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Chlordane Components and Metabolites in Six Arctic Seabird Species from the Northwater Polynya: Relationships between Enantioselective Analysis of Chlordane Metabolites and Trophic Level

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Introduction

Various components of the insecticide chlordane, including *cis*- and *trans*-chlordane, *cis*-nonachlor and *trans*-nonachlor and the metabolites heptachlor epoxide and oxychlordane, have been measured in the Arctic abiotic and biotic environments [1]. Many of these components bioaccumulate and biomagnify in aquatic food chains, and high concentrations have been measured in high trophic level organisms such as polar bears (*Ursus maritimus*)[2] and glaucous gulls (*Larus hyperboreus*)[3].

Polynyas are areas of open water which persist throughout the winter in polar seas. They are one of the most important and least understood phenomena in polar ecology. The Northwater (NOW) in northern Baffin Bay is the largest and most productive polynya in the Canadian Arctic, supporting large populations of seabirds and marine mammals. An extensive multi-disciplinary study on the NOW afforded the opportunity to collect a number of seabird species within the same area and time. Six species of seabirds: dovekie (*Alle alle*, DOVE), black guillemot (*Cepphus grylle*, BLGU), black-legged kittiwake (*Rissa tridactyla*, BLKI), northern fulmar (*Fulmaris glacialis*, NOFU), ivory gull (*Pagophila eburnea*, IVGU) and glaucous gull (GLGU), were collected to examine concentrations of chlordane components and enantiomeric fractions [EFs; EF = (+) / (+ and -)] of heptachlor epoxide and oxychlordane in liver. These species cover a range of trophic levels. Chlordane concentrations in liver were compared with trophic level determined from stable-nitrogen isotope measurements in muscle tissue.

Methods

Samples of liver were collected from DOVE (n=10), BLGU (n=9), BLKI (n=10), NOFU (n=10), IVGU (n=5) and GLGU (n=10) in May and June, 1999. Livers were removed from the birds shortly after death and frozen in Whirl Pak bags until analyzed. Extraction and clean-up methods are described in detail elsewhere [4]. Concentrations of chlordane components were quantified on an ECD-GC equipped with a 60 m DB-5 column. Enantioselective analysis of oxychlordane and heptachlor epoxide were performed on BGB-172 30 m chiral column (BGB Analytik) installed in an MSD. Stable isotope analysis methods have been described previously [5].

Results and Discussion

Concentrations (lipid basis) of Σchlordane in BLGU, BLKI, GLGU and NOFU are similar to those reported for eggs of the same species collected in the Canadian high arctic in 1993 [3,6] and liver collected in the European arctic [7]. No chlordane data for DOVE and IVGU could be found for

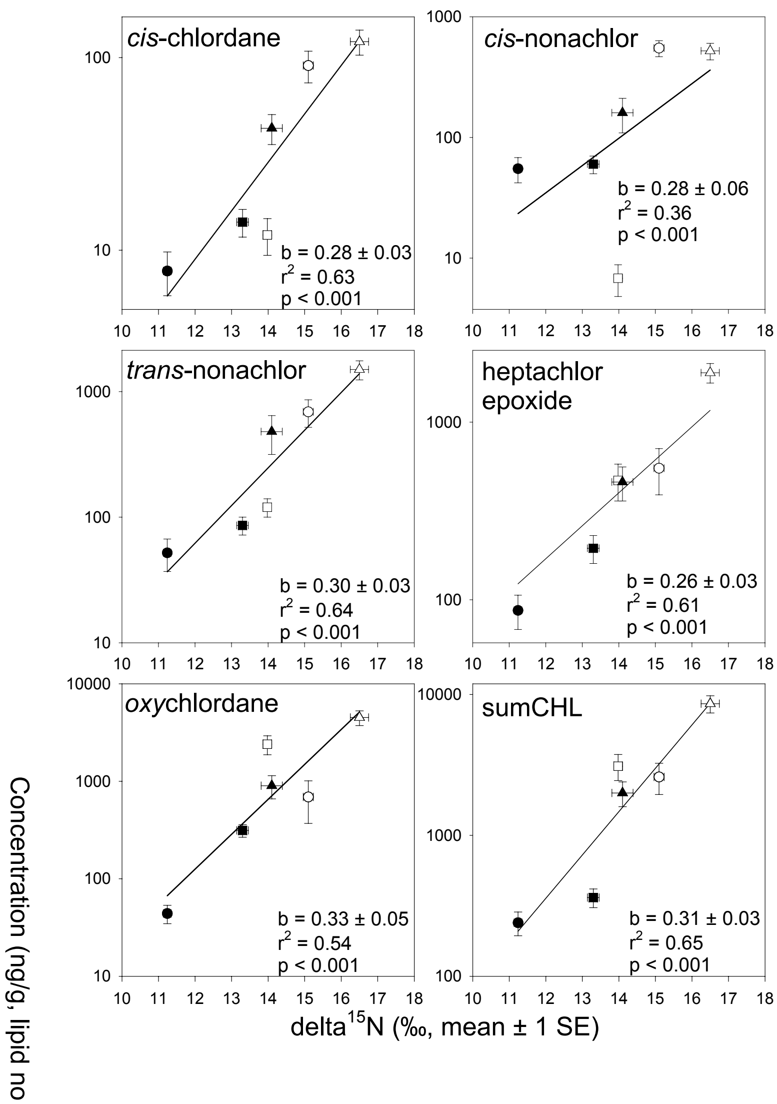

Figure 1: Relationships between concentrations (lipid normalized) of chlordane components and Σchlordane vs $\delta^{15}N$ in arctic seabirds of the NOW. Points represent mean ± 1 SE concentrations, regressions were based on $\delta^{15}N$-chlordane component concentrations for individual species (n = 46) (● - DOVE, O - BLGU, ■ - BLKI, ▯ - NOFU, ▲ - IVGU, Δ - GLGU).

comparison. Large differences in chlordane concentrations between species were observed and appear to be due mostly to trophic level, as described by relationships with $\delta^{15}N$ (Figure 1). Additional variation between species could be due to feeding habitats (e.g. inshore vs offshore), migration and/or reproductive state. One interesting result was the similar chlordane concentrations of BLGU compared with NOFU and IVGU. BLGUs are predominantly inshore benthic piscivores [8] and were expected to have lower concentrations than NOFU and IVGU, which are known to feed on carrion, such as seals. These results show the utility of using $\delta^{15}N$ to describe trophic level relationships with organochlorine concentrations in biota.

In food chains, biomagnification factors of a contaminant per trophic level can be estimated from slopes of log concentration vs $\delta^{15}N$ [9]. Good linear relationships between log chlordane component concentration vs $\delta^{15}N$ were obtained, indicating that chlordane concentrations increased concomitantly with trophic position of NOW seabirds (Figure 1). Slopes ranged from 0.26 to 0.33, similar to that (b = 0.49) estimated for Σchlordane in an arctic marine food chain that included marine mammals and seabirds [10]. These slopes, and those reported by Norstrom [10], are much greater than those calculated for aquatic food chains that only include fish but no birds or mammals [9], suggesting that seabirds and mammals accumulate chlordane components, and likely other OCs, at a much greater rate than fish or invertebrates.

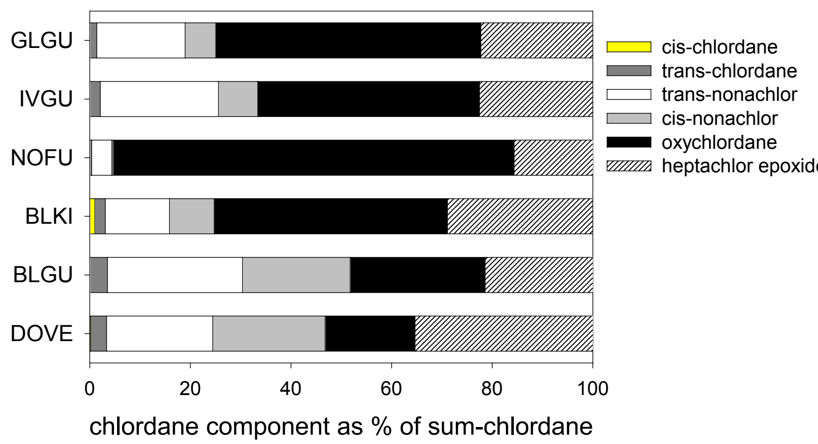

Figure 3: Components of Σchlordane in NOW seabirds.

The relative proportions of chlordane components as percentage of Σchlordane (Figure 2) suggest that the metabolic capabilities of alcids (DOVE and BLGU) are less than those of "gulls" (larids and closely related procellariids - NOFU, BLKI, IVGU and GLGU) because the relative proportion of the metabolite, oxychlordane, was higher in the gulls than alcids. Higher Σchlordane concentrations were found in the BLGU than BLKI, but BLKI had a higher proportion of oxychlordane, therefore differences in levels of chlordane accumulated do not account for the difference in oxychlordane percentage among species. Higher relative proportions of oxychlordane in gulls could also be due to feeding on dead marine mammals. Differences in EFs of chiral metabolites provides additional information on metabolic capability, as changes in EFs from technical mixtures or between trophic levels can be associated with biotransformation. It should be noted that these results are for livers and EFs could vary in other tissues or for the birds as a whole, and that bioaccumulation or diet could influence EFs. Differences in oxychlordane EFs between alcids and gulls are clear (Figure 3). EFs of hepatchlor epoxide (HE) do not appear to be related to phylogeny, as DOVE and BLGU, both alcids, had the highest and lowest EFs, respectively. The high EFs of HE in DOVE and BLKI, which were feeding at the lowest trophic, suggest that differences among food webs may be more important than biotransformation capability in determining EFs of HE in seabirds.

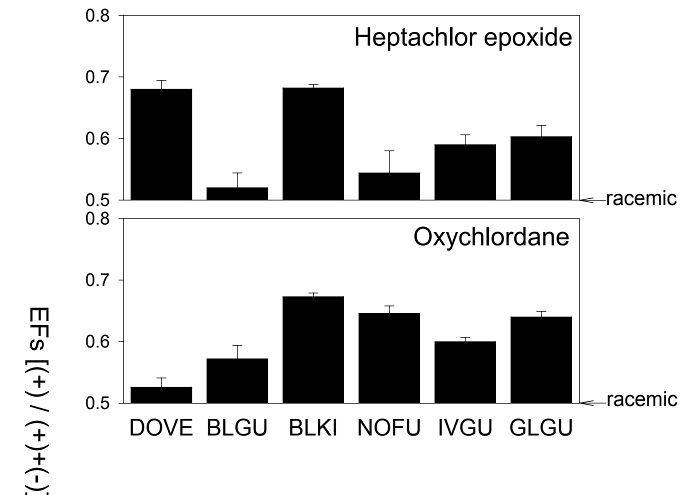

Figure 3: EFs of heptachlor epoxide and oxychlordane in NOW seabirds.

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References

[1] AMAP. 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, xii+859 pp.
[2] Norstrom RJ, *et al.* 1998. Arch. Environ. Contam. Toxicol. 35:354.
[3] Braune BM, 1994. Indian and Northern Affairs Canada, Ottawa, Environmental Studies 72, pp 305.

[4] Muir DCG, Ford CA, Grift NP, Metner DA, Lockhart WL. 1990. Arch Environ Contam Toxicol 19:530.
[5] Hobson KA, Piatt JF, Pitocchelli J. 1994. J Anim Ecol 63:786.
[6] Braune BM, 1994. Indian and Northern Affairs Canada, Ottawa, Environmental Studies 72, pp 312.
[7] Savinova TN, Polner A, Gabrielsen GW, Skaare JU. 1995. Sci Total Environ 160/161:497.
[8] Bradstreet MSW. 1980. Can J Zool 58: 2120.
[9] Kidd, K.A., R.H. Hesslein, B.J. Ross, K. Koczanski, G.R. Stephens and D.C.G. Muir. 1998. Environ. Pollut. 102:91-.
[10] Norstom RJ. 1994. Organohalogen Compounds 20: 541.