

The Origins of Organic Contaminants in Antarctica

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The continent of Antarctica is often described with words such as *pristine* and *untouched* due to its remote location and distance from the inhabited regions of earth. Environmental contaminants have, however, been detected^{1,2} in various Antarctic media since the 1960s. These early findings provided impetus for further study, confirming the ubiquity of contaminants in Antarctica but raising questions about how these chemicals came to exist in such a secluded area.^{3,4}

The isolation of the Antarctic continent has meant that it has endured very little contact with people throughout history, making it a rather unique case in the field of contaminant study. Traditionally, human activities in this area have been involved with either exploratory or scientific endeavours.⁵ More recently, the tourism industry has also brought noteworthy numbers of visitors to the Antarctic continent, thus increasing the likelihood of contamination.⁶ Collectively though, these activities still represent a relatively low level of human interaction and are generally confined to specific and restricted areas of the continent. As a result, the detection of contaminants throughout Antarctica conventionally has not been attributed to *in situ* human activity.⁷ Nonetheless, this assertion requires further analysis through consideration of specific contaminants and their distributions in Antarctica. The term *contaminant* encompasses a wide variety of chemicals, including heavy metals, hydrocarbons, radionuclides and so forth.⁸ A large proportion of the contaminant research in Antarctica focuses on the class of compounds known as Persistent Organic Pollutants (POPs). These are chemicals *that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment.*⁹

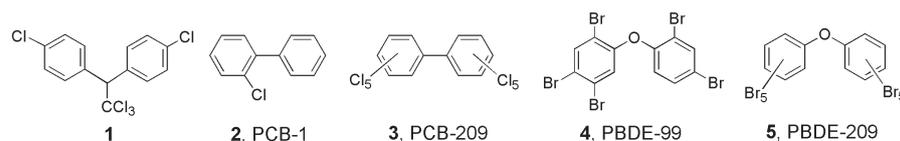
It is the potential detrimental impact on humans and wildlife that originally instigated interest in the global distribution of the POPs. The first organic contaminant detected in Antarctica was the pesticide 1,1-trichloro-2,2-di(*p*-chlorophenyl)ethane (DDT, **1**; Chart 1), as reported by Sladen *et al.*¹ in 1966. DDT was used extensively to control disease vectors throughout WWII and the subse-

quent two decades. Its discovery in Antarctica was regarded as highly significant because it signified that harmful contaminants had achieved a global distribution well beyond that previously anticipated. Moreover, the detection of DDT in Antarctica occurred not long after concerns about the biological effects of such pesticides were first raised in the book¹⁰ *Silent Spring* in 1962. Research at that time elicited concern for high trophic-level bird species, in which high concentrations of DDT were being measured because of biomagnification. It was also implicated in egg-shell thinning, which led to the fracturing of egg shells during incubation and decreased hatching rates.¹⁰ Thus, Sladen's publication¹ was ground-breaking in its time and it prompted an emerging environmental concern. The most prominent issue exposed was the question of how such chemicals came to be found in the Antarctic region without ever having been used there.

Based upon Sladen's initial measurements, the authors proposed various mechanisms by which DDT may have come to be found in Antarctica.¹ These were limited by a lack of information about the physical properties, degradation rates, and partitioning behaviour of DDT in the environment. Despite the limitations, the authors were able to estimate the effect of human activity in Antarctica and they concluded that this was unlikely to be responsible for the observed levels of DDT. Instead, they suggested that the pesticide may have reached Antarctica by ocean-, atmosphere- or biologically-mediated transport.¹

Subsequent research has furthered not only a better understanding of the physical properties of DDT but also of its distribution in Antarctica.^{11,12} The properties most relevant to the distribution of DDT, now accepted as entering the Antarctic by long-range atmospheric transport, are shown in Table 1;⁷ it has been detected in biota and sediments at most sites across Antarctica thereby decreasing the possibility of local point sources being responsible.^{13,14} Furthermore, the notion of atmospheric transport is supported by DDT's vapour pressure of 2×10^{-5} Pa (Table 1), which falls within the 1×10^{-5} to 100 Pa range for semi-volatile chemicals.¹¹

Table 1. Some physicochemical properties of persistent halogenated contaminants **1-5**.^a



Property	1, DDT	2, PCB-1	3, PCB-209	4, PBDE-99	5, PBDE-209
Vapour Pressure (Pa)	2×10^{-5}	1.84	1.4×10^{-6}	5×10^{-5}	5×10^{-11}
Log K_{ow}	6.19	4.56	8.20	6.71	11.15
Half-Life in Air (h)	170	170	55,000	467	7,620
Half-Life in Water (h)	5500	5,500	55,000	3,600	3,600

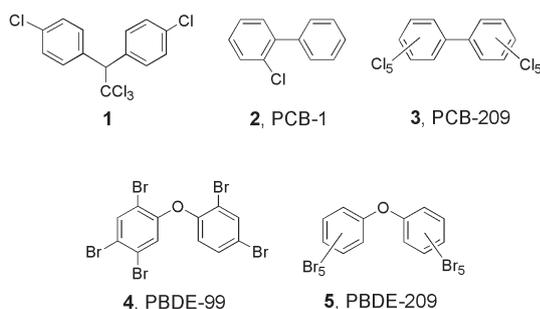
^aData for **1-3** are taken from ref 11; data for **4-5** are taken from ref 23.

Semi-volatile chemicals tend to enter the air in the warmer regions of earth where they also tend to be used. Provided that the chemical is sufficiently air-stable, which is true for DDT (Table 1), it will be transported in the direction of the prevailing wind. On a global scale, atmospheric circulation transports air from the equator towards the poles so that the chemicals eventually make their way to the polar ice caps. The temperatures in these regions are significantly lower than at the site of use and thus the molecules condense¹⁵ thereby explaining the detection of semi-volatile chemicals in cold remote regions where they have never been used in notable quantities.

The fate of atmospherically deposited semi-volatile chemicals is dependent upon their partitioning characteristics. The medium of greatest interest for organic contaminants is biological tissue since this is where they exhibit their toxic effects. The parameter that best quantifies the tendency of a molecule to bioaccumulate in living systems is the octanol-water partition coefficient (K_{ow}). Log K_{ow} for DDT is 6.19 and it is therefore expected to bioaccumulate because chemicals with a log $K_{ow} \geq 4$ are considered lipophilic.¹⁶ This lipophilicity is particularly significant for Antarctic organisms because many of them must store energy in the form of fatty adipose tissue in order to survive the winter and, therefore, have relatively large quantities of lipids. This hydrophobic tissue is ideal for accumulation of compounds such as DDT that already show considerable potential for bioaccumulation, and this explains the numerous reports of measurable levels of DDT found in Antarctic biota.^{1,2,13}

The polychlorinated biphenyls (PCBs) were the next class of semi-volatile organic contaminants to be measured in Antarctica. PCBs consist of a biphenyl core with varying degrees of chlorination that can give rise to as many as 209 possible structures, termed *congeners*, e.g. **2** and **3** (Chart 1). Following their discovery in the 1920s, PCBs had wide-ranging applications throughout industry, based largely upon their desirable properties of low flammability and high boiling points. However, as time progressed, various detrimental health effects, including chloracne, skin rashes, and liver damage were observed in people who had experienced high exposures to PCBs.¹⁷ As a result of these observations, PCBs were banned from use in the developed countries in the 1970s.

Chart 1



PCBs have been detected in samples from Antarctica since 1976. However, their origin was not as easily discernible as that of DDT because of local sources,⁴ one of the most obvious being the historical dumping ground at

McMurdo Base in the Winter Quarters Bay. A variety of PCB-containing materials were disposed of directly into this bay giving rise to considerable contamination in the area.¹⁸ In order to establish whether local sources such as these have a notable effect, or whether long-range atmospheric transport again is responsible, it is necessary to consider the properties of different PCBs.

The properties of the PCB molecules change as the degree of chlorination increases and two molecules were selected for comparison, namely congeners **1** (**2**) and **209** (**3**) (Chart 1). The vapour pressure of a PCB decreases as the degree of chlorination increases (Table 1) because of the increasing van der Waals attraction between the molecules. The progressive change is so significant that whilst the lower chlorinated congeners such as PCB-1 (**2**) have vapour pressures that allow them to be classified as semi-volatile, the heavier congeners such as PCB-209 (**3**) have vapour pressures that place them outside the accepted range. This is a key factor in the elucidation of the source of PCBs in the Antarctic as it means that the larger congeners would not be expected to undergo efficient long-range atmospheric transport. Therefore, larger congeners are associated with local sources whilst lighter congeners are associated with long-range atmospheric transport.

Numerous studies were conducted into the levels of PCBs found in a variety of Antarctic biota collected from Terra Nova Bay during the 1990s. The congener profiles were compared to those in common commercial PCB mixtures, and those from biotic samples were found to contain more of the less-chlorinated congeners than was found in the commercial mixtures.^{14,19} Based on their K_{ow} values, all PCB congeners are expected to bioaccumulate. Thus, the observed congener profiles indicated that long-range atmospheric transport was largely responsible for the presence of PCBs in Antarctica. This conclusion was strengthened when similar congener profiles were found in sediment samples, removing the potentially confounding variable of biological uptake.²⁰

Banned, historic-use contaminants are no longer the only focus of contaminant research in Antarctica. Recent studies have revealed the potentially detrimental health effects of brominated fire retardants - polybrominated diphenyl ethers (PBDEs), e.g. **4** and **5** (Chart 1). These chemicals are used in a wide range of household items, particularly electronics, plastics and furniture. PBDEs have been identified as possible neurotoxins, causing their distribution in the natural environment increasingly to become a prominent human health and environmental issue.²¹

A recent publication has described the detection of PBDEs in Antarctic wildlife.²² Although they make up a relatively small proportion of the detected organic contaminants, at ca. 1%, their increasing usage in the Antarctic environment is cause for concern.²² Consideration of the structure of the PBDEs again is important in determining their origins. In analogy to the PCBs, PBDEs are brominated to varying degrees and there are again 209 possible congeners. The major commercial classes of these products are the penta-, octa- and deca-brominated compounds. One of the major constituents of the pentabromo formulation

is PBDE-99 (**4**) whereas PBDE-209 (**5**) is the principal constituent of the decabromo formulation.

The differing properties of the two compounds reported in (Table 1) illustrate the importance of the bromination level on the behaviour of a PBDE in the environment. The more heavily brominated **5** has a vapour pressure of 5×10^{-11} Pa that is well below the 1×10^{-5} Pa minimum for a semi-volatile compound.²³ In contrast, PBDE-99 at 5×10^{-5} Pa is semi-volatile and is expected to undergo long-range atmospheric transport.

In an early investigation on PBDE fate in the environment, computer modelling was used to determine that they are likely to undergo long-range atmospheric transport.²⁴ In a subsequent study, the low-brominated congeners were detected in three species of Antarctic penguin, leading the researchers to conclude that they had confirmed the proposed mechanism of long-range atmospheric transport.²² However, a more recent publication⁵ challenged this assertion by investigating the possibility that PBDEs may be originating predominantly from local sources, namely the Antarctic research bases, the major human activity centre in Antarctica.⁵ The aim of the authors' investigation was to *determine whether the indoor dust and wastewater sludge from Antarctic research bases contain substantial burdens of PBDEs* and to *establish whether PBDEs have been released locally*.⁵ In order to do this, they took dust and wastewater samples from two bases in McMurdo Sound, Scott Base (NZ) and McMurdo Station (US), and analysed the levels of PBDEs in these matrices.

The analysis revealed particularly high levels of PBDEs in the indoor dust samples - even higher than those commonly found in residential dwellings in developed countries, including NZ.²⁵ This validated the authors' hypothesis that Antarctic research bases may be local sources of PBDEs. However, a high PBDE concentration in indoor dust does not necessarily mean that the bases are polluting the environment. Thus, PBDEs were also measured in wastewater samples from the same two bases. The untreated wastewater would be expected to contain high levels of PBDEs since that used for cleaning would contain indoor dust, and it did. In contrast, the treated wastewaters had no detectable levels of PBDEs fully compatible with the bases under investigation not contributing PBDEs to McMurdo Sound.⁵ Nonetheless, the findings are highly significant for two reasons. Firstly, compared to the high-grade treatment facilities at Scott and McMurdo Bases, many Antarctic research bases fall short and often release untreated waste directly into the environment. Thus, based upon the untreated wastewater measurements, these other bases currently may be releasing notable amounts of PBDEs to the surrounding environment.⁵ Secondly, Scott Base and McMurdo Station had their treatment facilities upgraded some 18 months prior to sample collection and, given the long environmental half-life of the compounds, it is distinctly possible that PBDEs would still have been detectable in the area surrounding the bases due to the relatively recent release of PBDEs into the environment.

It was with this latter possibility in mind that the authors measured the levels of PBDEs found in sediments and

biota at sites of increasing distance from the wastewater outfall of McMurdo Station. The sum for congeners 47, 85, 99, 100, 153, and 154 (Σ PBDE6) - the major constituents of the pentabromo commercial product - was quantified in biological samples. In the sediment samples, both Σ PBDE6, and the concentration of PBDE-209, the major constituent of the decabromo analogue, was measured.

PBDE concentrations were found to decrease with increasing distance from the McMurdo wastewater outfall, thus providing strong evidence that prior to installation of the treatment facility, the wastewater from McMurdo Base was, in fact, releasing PBDEs to McMurdo Sound. The importance of these results cannot be underestimated as they indicate that long-range atmospheric transport may not be the primary source of PBDEs in Antarctic marine ecosystems. This is particularly noteworthy because, although little can be done about the presence of banned, historic-use chemicals like DDT and PCBs in Antarctica, PBDE inputs are on-going and current environmental management decisions may affect their fate and future impacts on Antarctic ecosystems.

Prior to the implementation of any mitigation plans, it would be wise to repeat a similar experiment to that described above at an Antarctic research base that does not treat its wastewater. This would provide further information and give a more logical basis for the formulation of a plan to reduce the anthropogenic inputs of contaminants to Antarctica. Further initiatives could also include research into the level of other chemical contaminants currently overlooked. Until very recently, research on contaminants in remote ecosystems focussed on banned, historic-use contaminants for which analytical methods are well-established. However, as the PBDE case illustrates, chemicals in current-use may be accumulating in these ecosystems without our knowledge. Other compounds of concern, which may be worthy of investigation due to their toxic properties, include *pharmaceuticals, fragrances and cleaners*.⁵ Without adequate knowledge of their distribution, these may be having untold effects on organisms within this unique ecosystem. It is clear that efforts directed at understanding the sources of contaminants in Antarctica are critically important to the future welfare of Antarctic ecosystems.

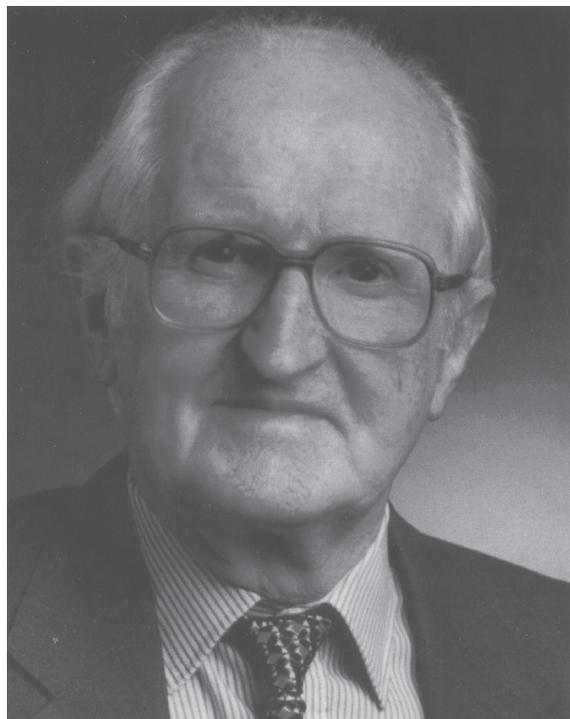
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OBITUARY

Rowland Albert (Roy) Kennerley – 9 March 1923 - 7 January 2009



The death occurred recently at the age of 85 of Roy Kennerley, a scientist with the former Chemistry Division of DSIR. Roy was born in Carterton, gained secondary education at Levin District High School, and joined the public service as a cadet. Initially assigned to the Public Service Commission Office in Wellington, he moved to the Social Security Head Office as a clerk, and then signed up for military service in 1941. He served first with 2nd Field Regiment and then the RNZAF as a radar operator in the Solomon Islands campaign.

After the war, Roy graduated with his MSc in chemistry from Victoria University and then joined DSIR's Dominion Laboratory in 1948, where he led a research team working on the inorganic chemistry of cement and concrete. This was particularly important in the era of public works construction following WWII, when millions of tonnes of cement and concrete were used in bridges, hydro dams, airport runways, geothermal projects, and public buildings. Roy and his colleagues at DSIR's inorganic materials unit at Gracefield played a vital part in these developments, testing materials, advising cement works, and ensuring standards were drafted and complied with.

By the time Roy retired in 1983, the inorganic materials team had grown to twelve, five of whom held PhD degrees. Retirement saw Roy begin a second career - as a technical manager and consultant to the Milburn NZ Ltd. cement company from which he retired permanently in 1998.

In addition to his science, Roy Kennerley's other great interest was music. He was a church organist, teacher, accompanist, ensemble leader and conductor who set high standards. He first sang in 1949 with the Eastbourne Lyric Singers conducted by Maxwell Fernie, and later formed or led choirs at Tawa, Upper Hutt, and, more recently at Eastbourne. After studying the organ, he began a career as an itinerant church organist, accompanying church services wherever the need arose. He also performed with Schola Polyphonica and the NZSO, which he accompanied on the Wellington Town Hall organ.

Roy is survived by his wife Agnes, and a son from an earlier marriage.

Ken MacKenzie

Help getting the message across

The British Science Media Centre has produced some one page brochures on communicating in soundbites. They have one entitled "Communicating risk in a sound bite" which can be freely downloaded at the address; www.sciencemediacentre.org/uploadDir/admincommunicating_risk.pdf

A second is entitled "Communicating uncertainty in a sound-

bite", available at the address www.sciencemediacentre.org/uploadDir/adminuncertainty_in_a_soundbite.pdf

They also have a tips brochure for working with the media. Some of this is less relevant to New Zealand but still has helpful suggestions. It can be found at the address; www.sciencemediacentre.org/uploadDir/admintop_tips.pdf