result, opportunities exist for retrospective analyses of tissues from key regions, especially as new chemicals become a concern (e.g., brominated flame retardants in Japanese marine mammals; Tanabe and Ramu 2012), or if new contaminants need to be tracked retrospectively (e.g., Borgmann and Whittle 1992). However, limitations and significant challenges exist for specimen banks especially in regards to long-term operation, national priorities, funding levels and access to limited samples (Braune et al. 2010).

Sources and Considerations for Catalogued Tissues Natural history museums, herbaria and other museum institutions holding NHC and biological materials often have multiple foci. Those can include the need for educating the public about regional flora and fauna, national and international collection interests of curators and research staff, and the institutional priorities as decided by its board and senior staff. In addition, collections can have inherent biases due to the goals during the sampling itself, such as obtaining type specimens and voucher specimens, which are essential for species description as per international taxonomy and species description standards. Therefore, obtaining sufficient samples from such collections for spatiotemporal continuity and robust experimental designs appropriate for contaminant research may not always be possible. The spatial, temporal and taxonomical content of catalogued collections can be diverse and wide-ranging, sometimes shifting over time with changing institutional priorities, making it difficult to design a research project without a thorough investigation of multiple catalogues. In fact, many researchers often find that they must consult the catalogues and visit many

museums and herbaria in order to collect a sufficient number of specimens for any single site and temporal period (e.g., Poulopoulos 2013). As a result, the types of tissues sampled tend to be restricted to a short list (Table 1), with feathers, fur, nails and muscle being the most common types of tissues used for analyses.

Most museums and herbaria are members of consortia, both national and international, which allow them to share their electronic catalogues and access to paper catalogues. Graham et al. (2004) tabulated a list of national and international NHC databases with corresponding websites, most of which are still current. It must be kept in mind that many museums and herbaria are also in the process of converting paper records and specimen labels into electronic databases, so many databases may still be incomplete. Often it is necessary for researchers to work closely with curators to track down and document specimens of interest during a research visit. Researchers wishing to investigate collections for potential samples can query databases listing the catalogued specimens and any ancillary information associated with those specimens. Two such international consortia compiling national databases around the world are the Global Biodiversity Information Facility (GBIF, URL: http://www.gbif.org/) and the more recent Scientific Collections International (SciColl, URL: http://www.scicoll.org/content/about-scicoll). Even so, not all institutions with NHC have contributed databases, and it is wise to individually contact curators and archivists in the region, especially to track down specimens of interest from smaller museums, universities and private collections (Casas-Marce et al. 2012).

It is important to understand that, for many NHC, conserving the structural integrity of each specimen is of paramount concern for curators and archivists for taxonomic and systematic purposes. This is often in direct conflict with environmental chemical research, because for many types of chemical analyses, the removal of a small tissue sample and destructive analytical techniques are required. Non-invasive techniques, which do not rely on destructive methods, such as x-ray fluorescence (XRF) and micro-XRF using synchrotron technology (Janssens et al. 2000), are usually preferred by curators and archivists whenever possible especially for rarer samples. Recent improvements in analytical techniques and corresponding lower detection limits have meant that increasingly small sample masses are now feasible for analyses which make it easier to take smaller tissue samples. Those technological improvements have helped with gaining access to high-value collections while ensuring minimal destruction. However, in recent times, due to the increasing focus on usefulness of museum and herbaria collections for long-term trend analyses of contaminants, chemical signatures, and genetic material, many curators have established policies for collections under their responsibility to facilitate "responsible destructive sampling" when there is scientific merit. Those policies can include retaining duplicate imperfect specimens and simplifying paperwork (Lister et al. 2011). A mutually beneficial relationship between the researcher and the curator is advised, including help with database entry, maintaining sample provenance in publications, updating and correcting data and respecting the sample integrity as per collection priorities at all times.

Another high priority for curators and archivists is maintaining provenance of specimens and documenting how collections are used to aid education and research,

especially if tissue must be removed from the specimen. This includes tracking the various uses of catalogued collections and any subsequent data derived from specimens. This additional information and meta-data will enhance the value of the specimens and the museum's role in research. As a result, it is highly recommended that all researchers include a list of specimen codes associated with each sampled specimen in their published output, such as an appendix in a thesis, online supplementary material accompanying a published journal article, or cited in any output with a freely available online document with permanent URL via a university or research website repository. These steps enhance the chain of provenance and the curators' ability to maintain meta-data related to each specimen and correct auxiliary data.

ESBs tend to be more focused on national priorities with particular taxon groups, regions, and/or times being targeted for intensive collecting and cataloguing. Sampling for specimen banks is frequently done specifically for environmental monitoring of contaminants and other chemical tracers, meaning that temporal continuity for selected sampling locations may be better established relative to samples obtained from many NHCs. Requests to access specimens in an ESB will usually be screened by a scientific committee who will consider several parameters, including scientific merit, whether the information can be obtained via other avenues, whether there is sufficient tissue remaining, and the requirement for all publications using ESB specimens acknowledge the source of tissues. Through the standardized banking of specimen tissues, important questions that can only be answered through retrospective analyses (Braune et al. 2010), as well as evaluating compliance with environmental regulations over time (Day et al. 2014), are made possible.

While the quality of samples and data from ESB may be more consistent, working with ESB samples has inherent challenges. Nearly all ESBs were established in the 1970s or later, meaning that samples in catalogued ESB collections may not date back to earlier years prior to the period of increasing industrial contamination. This is in contrast to many NHC that often contain specimens collected earlier, often to the early 1900s or even the 1800s in some cases. Furthermore, despite consistent sampling, ESB archives may not necessarily have the range of species and sampling locations required for a large spatiotemporal analytical project, a food web study, or large-scale biodiversity patterns. However, a robust study designed to maximize the value of samples collected within ESB's constraints can be valuable, not only scientifically, but also for policy and legislation formulation.

Data Interpretation and Cautions

Once samples are obtained from long-term catalogued collections and analysed, the data will need to be interpreted and presented. There are several inherent challenges that must be taken into consideration when presenting results. Those challenges include preservation methodology, storage of specimens, sampling bias, spatiotemporal patchiness of collections, and ethical considerations. A major challenge of using catalogued specimens is that the results may not be directly comparable to freshly

collected modern samples, or there is no experimental confirmation that such specimens can be comparable over time. All catalogued samples in long-term collections and specimen banks have been preserved by different means, e.g. chemical preservation (wet, dry), drying or freezing (Table 2). Each preservation method will affect the chemical structure and ratios of elements in different ways.

Of greatest concern for contaminant and trace element analyses of NHC specimens is chemical fixation and wet preservation of samples. The wet-chemical preservation process introduces more chemicals to the specimen, intended to preserve its structural integrity, but can significantly affect the chemical composition of its tissues. Formalin, which consists of about 37% formaldehyde in water with methanol, combines with nitrogen in proteins to form methylene bridge crosslinks in tissues (Kiernan 2000). The formation of crosslinks results in a hardening of tissues and preservation of tissue structures, hence the "fixation" step. Once fixation is done, the specimen will often then be immersed in ethanol or another alcohol for long-term preservation. There have been several experimental studies suggesting that tissues undergoing formalin fixation and ethanol preservation will have consistent and predictable changes in stable isotopes of C and N, which can then be adjusted to comparable modern values (Rennie et al. 2012; Schmidt 2009). Studies of preservative effects on mercury, trace elements, and contaminants in tissues, however, still are scarce despite the fast-growing number of publications using wet-preserved samples for trace elements. Hill et al. (2010) and Poulopoulos (2013) both carried out experiments indicating that mercury concentrations in wet-preserved tissues undergo consistent and predictable changes, which suggest that NHC ichthyological collections and other wet-preserved organisms may be used for mercury research. Furthermore, Poulopoulos (2013) assessed the effects of preservative on various trace metals in fish muscle over time using inductively coupled plasma—mass spectrometry (ICP MS), and found that most trace elements followed a similar temporal trend in fish muscle after preservation, and provided several recommendations for appropriate protocols for sampling and interpreting subsequent data from museum collections. Because ethanol can extract fatty tissues and organic chemicals from tissues, it is not highly recommended that NHC wet-preserved tissues are analysed for fatty acid or lipid-soluble organic contaminants without extensive prior laboratory experimentation as per Poulopoulos (2013) and Rennie (2012).

Dry preservation of biological specimens can be undertaken in several ways. First the specimen is skinned, and either the skin (with feathers, fur or other structures attached) or the skin with skull is dried around a cotton wool support. To prevent insect and rodent damage, the skin can be preserved with toxic powders (arsenic mercuric compounds, pesticides) or with borax (Schieweck et al. 2007). As a result, skins prepared prior to the 1960s may often have arsenic or mercury contamination (Hogstad et al. 2003), which needs to be carefully cleaned prior to trace metal analyses. Prepared skins are then kept in sealed drawers to minimize exposure to light, UV, insects and other pests. Skins are often prepared by removing internal organs and bones, then adding a preservative or pesticide to prevent damage to the skin over time before mounting over a cotton wool form (Hogstad et al. 2003). As a result, it is frequently recommended that feather, fur and external structures, such

Table 2 Most common preservative and storage methods to ensure longevity of catalogued specimens in Natural History Collections and Environmental Specimen Banks, and the associated advantages and disadvantages of each method

Preservative & fixative methods	Most common examples:	Taxa	Tissue types	Purpose	Advantages	Disadvantages	Cautions
Wet Chemical	• Formalin (fixative) • Ethanol • Isopropanol • Other alcohol formulations • Lugol's preservative (potassium iodine)	• Fish • Invertebrates • Phytoplankton	• Typically whole body • Can subsample whole-body for specific tissues such as muscle and inert tissues (scales, nails)	• To preserve taxonomic structures, inexpensive medium- to long-term storage.	• Very long-term storage if chemical refreshed occasionally, fixed tissue structures for taxonomy. • Relatively inexpensive compared to freezing.	• Loss of colour, distortion of shape and tissue due to chemical action. • Can affect chemical signatures and contaminant patterns.	• Interpretation of ecotracer and contaminant signatures must take into account "preservative effect", which can be significant for many elements. • Ethanol source can influence $\delta^{13}C$ value (e.g., corn, sugar beet, sugar cane) • Not all contaminants can be analysed, such as certain organochlorines.
Dry Chemical	• Arsenic • Mercuric powders • Organic pesticides • Mothballs	• Bird • Mammal • Fish • Reptile • Plant • Insects	• Skins with feather & fur. • Taxidermy mounts • Herbarium archives	• Preserved skins easier to store, retains characteristics of feather & fur structures. • Taxidermy mounts for display.	• Keeps insects, fungi and other organisms away from specimen	• Toxicity to handlers • Masks true contaminant concentrations in organism. • Need advanced washing and compound-specific or congener-specific analytical techniques.	• Arsenic, mercury and organic pesticides can mask contaminant concentrations in organism, need advanced washing and special analytical techniques, which does not work for all species (e.g.

Table 2 (continued)

							Hogstad et al., 2003) • Can use methylmercury, known isotope ratios / types of contaminants, and other indicators.
Dried or dry conditions with no chemical preservation	• Dehumidifiers • Desiccant cabinets with desiccant chemicals • Silica gel • Calcium sulfate	• Fish • Bird • Mammal • Reptile • Insects	• Muscle. • Ossified structures (bone, teeth) • Feathers	• Long-term storage of samples for analyses. • (note: mothballs often used in storage)	• Dried specimens can still be easily sampled and analysed for most contaminants and chemical tracers.	• Requires extensive preparation of most organism (e.g. removal of organs) resulting in loss of tissues potentially useful for analyses. • Mold and other pests can still result, altering specimen's chemical composition.	• Degradation of contaminant concentrations with time unknown.
Frozen	• Homogenized or subsampled tissues. • Frequently at one of the two temperatures: • -20°C • -80 ºC	• All taxa	• Whole body • Muscle • Blood • Urine • Organs • Egg contents	• Long-term storage of samples for analyses.	• Long-term storage, least alteration of tissues in regards to chemical and contaminant signatures. • Samples stored at -	• Expensive, requires significant investment in infrastructure, operating and maintenance. • Lower temperatures (e.g. -20oC) and repeated freezing & thawing of	• Access to samples can be highly restricted if held by ESBs. • Many species homogenized whole or specific tissues homogenized, meaning that tissue-specific analyses or taxonomic-

Table 2 (continued)

		80ºC or properly dried samples are preferred.. • High quality data and laboratory results.	samples may lead to uncertainty of sample integrity. • Loss of organ and cellular structure due to homogenizing typical for most specimen archive standard protocols.	specific analyses are not always possible.

as toe pads be sampled rather than the skin itself (Hogstad et al. 2003). Camphor (mothballs) or other pest deterrents may be kept in the drawers, possibly introducing additional contaminants to the samples.

Dried specimens are usually desiccated via air drying, drying in an oven, or by freeze-drying. Many types of samples such as moss, lichen, fur and feather samples are then stored dried with no further preservative, often over desiccant crystals, considerably simplifying the collection of trace analysis samples. Dried samples kept in desiccant conditions are highly stable (McFarland et al. 1995). However, a major issue is that most dried samples in NHC were not originally collected, prepared, mounted or stored with trace contaminant analyses in mind so they likely have been exposed to cross-contamination from other specimens or always-present dust (e.g., Oyarzun et al. 2007), which adds to the challenge of interpreting data derived from such samples. Extra cleaning and sampling considerations must be factored in to improve the quality of dried samples for contaminant and trace element analyses (Sigrun-Dahlin et al. 2012).

Biologically "inert" structures, i.e., ossified structures (bones, teeth), cartilage, and keratin, are typically air dried and not chemically preserved, and are thus amenable for contaminants research. External structures, such as baleen (Hobson et al. 2004) and teeth (Farmer et al. 2006), provide useable material for contaminant and trace element analyses with some cleaning of the specimen. Bones may be boiled or immersed in ammonia in a "degreasing" step, dried and mounted (Neves et al. 1995). As a result, analyses of archived skeletal materials, especially those that have been mounted, may provide challenges that have not yet been experimentally verified in the literature.

Frozen specimens are more commonly associated with ESB collections, and can be stored in ordinary −20°C freezers, −40°C cold rooms or ultra-low −80°C for genetic, fatty acid and other types of specialized analyses (Braune et al. 2010). Like dried specimens, frozen specimens may be among the most straightforward to analyze, although long-term storage effects are of concern with literature reviews showing mixed results for stability of organic contaminants and trace elements (McFarland et al. 1995; Day et al. 2014).

How a sample is stored and the length of storage are important considerations, depending on the analysis in question. Chemical changes, UV, degradation, and decomposition are all factors to keep in mind. Ethanol can extract organic material, and as a result, organic contaminants and carbon isotopes can be affected by length of storage. For dry samples, humidity and ultra-violet light are key factors in degradation of contaminant and chemical tracer concentrations and as such, storage type, and length are important factors to consider (McFarland et al. 1995. Most detailed methodology publications related to the effect of storage on samples are from medical and clinical studies (e.g., Cuhadar et al. 2013). In general, refrigeration has been shown to be sufficient to preserve trace elements in urine for ICP-MS analyses over a month (Bornhorst et al. 2005). Dried and freeze-dried samples also have been shown to conserve trace elements and mercury for several months to few years (McFarland et al. 1995). Likewise, organochlorine compounds tend to remain consistently stable in frozen samples at −80°C over several years and in

freeze-dried samples (McFarland et al. 1995), although there are some exceptions to this in the literature. One common constant by all authors is that the storage technique needs to be tested on the particular tissue type and contaminant of concern before commencing to use that technique.

Each collection has its own priorities, and therefore sampling bias will be a big factor in using long-term catalogued collection material for research. Often it is challenging to create a robust research design for a project prior to approaching curators and archivists as the number of species, size ranges or time periods may simply not be available. Researchers must be prepared to derive an experimental design based on what is present already in collections and acknowledge that spatiotemporal patchiness and paucity of key samples may be present. Furthermore, as space becomes more restricted over time, curators will be required to discard samples while conserving type and voucher specimens, so there may be a bias towards older original specimens in some collections due to this priority on taxonomically important specimens. There is also bias towards smaller representatives of many species due to storage issues: for example, many small fish can be stored in a single jar or many smaller birds and mammals can be stored in a small drawer—while only a few larger individuals can be stored in larger containers or on shelves making it difficult to get an appropriate size range for each species.

Tissue availability is another challenge. Curators may restrict sampling only to particular types of tissues or structures, which can make it logistically difficult to extrapolate data from one type of tissue to what is used for modern research techniques. Researchers may need to be prepared to use modern laboratory and field studies comparing contaminants in different types of tissues for a single individual when preparing to standardize data across tissues and time periods.

Ancillary data are essential—analyzing a sample without knowing location, species, or time of collection will result in poor data. Both ESB and NHM catalogued collections will have specimen labels and data detailing the date, species collected and in most cases, the name of the collector. Older specimens may only have ancillary data on a paper label with faded handwriting, or have incomplete information prior to establishment of standard protocols on accepting and maintaining collections, making it challenging to compile all information for each specimen.

Can we compare wet-preserved fish tissues from the early twentieth century to those of modern freshly-caught fish? Adjusting for probable changes in contaminant concentrations due to preservation, storage and tissue type all adds more uncertainty to the data. Currently, there is more focus on stable isotope data for archived and fresh samples, although researchers have started to investigate potential impacts of wet-preservation methods on mercury and metals (Hill et al. 2010; Poulopoulos 2013). Drying and storage length of dried tissues do not appear to have been investigated in the peer-review literature at this date, but it is very probable that changes occur over time. Freezing at temperatures below −80°C and repeated freezing-thawing of samples for subsampling is an issue as it can lead to decreased stability of the sample with significant differences in contaminant concentrations (Krystek and Ritsema 2005; Hale and Greaves 1992; Cuhadar et al. 2013). As a result, it is frequently recommended that the storage technique be consistent throughout the

archival lifespan of the catalogued specimen, and storage conditions should be kept constant.

Case Studies

To illustrate the successes and challenges of using catalogued specimens for contaminants research, we will present three case studies, the first two of which involved analyses of mercury in preserved animal tissues. Perhaps more than other contaminants, mercury has been measured in tissues from catalogued specimens for many studies conducted to infer pollution source and/or extend temporal trends. Dietz et al. (2009) provided a review of such studies that used bird and mammal specimens collected in the Arctic. Although we focus on mercury, similar successes and challenges are possible for other contaminants. The DDT studies presented in the introduction are a prime example of a major success of using museum specimens to understand a pollution problem. The third case study in this section focuses on organochlorine contamination in Lake Ontario.

Isle Royale—a Comparison of Multiple Records of Mercury Pollution

Isle Royale is an archipelago in Lake Superior that supports an ecosystem sensitive to atmospherically-deposited contaminants. The archipelago is protected from most human influences by its relative isolation within a Great Lake and by multiple designations as a national park, a wilderness area, and an international biosphere reserve. It was a surprising discovery in the 1970s that concentrations of organochlorine contaminants (Swain 1978) and mercury (Kelly et al. 1975) were higher in fish in "inland" lakes of Isle Royale than in surrounding waters of the Great Lakes, where discharges of untreated industrial and municipal wastewater were common. Among ecosystems, the relationship between contaminant loading and accumulation in biota is often not straightforward. Contaminant concentrations in Isle Royale fish were/are comparatively elevated because of food web dynamics that favor biomagnification (organochlorines) or water chemistry that enhances bioavailability (mercury) (Swackhamer and Hornbuckle 2004). For organochlorines, production bans cut off contamination at the source, and rates of atmospheric deposition (Baker and Hites 2000) and concentrations in fish (MDEQ 2014) declined at Isle Royale. For mercury, a naturally occurring element, human activities worldwide have released geological stores (mineral deposits and fossil fuels) resulting in a 3–5-fold enhancement (global average) in atmospheric deposition (Engstrom et al. 2014). In the Great Lakes region, controls on mercury emissions have gradually decreased rates of atmospheric deposition since the mid-1980s; however, mercury concentrations in fish have been uncoupled from deposition for 80+ years, determined by

investigations of mercury cycling at Isle Royale that featured the use of catalogued tissues.

The magnitude and rate of change of atmospheric mercury deposition to Isle Royale is largely known from lake sediment cores. Lake sediments are the most reliable archive of atmospheric mercury deposition (Biester et al. 2007), although because lakes also receive inputs of mercury from their watersheds, the relationship between atmospheric mercury deposition and sedimentary mercury accumulation is not always straightforward. Sediment cores collected from five lakes at Isle Royale show a cohesive 3-fold increase in mercury accumulation rates, beginning c. 1890 and continuing to the present (Drevnick et al. 2007) (Fig. 1a). The unabated increase is at odds with a region-wide analysis that found sedimentary Hg accumulation rates peaked in the mid-1980s, followed by a 20% decline (Drevnick et al. 2012).

A dataset of mercury in teeth from moose (*Alces alces*) (Vucetich et al. 2009) provides an important check on the lacustrine record. As part of a long-running study of predator-prey interactions at Isle Royale, teeth have been collected from moose carcasses since the early 1950s. The counting of cementum lines (layers of bonelike connective tissue covering the root of a tooth) was used to determine birth and death years of individuals, and teeth were "stored dry in paper bags inside wooden cabinets, and were never exposed to potential sources of contamination." Vucetich et al. (2009) measured mercury, as well as lanthanum and strontium to correct for any accumulation of mercury of geogenic origin, in adult and calf moose teeth and reported an abrupt 65% decline in Hg concentration between 1980 and 1986. The authors reported no trend in Hg concentration before or after this period, but a re-analysis of data from calves (which were defined as < 1 year old and thus had a narrow window of exposure) suggests a more gradual decline (of similar overall magnitude) from 1983 to the present (Fig. 1b). Ungulates accumulate mercury almost entirely from the plants they consume (Gnamus et al. 2000), and moose diet (plant selection, feeding location) has not changed in coincidence with the trend in tooth mercury. Having ruled out other contributing factors to the decline, Vucetich et al. (2009) concluded that the cause must be a drop in atmospheric mercury pollution. This conclusion agrees with the region-wide analysis, i.e., that mercury deposition is declining.

The discrepancy between the sediment and moose teeth records helps to constrain rates of atmospheric mercury deposition. Wet and dry mercury deposition rates were measured at Isle Royale during periods of 1997 and 1998 (U.S. NPS 2014), but only show a snapshot view. Using the model of Swain et al. (1992), the sediment record can be used to model total (wet + dry) mercury deposition long term (Fig. 1c), with a present estimate of 11.3 $\mu g/m^2/yr$. Aligning estimates for total mercury deposition with the broken-stick regression line for Hg/La in moose teeth shows the records were in strong agreement during the period 1958–1983, but diverge thereafter. Which record is correct? Data from measured rates of wet mercury deposition from a site in adjacent northeastern Minnesota fits in the wedge between the two records. An unknown is dry mercury deposition, which at Isle Royale may amount to 40% of wet mercury deposition (U.S. NPS 2014), allowing us to conclude that total mercury deposition remains in the wedge (of Fig. 1c) and,

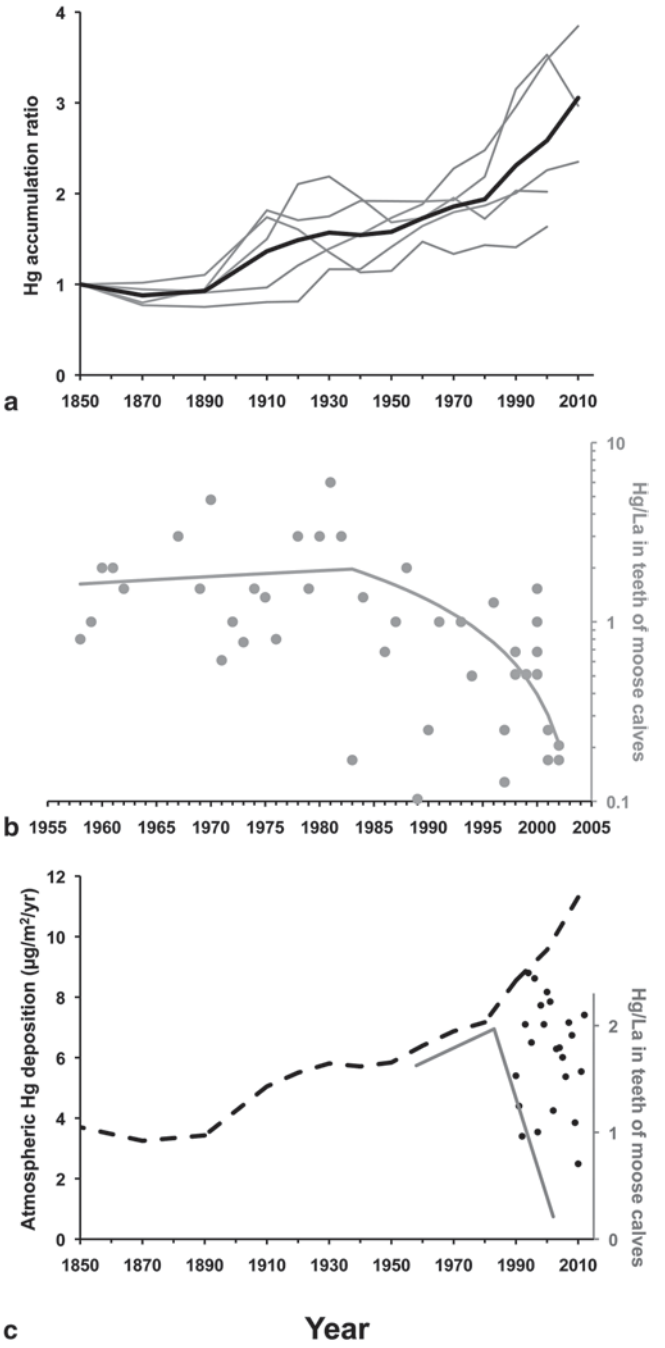

Fig. 1 **a** represents sedimentary mercury accumulation rate for a given period compared to a background (1850) rate. The *thin*, *gray* lines are for cores collected from five lakes at Isle Royale. Lakes include Intermediate, Richie, Sargent, Siskiwit, and Whittlesey. The thick, *black* line repre-

importantly, appears to have declined. Using data from the sediment cores for modeling atmospheric mercury deposition resulted in overestimation of actual rates. The sediment data may be affected by increased output of mercury from watersheds, either from a change in the retention of "new" mercury (recently-deposited) or from output of "old" mercury (from a legacy of past deposition).

Mercury concentrations in fish tell another story, beginning with a wealth of catalogued fish samples. In 1929, Walter Norman Koelz of the University of Michigan Museum of Zoology (UMMZ) led a sampling expedition to the inland lakes of Isle Royale and collected nearly 15,000 fish for the museum's research collection. The fish were preserved in formalin and transferred for storage in ethanol, both solutions free of added mercury (Kelly et al. 1975). To fairly compare mercury concentrations in these specimens to fresh fish, it is necessary to correct for an approximate 30% weight loss in ethanol. Kelly et al. (1975) and Drevnick et al. (2007) have used these specimens for mercury-related research, and a sample of the data is shown in Fig. 2. From 1929 to 1971, the median mercury concentration (expressed in wet weight) in axial muscle of walleyes (*Sander vitreus*) increased from 0.2 to 0.7 μg/g (a 3.5-fold increase). For comparison, during that same time period sedimentary mercury accumulation increased 1.2 fold. The additional increase in fish mercury compared to mercury loading to lakes (also observed in adjacent northeastern Minnesota by Swain and Helwig 1989) is hypothesized to have resulted from sulfate in acid rain that stimulated ecosystem production of methylmercury, the form of mercury that accumulates in fish. Methylmercury is not preserved in sediment and thus does not provide a record of methylmercury production; however, products of sulfate reduction (the process that results in the production of methylmercury) can be stored in sediment. There is a strong correlation among lakes and time between concentrations of chromium reducible sulfur (an operational term that represents products of sulfate reduction) and concentrations of mercury in fish. With mercury loading to lakes continuing unabated (as evidenced from the sediment data), declines in mercury concentrations in walleye, northern pike (*Esox lucius*), and other fish species since the mid-1980s appear to be solely attributed to controls on sulfate deposition (Drevnick et al. 2007).

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sents the mean. The data show sedimentary mercury accumulation rate is increasing to the present. Data from Drevnick et al. (2007). **b** represents mercury/lanthanum data from moose calves at Isle Royale (Vucetich et al. 2009). The regression line is from a "broken stick" model with the following equation: Hg/La = −25.2 + 0.0137(year)—0.106(year-1983). The model shows no significant trend pre 1983 ($p = 0.61$), but a significant decline since 1983 ($p = 0.038$). **c** has three components. The dashed, *black* line shows the modeled atmospheric Hg deposition, based on the sediment record. The model is from Swain et al. (1992): sedimentary mercury accumulation = 3.7 + 0.83(watershed area/ lake area), where the intercept (3.7) represents atmospheric mercury deposition to a lake with no watershed. For this analysis, estimates of atmospheric mercury deposition were made by multiplying the mercury accumulation ratio (see Fig. 1a) by 3.7, assuming there has been no change in watershed retention of atmospherically deposited mercury. The gray line is the broken stick regression line from the moose data; the line appears different from Fig. 1b because of a change is scale. The *black* circles show measured wet mercury deposition from site MN 18 of the National Atmospheric Deposition Program (NADP). Data were retrieved from Glass and Sorensen (1999) and the NADP website (http://nadp.sws.uiuc.edu/)

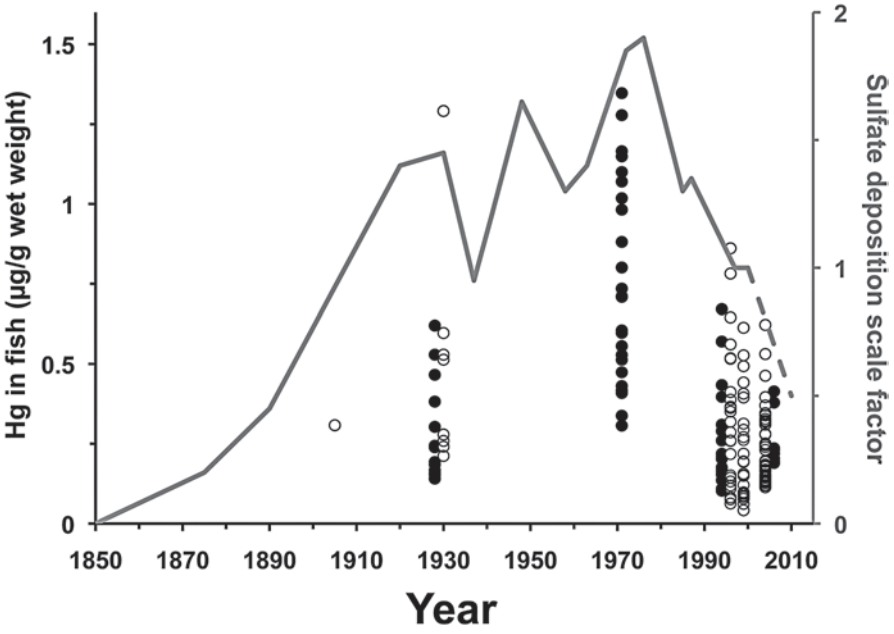

Fig. 2 has two components. The circles represent concentrations of mercury in skin-on axial muscle from fish from lakes of Isle Royale: *black* for walleye from Chickenbone, Dustin, and Whittlesey and *white* for northern pike from Eva, Richie, and Sargent. Data sources include Kelly et al. (1975), Kallemeyn (2000), Gorski et al. (2003), and Drevnick et al. (2007). Data points early in the record (1905, 1929) are from catalogued fish samples at the University of Michigan Museum of Zoology. The *gray* line shows the history of sulfate deposition in the Great Lakes region, as estimated by Aherne et al. (2003). The solid line indicates estimates are based on empirical observations. Dashed line is a model forecast. The scale factor is unitless; a factor of 1.0 is equivalent to a deposition rate of 13.2 kg S/ha/yr (measured rate in 1997)

In total, the use of catalogued tissues for mercury research at Isle Royale allowed insight that otherwise was not possible. The record from moose teeth indicates rates of atmospheric mercury deposition are declining. Mercury concentrations in fish are also declining because rates of atmospheric sulfate deposition are declining. Management of atmospheric mercury and sulfur emissions, largely via regulations on coal combustion for electricity generation, are making significant progress towards recovery of lake ecosystems from mercury contamination at Isle Royale and likely elsewhere in the Great Lakes region.

Mercury in Tuna, Revisited

Miller et al. (1972) tested the seemingly straightforward hypothesis that there is no difference in mercury concentration in tuna between museum specimens (dating from 1878–1909) and samples caught "recently" (1970–1971). Results of mercury analyses, 0.38 ± 0.14 µg/g in museum specimens ($n = 7$) and 0.29 ± 0.14 µg/g in recent samples ($n = 5$) (both expressed as wet weight), did not allow the authors to

reject their null hypothesis. Rather, the results were used as evidence to support the ideas that mercury pollution since 1900 could only result in a negligible increase in mercury concentration in open ocean waters and that mercury in wide-ranging ocean fish is of natural origin (Hammond 1971). The first of these ideas was based on faulty data; before the advent of clean sampling techniques, it was accepted that the mercury concentrations of open ocean waters ranged in the low parts-per-billion, whereas we now know that a typical mercury concentration is ~200 parts-per-quadrillion (Lamborg et al. 2012). Current models of global mercury cycling unanimously agree upon an increase in mercury concentration in ocean water since preindustrial times (Black et al. 2012). Validation of this increase, however, requires an independent record of oceanic mercury, and a common approach has been to measure temporal changes in biota. For this purpose, museum collections have repeatedly been revisited for bird feathers, and recently Vo et al. (2011) reported a post-1940 increase in mercury concentrations in feathers from black-footed albatross (*Phoebastria nigripes*) while accounting for changes in mercury exposure from diet or food web shifts, with analyses of carbon and nitrogen stable isotopes. Finding a similar increase in fish has proven elusive. Kraepiel et al. (2003) compared mercury concentrations in yellowfin tuna (*Thunnus albacares*) caught off Hawaii in 1971 and 1998, found no recent increase, and (to come full circle with Miller et al. 1972) concluded that methylmercury (the form of mercury that accumulates in fish) forms from mercury naturally present in deep waters, sediments, or possibly hydrothermal vents. This idea has been challenged by three independent lines of data (see Blum et al. 2013, Lamborg et al. 2006, and Sunderland et al. 2009), but nonetheless was key in a court ruling that exempted tuna companies from warning consumers of a reproductive toxin (methylmercury) in their products (State of California v. Tri-Union Seafoods, 171 Cal. App. 4th 1549, 90 Cal. Rptr. 3d 644 2009). The court stated that "virtually all methylmercury [in tuna] is naturally occurring."

Why is there confusion about mercury in tuna? At center is a dispute about the risk of mercury in fish to human consumers, between tuna companies (consumer freedom) and governmental health agencies (consumer protection). What level of mercury is toxic to humans? Toxicity values (e.g., reference dose) are debatable because of the many potential studies that can be considered as the base of the calculations and because of uncertainty factors that modify the final product. However, unbiased science should be able to inform the public about the mercury content in tuna. Success in that task has been questionable, though. With all of the tuna caught annually, it should be straightforward to design monitoring programs to answer the appropriate questions. The U.S. Food and Drug Administration, for example, has a monitoring program in place and allows the public to see the data (U.S. FDA 2014), but information is not provided that would allow for an analysis to determine whether mercury concentrations are changing with time.

To determine whether mercury concentrations in tuna are changing with time, it is necessary to examine the data in context, especially with fish age and size. As fish grow older and larger, their mercury concentration increases because methylmercury is readily accumulated (via the diet) but difficult to eliminate. Further, as fish grow larger they may switch to diet items that have higher mercury content. It

is common practice to standardize mercury concentrations to a specific length or weight, so for a given species datasets can be fairly compared across space and time.

Miller et al. (1972) gave very limited information about the ages and sizes of the museum specimens in their study ("each slightly under 0.6 m in length") and no information about the age or size of the recent samples, which reinforces the need for all researchers using museum collections to indicate specimen numbers as part of their metadata. Placing the data in context (Fig. 3) reveals some surprises. For albacore tuna (*Thunnus alalunga*), the mercury concentration of a specimen caught off the California coast in 1880 is a statistical outlier when compared to a larger dataset for individuals from California, Oregon, and Washington (Morrissey et al. 2004). The data point is biased high (i.e., high mercury for given length), which could be a real phenomenon or may be an artifact of museum preservation. The authors addressed the issue of mercury in preservative and could not "rigorously exclude" the possibility, but it does not appear to be an issue in any of their data. Rather, if the data point is corrected for 30% lipid loss (Kelly et al. 1975), which has the effect of concentrating mercury in the remaining tissue, the mercury concentration would fall into place in the length-mercury relationship. It is unclear, however, what is an appropriate correction factor for tuna, and Gibbs et al. (1974) warned that, until preservation effects are understood, comparisons between museum specimens and unpreserved samples "must be considered unreliable." For skipjack tuna (*Katsuwonus pelamis*) and Atlantic bluefin tuna (*Thunnus thynnus*), the data from Miller et al. (1972) fit neatly with larger datasets. Although, if lipid loss is important in the museum specimens, the data points for these two species would be biased low, opening up the possibility that mercury concentrations have increased since the late nineteenth century and early twentieth century. In fresh tuna, Balshaw et al. (2008) determined that mercury and lipid content in muscle tissue are inversely related, with mercury decreasing at a rate of −0.0046 µg/g (wet weight) per percent lipid. For Atlantic bluefin tuna, the one museum specimen (caught off the Massachusetts coast in 1886) is at the far left side of a length distribution that is considerably larger than shown; Fig. 3C only shows age-1 fish (Mather and Schuck 1960). Mercury concentrations at this young age are low and highly variably (Cumont et al. 1975) and therefore rather insensitive to use for detecting temporal change.

The study by Miller et al. (1972) was an early attempt at a difficult and contentious issue. Other problems with the study include small sample sizes (a common drawback of contaminants research involving museum specimens) and the failure to account for changes in trophic position. The shortening of food webs, shown to occur in ocean fisheries since *c.* 1950 (Pauly et al. 1998), reduces the biomagnification of mercury (Cabana and Rasmussen 1994). This oversight is excusable because in 1972 a simple method to determine trophic position (i.e., analyses of carbon and nitrogen stable isotopes) had not yet been discovered. Going forward, there are no excuses for poor collection or representation of data. Mercury contamination of ocean fish is a serious global health issue, now being tackled by the UN Minamata Convention on Mercury that must be guided by valid data (Selin 2014).

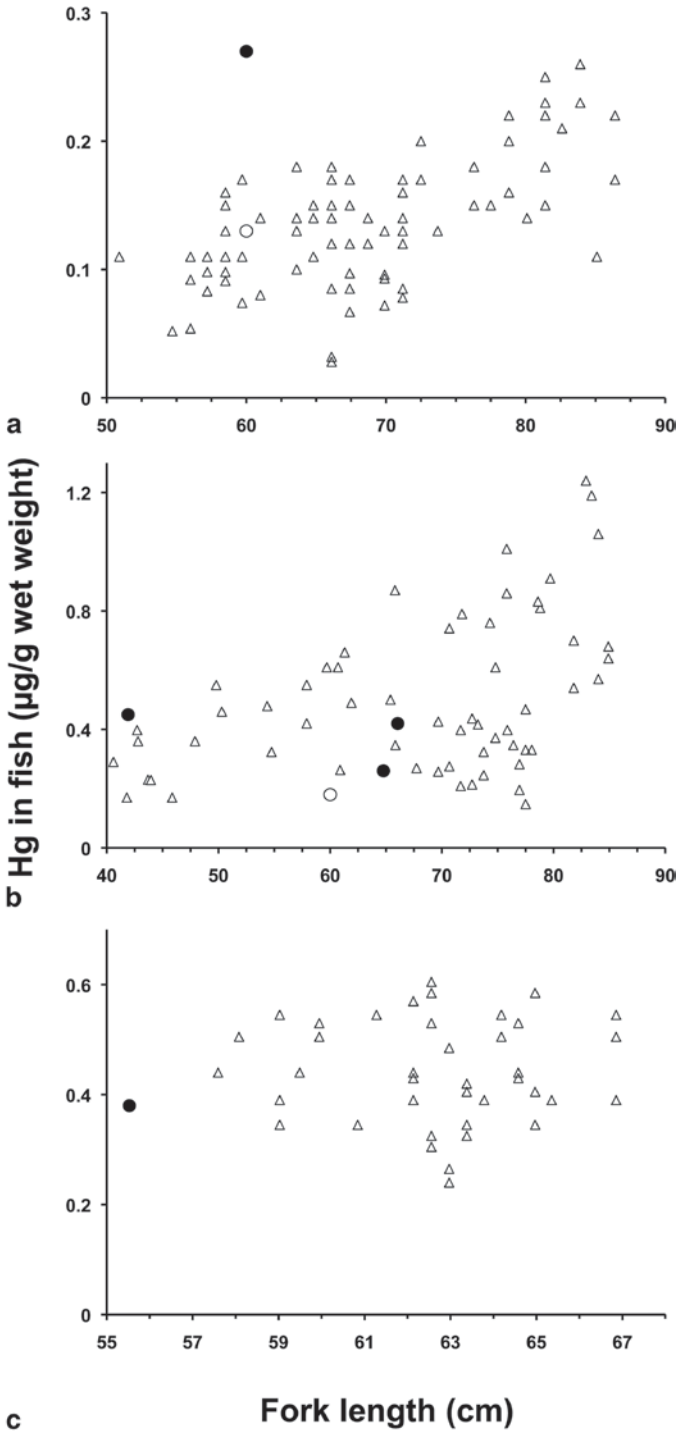

Fig. 3 Mercury concentrations in muscle tissue of tuna from Miller et al. (1972) (circles), placed in the context of larger datasets (triangles). Solid circles represent museum specimens dating from

Chlorinated Hydrocarbons in Gull Eggs from Scotch Bonnet Island, Lake Ontario

Herring gull (*Larus argentatus*) eggs from Scotch Bonnet Island, collected annually since 1971 and archived in the Canadian Wildlife Service Specimen Bank, have been instrumental in understanding biotic exposure and effects from organochlorine contaminants in Lake Ontario. Fresh eggs have been analyzed at regular intervals, but because of changes in analytical methodology during the course of the program, early data are not directly comparable to more recent data. A re-analysis of eggs from the specimen bank has remedied this problem (Norstrom and Hebert 2006). Concentrations of individual organochlorine contaminants were at their highest at the beginning of the record, and controls on production and/or release have resulted in steady decreases in 2,3,7,8-TCDD (dioxin) (see Fig. 2 in Norstrom and Hebert 2006), chlorobenzenes, chlorostyrenes, and dieldrin. From the mid-1960s to the mid-1970s, reproductive success of herring gulls on Scotch Bonnet Island was poor, averaging 0.1 chicks per nesting pair. Poor reproductive success was due to egg disappearance—from inattentive parenting—and embryo mortality (Peakall and Fox 1987). With significant declines in organochlorine exposure by the late 1970s, the average number of chicks per nesting pair increased to >1, similar to herring gulls in other Great Lakes and strongly suggested that exposure caused effects.

Cook et al. (2003) used the herring gull egg record from Scotch Bonnet Island and nearby sediment core records to model lake trout (*Salvelinus namaycush*) fry mortality in Lake Ontario. Lake trout were extirpated from Lake Ontario *c.* 1960 and attempts to re-establish the population via stocking failed because of sac fry mortality. 2,3,7,8-TCDD and similarly structured chemicals (e.g., PCBs) bind to the aryl hydrocarbon receptor, which (when bound) activates phase I and phase II metabolism—processes that are intended to detoxify and eliminate xenobiotics, but can instead result in activation (increased toxicity). Such is the case for these chemicals. Lake trout sac fry exposed to 2,3,7,8-TCDD show overt toxicity that results in death (King-Heiden et al. 2012). Cook et al. (2003) compiled a 60-year record of toxicity equivalent concentrations (TEC) for 2,3,7,8-TCDD and other organochlorines that bind the aryl hydrocarbon receptor, from sediment core records (prior to 1971) and herring gull egg record (1971 onward), with appropriate conversion factors and assuming these records ran in parallel with lake trout exposure. TECs from 1940 to 1980 were sufficiently high to result in 100% mortality to lake trout fry, hence the extirpation of lake trout from the lake post 1980, with significant declines in contaminant concentrations, stocking programs have had success, and a viable lake trout population now again inhabits Lake Ontario.

1878–1909; open circles represent samples caught "recently" (1970–1971). Kris Murphy, Division of Fishes, Smithsonian Institution, re-measured lengths of the museum specimens and has added this information to the museum's electronic catalog, accessible at < http://collections.mnh.si.edu/search/fishes/>. For all data from "recently" caught specimens from Miller et al. (1972), a fork length of 60 cm was assumed (see text). Panel A shows data for albacore tuna from the U.S. Pacific coast (CA, OR, WA), with the larger dataset from Morrissey et al. (2004). Panel B shows data for skipjack tuna from the Indian and North Pacific oceans, with the larger dataset from Choy et al. (2009) and Kojadinovic et al. (2006). Panel C shows data for Atlantic bluefin tuna from the North Atlantic Ocean, excluding the Mediterranean Sea, with the larger dataset from Cumont et al. 1975

Recommendations and Conclusions

Success in using catalogued specimens for contaminants research requires finding samples that have the potential to provide information to answer the research question (source, temporal trends, effects) and then ensuring that the samples provide results that reflect reality. Validation must involve either in-house experiments, e.g., as performed by Hill et al. (2010) and Poulopoulos (2013) to understand the impacts of preservation on contaminant concentration, or referring to the work of others. A valid comparison of catalogued sample data to results from modern samples also requires understanding (and adjusting for) changes in the ecosystem, as done by Vo et al. (2011) with the ancillary analysis of carbon and nitrogen stable isotopes to account for changes in mercury exposure in albatross from shifts in the food web. When reporting data from catalogued specimens, it is advised to list the sources (e.g., museums) where the samples were obtained and also the identification code for each sample, in supplementary materials if necessary. This information is important for curators and archivists and also allows others the potential to repeat the work—a requirement of peer-reviewed science. The information given in Miller et al. (1972), for example, allowed us to revisit the samples for the case study on mercury in tuna.

NHC and ESB catalogued specimens offer a powerful medium for making or extending (when monitoring data are available) timelines of biotic exposure to contaminants. Curators and archivists are increasingly becoming aware of the additional value of NHC specimens as a repository of long-term contaminant and chemical tracer information, which are resulting in changing collection policies and management. Preservation and storage remains a challenge especially with the high cost of low-temperature storage, although great strides have been made in quantifying the effects of long-term preservation and storage on chemical signatures in biological tissues over recent years. Provenance remains a significant priority especially for curators of key collections, so it is necessary for researchers to cooperate with curators and ensure the traceability of their sample analyses (through lists of specimen codes and sources) in their publications and the metadata accompanying all databases. Catalogued specimens have already provided significant insights into long-term trends of environmental contaminants in biological tissues, and with better sampling protocols, metadata management and storage techniques, this potential will continue to grow in the near future.

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