

the latent lactotropes, thus avoiding unnecessary waste in the extracellular spaces.

Such a biological activity for the free α subunit may explain hitherto unconnected observations. For example, in human anencephaly the large number of lactotropes in the absence of hypothalamic GnRH (3) would be due to the exceptionally high concentration of α subunit in pituitary because of the almost complete absence of intact hormone (4, 5). In cultures of human fetal pituitaries, the secretion of α subunit but not intact LH persists and even increases after several weeks (15). This could occur in connection with an increase in the secretion of prolactin observed under similar conditions (16).

In clinical investigation a role of the α subunit should be considered. Indeed, in some pituitary adenomas with markedly elevated concentrations of serum α subunit, the amounts of serum prolactin were also elevated (17). Injection of GnRH gave a greater increase in the concentration of serum α subunit in these hyperprolactinemic patients than in normal controls (18). In contrast, bromocriptine therapy, which reduces serum prolactin, also reduced the peak serum concentration of α subunit (18). As yet, a possibly direct relation between the abnormal secretion of α subunit and hyperprolactinemia has not been considered. These variations should be studied further to appreciate fully their clinical implications.

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Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Sediments from Siskiwit Lake, Isle Royale

Abstract. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans were found in sediment from Siskiwit Lake on Isle Royale, Lake Superior, a location which can receive only atmospheric inputs. The source of these compounds is the atmospheric transport of dioxins and furans formed by combustion of domestic and chemical waste.

The reputation of chlorinated dioxins and dibenzofurans as extremely toxic chemicals to man (1) is largely based on the ability of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and -furan to kill guinea pigs at very low doses (0.6 μ g/kg) (2). Dioxins and dibenzofurans have several sources and can thus enter the environment either through the atmosphere or through the water. Examples of the atmospheric path include the explosion of a trichlorophenol reactor at Seveso, Italy (3), and the incineration of chlorinated waste

chemicals (4). Examples of the aquatic path include direct industrial discharge into a river (5) and leaching at a hazardous waste facility (6). Distinguishing between these paths has obvious regulatory implications but is not easy.

We have investigated the atmospheric path by measuring polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in sediments from Siskiwit Lake, which is located on Isle Royale in northern Lake Superior. This island has been a national

Table 1. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in Siskiwit Lake sediment and in two air particulate samples. The three sediment depths correspond to depositional dates of 1982 for 0 to 0.5 cm, 1953 for 5 to 6 cm, and 1935 for 8 to 9 cm. Abbreviations for the various PCDF and PCDD are: tetrachlorofuran, TCDF; pentachlorofuran, PnCDF; hexachlorofuran, HxCDF; heptachlorofuran, HpCDF; octachlorofuran, OCDF; tetrachlorodioxin, TCDD; pentachlorodioxin, PnCDD; hexachlorodioxin, HxCDD; heptachlorodioxin, HpCDD; and octachlorodioxin, OCDD. Concentrations are given as parts per dry weight extracted; ppt, parts per trillion; ppb, parts per billion.

Compound	Sediment (ppt)			Air (ppb)	
	0 to 0.5 cm	5 to 6 cm	8 to 9 cm	Washing-ton, D.C.	St. Louis
TCDF	15	18	N.D.*	1.3	0.2
PnCDF	5	2	N.D.	1.2	0.2
HxCDF	2	2	N.D.	0.8	0.3
1,2,3,4,6,7,8-HpCDF	8.2	12	1.6	9	4.3
1,2,3,4,6,8,9-HpCDF	11	5	N.D.	8.5	7.4
1,2,3,4,7,8,9-HpCDF	1	0.4	N.D.	0.5	0.4
OCDF	4	3.2	1.1	6.2	0.5
TCDD	26	12	N.D.	0.5	1.1
PnCDD	12	11	N.D.	6.4	0.2
HxCDD	10	8	N.D.	1.6	1.2
1,2,3,4,6,7,9-HpCDD	32	20	3.7	9.2	11
1,2,3,4,6,7,8-HpCDD	38	26	4.5	12	14
OCDD	560	390	54	200	170

*Not determined (N.D.), <0.4 ppt.

park since 1940. Because the water level in Siskiwit Lake is 17 m higher than that in Lake Superior, there is no movement of water from Lake Superior into Siskiwit Lake. Also there are virtually no anthropogenic inputs in the drainage basin of Siskiwit Lake, making the atmosphere the only source of anthropogenic chemicals in this lake. Once such inputs cross the air-water interface (either as vapors or particulates), the nonvolatile compounds will move through the water column to the sediment. Thus, our strategy has been to measure the congener distributions of PCDD and PCDF in Siskiwit Lake sediments and to compare these data with those found in the atmosphere.

A sediment core was collected from Siskiwit Lake (48°0'N, 88°46'W) and immediately sliced into 0.5- to 1-cm sections. The wet sediment (~10 g) was later extracted in a Soxhlet apparatus with isopropanol and then with dichloromethane. Both PCDD and PCDF were isolated with the use of elemental copper, silica, and alumina chromatography as described by Czuczwa and Hites (7). The final extracts were analyzed by gas chromatographic-mass spectrometry with negative ion methane chemical ionization and selected ion monitoring (7).

The concentrations of PCDD and PCDF found in three sections of Siskiwit Lake sediment core are given in Table 1. In all three sections, octachlorodioxin (OCDD) predominates; the heptachlorodioxins (HpCDD) and the heptachlorofurans (HpCDF) are also abundant congeners. Table 1 gives the concentrations of specific heptachloro isomers. We note that 1,2,3,4,6,7,8-HpCDD constitutes about 55 percent of its congener class in all three sections. There is a considerable decrease in concentration of all PCDD and PCDF between 6 and 8 cm deep in the core. This change is a result of the "1940 horizon" (7).

If PCDD and PCDF travel through the atmosphere, then these compounds should be present in the atmosphere (especially on airborne particulates) at locations which are remote from Siskiwit Lake. We analyzed air particulate samples from St. Louis, Missouri, and Washington, D.C., which are available from the National Bureau of Standards (standard reference materials 1648 and 1649, respectively) (Table 1). Although it is not yet possible to correlate the absolute PCDD or PCDF concentrations on particulates with those in sediments (be-

cause of dilution by mineral grains), the correlation of the relative abundances is very good. For example, OCDD is by far the most abundant compound in both the airborne particulate samples and in the sediment sample. The heptachlorodioxins and furans also predominate in all samples. In addition, the 1,2,3,4,6,7,8-HpCDD isomer is about 55 percent of its congener class, just as it was in the sediments. The ten correlation coefficients in the correlation coefficient matrix are always greater than 0.997, which is statistically significant at the 1 percent level.

Because of these similarities and because of the location of Siskiwit Lake, we conclude that the dioxins and furans in the Siskiwit Lake sediment arrived there by atmospheric transport. Other anthropogenic pollutants also reach Siskiwit Lake by atmospheric transport. Polycyclic aromatic hydrocarbons, known to be associated with combustion particulates and transported in the atmosphere, have been found in Siskiwit Lake sediments (8). Swain (9) reported that polychlorinated biphenyls, now recognized to be transported in the vapor phase through the atmosphere, were found in water, trout, and snow samples from Siskiwit Lake.

These results suggest that PCDD and PCDF are ubiquitous environmental contaminants that are transported through the atmosphere much in the same way as pesticides and certain heavy metals. Unlike the latter two substances, however, PCDD and PCDF have never been intentionally produced. How, then, did they get in the atmosphere? We can certainly rule out natural combustion (for example, forest fires). The historical record of dioxin and furan deposition is preserved in sediments (7), and this record shows that dioxins and furans were virtually absent from sediments until about 1940. Clearly, this record is inconsistent with natural combustion. We can also rule out direct atmospheric discharges such as a Seveso-type explosion. No such event has ever been reported in the United States. In addition, such an event would probably release large quantities of tetrachlorodioxins, compounds that were not abundant in the sediment studied. Although we cannot completely rule out chronic, low-level atmospheric releases from chlorophenol manufacturing, we believe them to be slight (10).

The most significant source of PCDD

and PCDF to the atmosphere is the combustion of wastes that contain chlorinated compounds. These wastes can be domestic trash or chemical refuse. For example, particulates from a midwestern municipal trash incinerator contained 440 parts per billion (ppb) of OCDD and 310 ppb of HpCDD's (7), and particulates from a chemical waste incinerator in Midland, Michigan, had 260,000 ppb of OCDD and 170,000 ppb of HpCDD's (11). These high concentrations suggest that the combustion of domestic and chemical waste, which is extensive in the Great Lakes' basin, is the major source of dioxins and furans in the atmosphere.

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10. We have found fluxes of PCDD and PCDF to Great Lakes sediments to be approximately $0.1 \text{ ng cm}^{-2} \text{ year}^{-1}$. The area of the sedimenting zones of the Great Lakes basin is about $2.4 \times 10^{15} \text{ cm}^2$ (12). Thus, we calculate a total load rate of dioxins and furans to the Great Lakes of 240 kg per year. The total U.S. production of pentachlorophenol in 1976 was $22 \times 10^6 \text{ kg}$ (13). If 0.1 percent of the pentachlorophenol produced enters the atmosphere (13) and the concentration of dioxins and furans in pentachlorophenol is 130 parts per million (14), one would expect a total input of PCDD and PCDF into the U.S. atmosphere of 2.9 kg per year. This is small compared to the sediment load rate of 240 kg per year. Therefore, atmospheric releases from chlorophenol manufacturing cannot account for the levels of dioxins and furans we find in the Great Lakes.
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