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Historic Trends in the Concentrations of Persistent Organohalogenated Pollutants in Australian Butter and the Impact of Regulation

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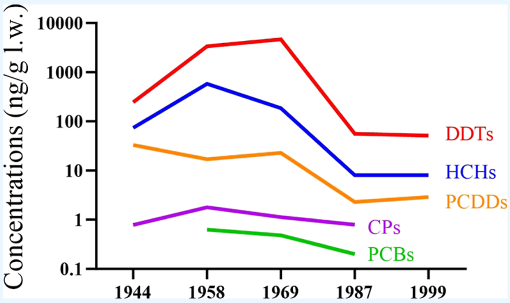
ABSTRACT: Analysis of historically sealed dairy products offers a novel method for tracking persistent organic pollutant (POP) contamination over time. This study examined Australian canned butter samples from 1944, 1958, 1969, and 1987, sourced from museum collections, Antarctic expeditions, and storage facilities. Samples were analyzed for a broad range of POPs, including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated alkanes (PCAs). OCP concentrations peaked in the 1950s and 1960s, before sharply declining post-1980s bans. Similar declining trends occurred for PCBs and PCAs, although at lower concentrations than for OCPs. PBDEs were consistently not detected in all of the historic samples. In contrast, highly chlorinated dioxins exhibited unique behavior, where their concentrations peaked in the 1944 sample, remained at high levels through the 1950s–1960s, and decreased to current levels afterward. The source of these elevated levels of dioxins remains unknown. The study revealed distinct temporal pollution patterns influenced by chemical properties, environmental behavior, and regulatory effectiveness. All monitored POPs exhibited declining trends, following regulatory restrictions on their production. These findings highlight the value of archived food samples in reconstructing contamination timelines.



1. INTRODUCTION

Persistent organic pollutants (POPs) are a group of organic substances that persist in the environment, accumulate in living organisms, and pose a risk to human health and the environment. Initially, under the Stockholm Convention on POPs, 12 chemicals were identified as POPs, including organochlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-dioxins and -furans (PCDD/Fs).[1] Later, new chemicals were also added, such as polybrominated diphenyl ethers (PBDEs) and polychlorinated alkanes (PCAs, also within the chlorinated paraffins, CPs, chemical group). A key exposure pathway for many POPs is via the food chain.[2−4] Analysis of dairy samples, such as breast milk and butter, has thus become a suitable approach to compare environmental/atmospheric levels of these pollutants on a spatial and temporal basis[5] and enabled the identification of specific contamination sources with unique "fingerprint" congener profiles. There are many examples over the last 30 years of contamination occurring via (accidental) waste additions or contaminated feed additions to cattle and aquaculture feed and therefore milk and meat production. For example, Covaci et al.[6] have linked the increased concentrations of PCBs and PCDD/Fs found in milk, including butter, to contaminated animal feed after the Belgian PCB/dioxin crisis, where PCBs and dioxins were accidently added to the feed.

Over the last few decades, an understanding of exposure to POPs has deeply depended upon the development of analytical methods and, in particular, gas and liquid chromatography and mass spectrometry. Analysis of PCBs and OCPs was established in the 1960s and rapidly adopted for assessing these chemicals in lipophilic matrices, including butter.[7] Methods for PCDD/Fs were established in the 1970s, advancing in the 1980s, such that routine monitoring programs were able to systematically evaluate associated human risks from exposure.[8] Monitoring programs on POPs in breastmilk further led to the discovery of PBDEs in the late 1990s, in samples archived through the 80s and 90s, which, in contrast to legacy POPs, showed increases in exposure,[9] with different environment exposure patterns to those of the legacy POPs, at that time. These analytical methods, particularly GC−MS, have also been applied to butter samples at different time

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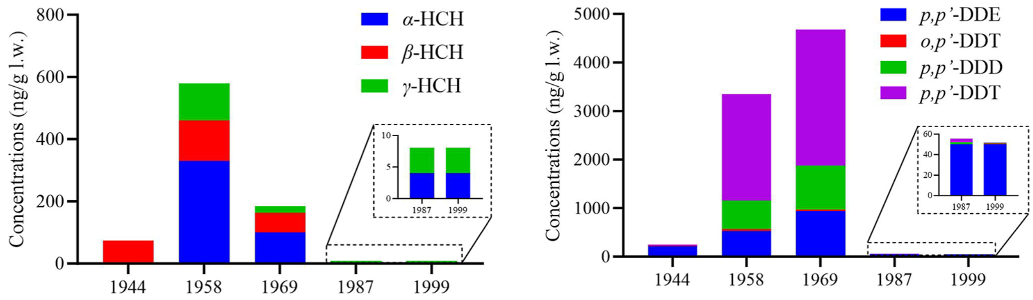

Figure 1. Concentration and isomer distribution of HCHs (left panel) and DDTs (right panel) in historical Australian butter samples.

points,[5,7,10,11] reflecting the different levels of POPs in the environment.

The history of environmental and dietary exposure to POPs in the early phase of their use is little documented. Sediment cores have provided some insights but are often associated with relatively large uncertainties, i.e., time between release and deposition in sediments, dating, bioturbation, and sedimentation rates.[12,13] A preliminary study of historic canned olive and vegetable oils indicated the potential value of OCP analyses to demonstrate the more recent contamination issues, compared to historic samples, prior to the use of DDT.[14] However, animal products such as canned butter offer even greater insight. As animal-derived food products are potentially exposed to contaminants throughout the food chain, they capture a wider range of contamination profiles and may eventually lead to associated dietary residue hazards. Furthermore, because animal food products for human consumption reflect contamination accumulated during the period in which the animals were farmed, they provide more accurate information on the contaminant's temporal trends. This makes them particularly valuable for assessing the historical environmental and temporal trends of POPs.

The difficulties in the use of butter samples are related to the availability and storage of the samples. The aim of this study was to obtain sealed (in cans) historic butter samples from Australia and establish time trends for concentrations of POPs for a period for which POP exposure trends are limited.

2. MATERIALS AND METHODS

2.1. Sample Collection. A series of historic butter samples were obtained from the Australian War Memorial and waste disposal sites near stations in the Australian Antarctic Territory. All samples were preserved and sealed in tin-coated steel cans since manufacture.

The oldest sample, a single can donated to a museum by a World War II veteran, was brought back at the end of the war. Consultation with the dairy industry indicated this sample was likely canned ca. 1944. The butter was derived from milk sourced across New South Wales (Southeast Australia), and archival evidence suggests it was stored predominantly at ambient temperatures since the 1940s.

The remaining samples originated primarily from Queensland (Northeast Australia) and were obtained through the Australian Antarctic Division. These samples were stored under frozen or refrigerated conditions for most of their storage period. Based on dates inscribed on cans or associated packaging materials recovered in Antarctica, these samples are estimated to correspond to milk collection years 1958, 1969, and 1987. A reference sample (1999) from the Antarctic Division's current supplies was also included.

2.2. Chemical Analysis. To extract the butter, cans were gently heated in a water bath, after which two perforations were made to drain the contents into solvent-washed glass jars. The homogenized samples were refrigerated at QAEHS (University of Queensland, Australia) until analysis. An aliquot of the samples was sent to ERGO-Forschungsgesellschaft (Germany) for analysis of PCDD/PCDFs and dioxin-like PCBs, and another aliquot was sent to the Toxicological Center (University of Antwerp, Belgium) for analysis of OCPs, nondioxin-like PCBs, and PBDEs. PCAs were analyzed at QAEHS.

Analysis for pollutants was undertaken using the isotopic dilution method in all the laboratories, where those methods were well-established and recognized.[15−18] Detailed analytical methods are provided in the Supporting Information.

2.3. Quality Assurance/Quality Control. All laboratories employed standardized QA/QC protocols to ensure analytical reliability. Procedural blanks ($n = 3$) were prepared and analyzed alongside the butter samples to account for potential background contamination, and blank correction was subsequently applied to all samples. Limits of detection (LODs) were defined as the average concentrations of the blanks plus three times their standard deviation. The LODs for selected chemicals ranged from 0.0020 to 0.28 ng/g lipid weight (lw) (Table S1). Spiked QC and certified reference materials (CRM 349 and 350) were included and analyzed together with butter samples, with the difference to the assigned results <15%. Additionally, QC was also assured by the successful participation of multiple interlaboratory tests.[19−21] Data are reported only when they pass all QA/QC criteria. The recoveries of internal standards ranged from 76 to 108%, and no recovery correction was conducted for any analyte. Spiked QC samples were also included in the analysis and were prepared by spiking known amounts of chemicals into a butter sample. The accuracy of the spiked samples, shown as the ratio between the calculated concentrations and assigned concentrations, ranged from 81 to 87%. Replicate samples were also analyzed, where the relative differences were all below 20%, and the average concentrations were used in this study.

3. RESULTS AND DISCUSSION

In total, six groups of halogenated POPs were analyzed, including 13 OCPs, 31 PCBs, 8 PBDEs, 3 PCAs, 7 PCDDs, and 9 PCDFs. Butter samples from 1958, 1969, and 1987 were analyzed for all analytes above; a sample from 1944 was also analyzed for most of them, except for dioxin-like (DL)-PCBs. A recent sample from 1999 was analyzed for OCPs, PBDEs, and non-DL-PCBs, as part of another study, but not analyzed for DL-PCBs and PCAs due to the accessibility in different laboratories. For the comparison, results of PCDD/Fs in butter samples collected in Australia in 1999 were also included from a previous study,[15] and average data from nine samples collected from different states were used. Detailed results are provided in Table S1.

3.1. Organochlorinated Pesticides. OCPs were detectable in all samples, covering butter samples from 1944 to 1987. For example, hexachlorocyclohexane isomers (HCHs) were detectable in all samples, increasing from 74 ng/g lw in 1944 to 580 ng/g lw in 1958 but decreasing to 190 ng/g lw in 1969, 2.0 ng/g lw in 1987, and less than 0.30 ng/g lw in 1999 (Figure 1, left panel). Compared with other studies, the concentrations of HCHs in Australian butters reported here were lower than that collected in India during 1978 and 1981 (100−12,000 ng/g).[22] β-HCH was the predominant congener in the 1944 sample, accounting for 98% of $\sum$HCHs. This was due to the greater persistence and resistance to degradation compared to other isomers.[23,24] In contrast, the profile of HCHs shifted in samples from 1958 and 1969, where α-HCH dominated. This change was reflected in the increasing α-HCH/γ-HCH ratio, which increased from 0.44 in 1944 to 2.7 in 1958 and further to 4.6 in 1969, indicative of the widespread use of technical HCH mixtures during this period.[25] The peak concentration was observed in the 1958 sample, consistent with historical usage patterns and policy interventions in Australia during the mid-20th century, when HCHs were extensively applied in agriculture (peaking in the 1950s−1960s).[26] A notable decline in HCH concentrations was observed after 1969, with average half-lives of 8.2 years during the 1950s and 1960s and 9.1 years during the 1960s and 1980s, likely reflecting the effectiveness of regulatory actions implemented in Australia, such as the Australian Pesticides Act in 1975.

Similarly, the concentrations of DDTs (Figure 1, right panel) increased from 250 ng/g of lw in 1944 to 3400 ng/g of lw in 1958 and further to 4700 ng/g of lw in 1969. This was followed by a sharp decline of over 200-fold, reaching 22 ng/g lw in 1987 and 8.0 ng/g lw in 1999. The higher concentrations of DDTs detected in 1958 and 1969, in this study, were in the same order of magnitude as butter collected from India during 1978 and 1982 (100−8300 ng/g for *p,p′*-DDE and 40−3700 ng/g for *p,p′*-DDT),[22] but higher than those collected in Mexico during 1994 and 2001 (44−60 ng/g).[27,28] However, the higher concentrations observed in more recent studies do not necessarily indicate increasing trends of DDTs use worldwide but also reflect local usage in combination with differences in regional regulations and enforcement. Regarding individual DDT compounds, the parent compound, *p,p′*-DDT, was predominant in samples from the 1958 and 1969, consistent with its extensive agricultural use during that era.[29] In contrast, *p,p′*-DDE, a persistent metabolite of DDT, was the predominant compound in both the earliest (1944) and later (1987 and 1999) samples. This shift in the profile is a result of the degradation of parent DDT over time and reflects the impact of Australia's restriction of DDT. The introduction of the Australian Pesticides Act in 1975 initiated restrictions on the registration and sale of problematic pesticides, followed by the complete ban on DDT in 1987, directly leading to a decline of over 95% in DDT concentrations in the butters by the 1980s. The prevalence of *p,p′*-DDE in later samples is indicative of aged DDT residues, resulting from historical use and subsequent environmental transformation processes.

For other OCPs, a similar temporal pattern was observed, with peak concentrations occurring between 1958 and 1969 for hexachlorobenzene, oxychlordane, *trans*-chlordane, *trans*-nonachlor, and *cis*-chlordane. This pattern consisted of the introduction of stricter regulations on pesticides starting in the 1970s. However, pentachlorobenzene (PeCB) showed higher concentrations from 1944 to 1958 (ranging from 1.1 to 1.2 ng/g of lw), followed by a rapid decrease to 0.35 ng/g of lw by 1969. PeCB had very limited direct application in Australia and was primarily presented as an impurity or byproduct of other chemical processes. Given the low concentrations detected in the butter samples, the production and import of PeCB in Australia were limited during this period.

3.2. Polychlorinated Biphenyls. A suite of 27 PCB congeners, including non-DL-PCBs and mono-ortho DL-PCBs, were analyzed at the Toxicology Center, while other DL-PCBs were analyzed at ERGO. Combining the two data sets obtained from the two laboratories demonstrates that levels of PCBs were the highest in the 1958 and 1969 (Figure 2). PCBs were banned in 1975 in Australia,[30] resulting in a consistent decreasing trend since the 1970s (approximately 70% decrease), which was far less accentuated than the drop of DDTs (approximately 99%) and HCH (approximately 90%), certainly due to the continuing persistent presence and high stability of PCBs. Considering their similar persistence in the environment, the higher concentrations detected in the 1960s and 1980s may indicate continued environmental leakage from PCB-containing equipment.[31]

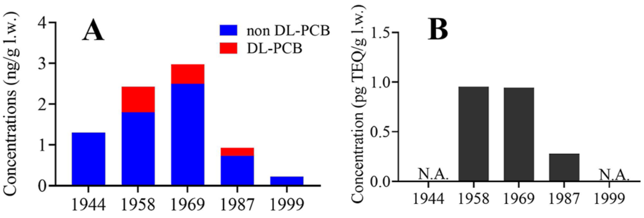

Figure 2. Concentrations (A) and WHO-TEQ (B) of PCBs in historical Australian butter samples.

The total toxicity equivalent (WHO-TEQ) value calculated based on a previous study[32] also reached approximately 1.0 pg-TEQ/g during 1958 and 1969 and then dropped to 0.28 pg-TEQ/g in 1987 (Figure 2). While DL-PCBs were not analyzed for the 1944 sample, the low concentrations of non-DL-PCBs might be an indication of the low concentrations of PCBs. The profiles of PCBs detected in the butter are shown in Figure S1. Similar patterns were observed for samples collected from 1958, 1969, and 1987, with the predominance of CB-101, -138, -153, and -118, indicating the usage and dumping of Aroclor 1254 in that period.[33] In contrast, notable differences were observed in the 1944 sample, characterized by elevated relative abundance of PCB-101 (60% higher than the average in other samples) and reduced contributions from PCB-138 and -153 (approximately 40% lower). This difference suggests a different usage pattern prior to the 1950s, possibly reflecting imported products from the 1950s. PCBs were banned in 1975 in Australia,[30] leading to a consistent decreasing trend from the 1970s onward.

Compared with other studies, PCBs have been detected in butter since the 1960s.[34] In Europe, consistent decreasing trends have been reported since the 1960s. For example, in Germany, the concentrations of $\sum$PCBs in butter decreased from approximately 150 ng/g lw in 1970s[35] to 20 ng/g lw in the 1980s[10] and were reported to continue to drop to 2.1−6.8 ng/g ($\sum_{14}$PCBs) in Spain in 1999.[36] While different congeners were measured in the latter studies, it is notable that this temporal trend is in line with that found in our study. However, over the same time period, the concentrations of PCBs detected in Australian butter were 10 times lower (i.e., 0.95 ng/g $\sum$PCBs in 1987). This is also in agreement with a more recent study from 1998/1999, which showed that concentrations of PCBs in butter in Australia decreased to <1 ng/g lw (mean of 0.74 ng/g lw), while data reported from North America (1.2−2.3 ng/g lw) and Europe (3.1−14 ng/g lw) at the same time, was substantially higher,[37] indicating evident lower historic usage of PCBs in Australia.

3.3. Polychlorinated Dibenzo-Dioxins and -Furans. PCDD/Fs were detectable in all samples from 1944 to 1987 (Figure 3). In addition, we have previously reported the concentrations of PCDD/Fs in several butter samples collected from Australia nation-wide during 1999/2000.[15] These data are also included here, with respect to the investigation of the temporal trends. The concentrations of dioxins expressed as TEQ levels[38] were 0.53−0.54 pg-TEQ/g lw in the samples collected from 1944 and 1958, with the highest concentrations in the sample from 1969 (0.95 pg-TEQ/g lw) and the lowest concentration in the 1999/2020 samples (mean 0.19 pg-TEQ/g lw). To our knowledge, no data are available for PCDD/F concentrations in historic butter (prior to 1990s) from elsewhere, but one may assume that the concentrations of these chemicals in the 1960s and 1970s were higher, on the basis of historic environmental evidence and understanding. In light of this, the highest concentration in the 1969 sample might be considered to be relatively low. This was in agreement with the study on the butter samples collected in 2000, which indicated that levels in butter from Australia were relatively low compared to butter from many other regions, including Europe and USA, which were more industrialized and had relied on waste incineration.[2,5,39,40]

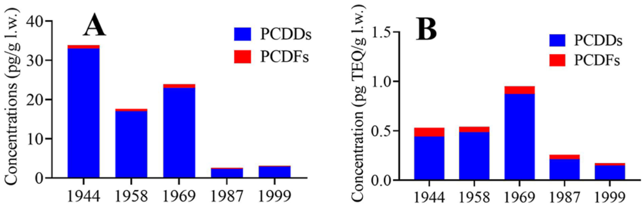

Figure 3. Concentrations (A) and TEQ (B) of PCDD/Fs in historical butter samples from Australia.

The concentrations of $\sum$PCDD/Fs in the butter were 33, 18, 24, 2.6, and 2.3 pg/g lw in samples collected in 1944, 1958, 1969, 1987, and 1999/2000, respectively, with the highest concentrations detected in the 1944 sample. The different temporal trends between the concentrations expressed as ng/g lw and pg-TEQ/g lw indicated an interesting trend for the higher chlorinated PCDDs (Figure S2). For example, the 1944 sample stood out with a concentration of OCDD of about 26 pg/g lw, while it was 14 and 17 pg/g lw in the 1958 and 1969 sample, respectively, both concentrations being much higher than that typically observed in butter samples from other countries (usually <1 pg/g lw). Also, the 2001 study on butters from Australia observed elevated levels of OCDD.[15] The decrease of OCDD concentrations from 1944 compared to the 1999/2000 sample may suggest decreased waste production since the 1940s. The congener profile of PCDD/Fs in the 1944 sample, which was dominated by OCDD, provides valuable insights into the temporal aging and degradation of these contaminants. This pattern was likely the result of differential environmental behavior of dioxin congeners. Lower-chlorinated PCDD/Fs are more volatile and susceptible to photolytic and microbial degradation over time, while highly chlorinated congeners, particularly OCDD, are extremely persistent and resistant to breakdown.[41] The profile in the 1944 sample therefore likely represented the residue from PCDD/F sources prior to the 1940s, where the original mixture had undergone extensive degradation, enriching the relative proportion of OCDD.

The temporal trend of PCDD/Fs reflected the interplay of historical emission sources and subsequent regulatory control. The high concentration between 1944 and 1969 coincided with a period of intensive industrialization and the widespread use of processes that unintentionally generate PCDD/Fs.[42] The decline in concentrations observed after 1969 is attributed to the implementation of stringent environmental regulations from the 1970s onward, which mandated the adoption of advanced emission control technologies and restricted the use of heavily contaminated industrial chemicals.[43]

3.4. Polybrominated Diphenyl Ether. PBDE concentrations in the butter samples were consistently below the LOD, and the sum of 8 PBDEs was <0.05 ng/g lw. To the best of the authors' knowledge, there is no data on PBDE levels in butter prior to 2000. The earliest data came from 2000s, with the mean concentrations of 0.53 ng/g lw, 1.2 ng/g lw, 0.52 ng/g lw, and 0.10 ng/g lw in butter samples collected from US,[44] Spain,[45] China,[46] and Poland,[47] respectively. PBDEs were not intentionally produced until the 1970s, which may explain their levels below the LOD before 1970s, while those low concentrations after the 1970s might indicate the low usage of PBDEs in Australia until the late 1980s. In Australia, the low concentrations of PBDEs were also evidenced by a sediment core study from the Sydney estuary, where concentrations remained < LODs or at very low concentration until the 2000s.[12]

3.5. Polychlorinated Alkanes. The concentrations of $\sum$PCAs-C$_{10-21}$ (PCA congeners with carbon chain length between 10 and 21) were 0.78, 1.8, 1.1, and 0.79 ng/g lw in samples collected in 1944, 1958, 1969, and 1987, respectively (Figure 4). $\sum$PCAs-C$_{14-17}$ (formally reported as medium chain chlorinated paraffins, MCCPs) showed the highest contribution in all samples, with concentrations of 0.58, 0.88, 0.66, and 0.59 ng/g lw, respectively. Concentrations of $\sum$PCAs-C$_{10-13}$ (formally reported as short chain chlorinated paraffins, SCCPs) in samples from 1944 and 1987 were both <LOD (0.12 ng/g lw), while they were detected at 0.54 and

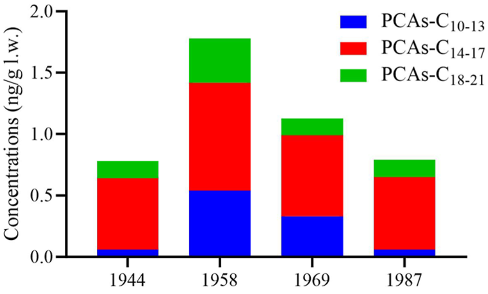

Figure 4. Concentrations of PCAs in historic Australian butter from 1944 to 1987.

0.33 ng/g lw in samples from 1958 and 1969, respectively. $\sum$PCAs-C_{18-21} (formally reported as long chain chlorinated paraffins, LCCPs) was only detected in the sample from 1958 (0.36 ng/g lw) and was <0.28 ng/g lw in other samples. The butter sample from 1999 was not analyzed for PCAs. The chlorine content was 40%, 43%, 42%, and 40% in the butter samples collected from 1944, 1958, 1969, and 1987, respectively. Congeners with 3 Cl atoms (Cl_3) were the predominant groups in all samples, accounting for >45% of total concentrations of PCAs analyzed. The predominance of Cl_3 groups in the butter samples was different from that of profiles in environmental and biota samples after 2000, both of which are dominated by Cl_{5-6}. It is notable that Cl_{1-2} congeners were also detected in the butter samples, but we were unable to quantify them due to analytical limitations. As such, the overall concentrations of PCAs may have been slightly underestimated.

Compared with other POPs, $\sum$PCA concentrations in butter were 2−3 orders of magnitude lower than those of DDT and HCHs, slightly lower than PCBs, but 2−3 orders of magnitude higher than PCDD/Fs. A recent multinational study of human milk collected between 2012 and 2019 reported that PCA accounted for 50% of the total POP burden, with levels approximately 5 times higher than those of PCBs.[48] In contrast, our results showed that $\sum$PCAs were, on average, 34% lower than $\sum$PCBs. This might be attributed to the substantial increase in global PCA production after the 1990s, particularly in China, whereas annual production remained stable at around 100,000 tons from the 1930s to the 1980s, which was comparable to PCB production during that period. Moreover, the relative concentration of PCA-C_{10-13} was consistently around 30% in both the 1958 and 1969 samples, resembling a compositional profile typically produced in North America, indicating that the use of PCAs in Australia prior to the 1990s was likely more influenced by North American products.[49]

A few studies also reported the concentrations of PCAs in butter collected elsewhere after 2000. For example, $\sum$PCAs-C_{10-13} was detected in butter samples from Denmark at 1.2 ng/g lw and from Ireland at 2.7 ng/g lw, while $\sum$PCAs-C_{14-17} was also detected in butter samples from Denmark (11 ng/g lw), Wales (8.8 ng/g lw), and Ireland (52 ng/g lw).[50] $\sum$PCAs-C_{10-13} and $\sum$PCAs-C_{14-17} were also detected in butter collected in the UK in 2007, with the concentrations of 1.2 and 2.8 ng/g lw, respectively.[51] However, these higher concentrations in butters collected in more recent European studies did not necessarily indicate the significant increase of PCA concentrations in butters, as the analytical issues, including using different extraction and instrumental methods, could lead to variation with respect to the detected PCA concentrations and thus a degree of uncertainty in comparative analyses. Additionally, the sealing process for butter cans primarily involved solder-based technology, which inevitably required the use of certain sealants.[52] However, specific information about the types of sealants used is unavailable. Consequently, their potential impact on PCA levels in butter could not be determined. Nevertheless, the highest concentration of PCAs was found in the sample from 1958, followed by decreases to 1969 and 1987, with all PCA groups following the same trends. Production and use of PCAs were first reported during the period of World War I (1914−1918),[53] whereas large-scale commercial production started around 1930.[54] Annual global production of PCAs slowly increased from the 1940s (18,000 t/year) to early 1970 (45,000 t/year), followed by a rapid increase to 220,000 t/year in 1978.[55] However, there are no available data on the historic production and use of PCAs in Australia. Our results might indicate that $\sum$PCAs-C_{10-13} release peaked in the 1960s and 1970s during the studied period. However, the $\sum$PCAs-C_{14-17} concentrations in butter remained relatively consistent from the 1940s to the late 1980s. It was worth noting that the global production of PCAs increased dramatically after the 1990s, leading to substantially increased concentrations in the environment and biota.[56,57] However, this was not covered by this study.

PCAs present a contrasting regulatory case. Despite being listed under the Stockholm Convention on POPs recently (particularly PCAs-C_{10-13}),[58] Australia maintained minimal restrictions until 2020.[18] This regulatory gap correlated with PCAs being the only contaminant group showing higher concentrations in the 1980s than in the 1940s.

3.6. Associations between Temporal Trends of Chemicals and Historic Production.

The peak concentrations of DDTs and PCBs and PCDD/Fs occurred in the 1960s, with estimated average half-lives of 9.0, 13, and 10 years, respectively, estimated by the different concentrations of analytes detected over 1987 and 1969 samples. HCH and PCA concentrations peaked in the 1950s, followed by a quick decline during the 1950s and 1960s, with average half-lives of 8.2 and 14 years, respectively, which extended to 9.1 and 32 years between the 1960s and 1980s. These temporal trends observed in butter exhibited similar trends with historical use and policy interventions in Australia during the mid-20th century, when DDT and HCHs were extensively applied as pesticides in agriculture (peaking 1950s−1960s), while PCBs and PCDD/Fs reached their highest (waste) production and use in the 1960s−1970s.[59−61] It was worth noting that due to the limited sample size in this study and regional variations in the production areas of different butter samples, the temporal trend identified in this research may carry a certain degree of uncertainty. However, obtaining these well-preserved historical samples was inherently challenging and rare, making the data from this study invaluable for providing critical evidence to fill in gaps in the historical environmental trends of persistent pollutants.

Regulatory interventions initiated in the 1970s drove significant declines in contamination levels. The introduction of the Australian Pesticides Act in 1975 initiated restrictions on the registration and sale of problematic pesticides, followed by a complete ban on DDT in 1987, which directly led to a decline of over 95% in DDT concentrations in butter by the 1980s. Similarly, PCBs were banned in 1975 in Australia,[30] resulting in a consistent decreasing trend since the 1970s. No specific regulations on PCAs were in effect during the studied period, resulting in the fact that the PCSs were the only contaminant group showing higher concentrations in the 1980s than in the 1940s.

The differential temporal trends between chemicals highlighted the importance of chemical properties, environmental fate and distribution, and regulations. While all monitored POPs showed postregulation declines, substances with ongoing secondary emission sources (PCBs) or weak regulatory control (PCAs) demonstrated prolonged environmental persistence, emphasizing the necessity of comprehensive and thoughtful bans and active monitoring systems to achieve meaningful contamination reduction. The findings further demonstrated that historical chemical usage contributed minimally to butter contamination, with environmental reservoirs becoming significant exposure sources only after the complete cessation of production and use.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c05330.

> Detailed information on the instrumental analysis, and detailed data on POPs in each sample (PDF)

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Author Contributions

This manuscript was written with contributions of all authors. J.M. and C.G. designed the research. C.H., A.C., M.N.J., and O.P. performed research and analyzed data, and conducted relevant preceding studies. All authors have modified and given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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