The Historical Record of PCDDs, PCDFs, PAHs, PCBs, and Lead in Green Lake, New York - 1860 to 1990

Smith, R.M., O'Keefe, P.W., Hilker, D.R., Bush, B., Connor, S., Donnelly, R., Storm, R., Liddle, M.
New York State Department of Health, Wadsworth Center for Laboratories and Research, Empire State Plaza, P.O. Box 509, Albany, NY 12201-0509, USA

INTRODUCTION

We reported preliminary data on PCDD/F in Green Lake sediments at Dioxin '91. In the present study, we update that information.

Green Lake is a small lake located approximately 15 km east of Syracuse. It has been the subject of numerous physical, chemical and biological studies[1]. Located in a rural setting, there are no industries, motorboats or known sources of local contamination. Each summer it precipitates a relatively constant amount of $CaCO_3$ (2 mm) resulting in a stratified, compact, sediment. There is little or no mixing between sediment layers because the lake is deep and the sediment is anaerobic year round with few organisms, making it ideal for our purposes.

Our main interest is the PCDDs and PCDFs. They have been reported in air and sediment samples from many areas of the world although few studies of the historical record have been done. We have reported the levels of PCDDs and PCDFs in air samples from urban areas and also in sediment samples from several New York lakes[2,3].

Our objectives were: 1) to study the deposition of PCDDs and PCDFs in Green Lake sediments to see what changes have occurred since the beginning of the industrial era; 2) to obtain an accurate record of PCDD/F deposition for the years near present; 3) to study the deposition of related organic pollutants; 4) to obtain the record of lead as an automotive indicator and 5) to see if there were changes in the isomer/homolog patterns with depth of sediment.

EXPERIMENTAL

Sampling Core samples (30-45 cm long) were collected at 200 ft depth with a gravity corer. Following partial drying and removal of the outer surface, each annual varve layer was cut away using a stainless steel blade, then dried in a desiccator at 25°C. Layers were combined to represent 2 to 8 years. Sections were dated by layer counting, ^{137}Cs counting, and sedimentation rates.

Analytical Methods One to three grams of dried sediment was spiked with ten ^{13}C-labeled PCDD/Fs. Samples were then Soxhlet extracted for 16 h with benzene. PAHs were analyzed, with no cleanup, by SIM GC/LRMS. PCDD/F extracts were purified with: 1) Cu, H_2SO_4, KSil, Sil gel; 2) acid alumina; 3) AX21 carbon and 4) Sil/2OH Bondesil prior to SIM DB5 GC/HRMS. PCB extracts were purified with columns 1,2,Hg^0 and Florisil prior to GC/EC. Dry sediment was digested with HNO_3 and analyzed for Pb by graphite furnace AA.

RESULTS AND DISCUSSION

Prior to 1900, the PCDD and PCDF concentrations in Green Lake sediments were at or below 10 pg/g (Figure 1). Little change is seen until the mid-1930's where we see a dramatic increase in both PCDDs and PCDFs similar to that reported for Great Lakes sediment[4], Swiss lake sediments[5], and British archived soils[6]. PCDD/F concentrations increase through the 1940's and 50's, reaching a sharp peak in the 1960's when sediment concentrations reached a maximum of 1545 pg/g. The concentrations of these compounds then decline rapidly to the present (1986-90) when the total concentrations of PCDD/F were measured at 750 pg/g. Thus, if sediment is an accurate representation of atmospheric concentrations, the PCDD/F concentrations in air have dropped to levels that existed between 1940 to 1960. Presumably, this reduction is the result of the clean air legislation enacted since the 1970's.

From our sediment data, we were able to calculate the corresponding atmospheric deposition rates for any given year. The deposition rate for our most recent sediment (1986-90) corresponds to 32.6 pg/cm^2/yr total PCDD and 4.9 for PCDF. This is about half of that which occurred during the peak years. (Siskiwit Lake = 22 pg/cm^2/yr for PCDD and 1.5 for PCDF.[7])

The homolog distribution patterns for PCDD/F were found to change throughout the length of a core. Since about 1970, we see a constant pattern predominated by OCDD (Figure 2). Prior to that, however, OCDD predominates but the lower chlorinated congeners were relatively more abundant.

PAHs (Figure 3), PCBs and Lead each had their own characteristic curve of deposition vs time. All were observed to increase rapidly in concentration reaching a maximum between 1960 and 1980, and declining thereafter.

CONCLUSIONS

The changes in concentrations of the above compounds reflected in the sediment core profile seems to be consistent with what we would expect from increased combustion, energy use, and pollution control legislation in the twentieth century. We find that the annual atmospheric deposition of these compounds is presently decreasing in the Syracuse area.

1 Ludlam SD. *Limnol and Oceanog* **1969**; 14:848-857.
2 Smith RM, O'Keefe PW, Aldous KM, Valente H, Connor SP, Donnelly RJ. *Environ Sci Technol* **1990**; 24:1502-1506.
3 O'Keefe PW, Smith RM, Connor S, Aldous K, Valente H, Donnelly R. *Chemosphere* **1992**; Dioxin '90 Short Papers.
4 Czuczwa JM, Hites RA. *Environ Sci Technol* **1984**; 18:444-450.
5 Czuczwa JM, Niessen F, Hites R. *Chemosphere* **1985**; 14:1175-1179.
6 Kjeller L-O, Jones KC, Johnston AE, Rappe C. *Chemosphere* **1991**; 25: 1619-1627.
7 Czuczwa JM, McVeety BD, Hites RA. *Science* **1984**; 226:568-569.

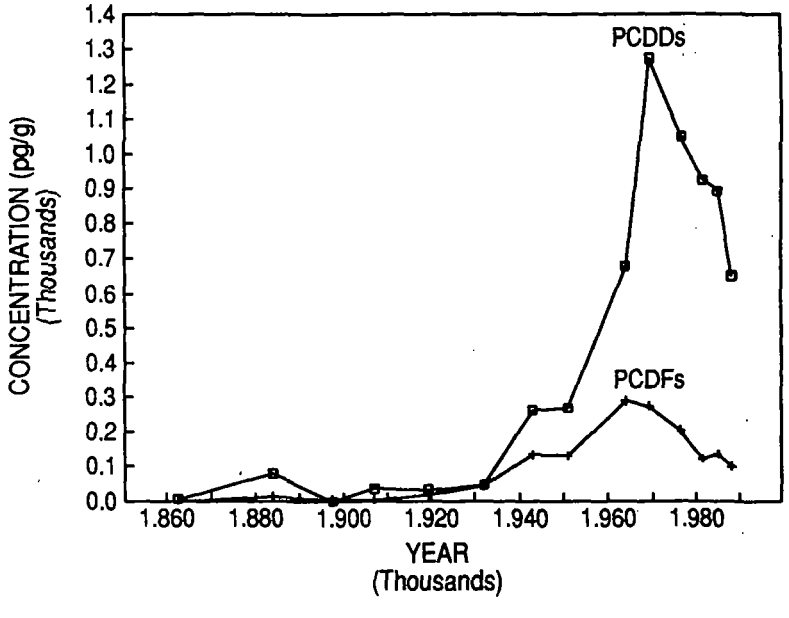

Figure 1: Historical Record of PCDDs and PCDFs

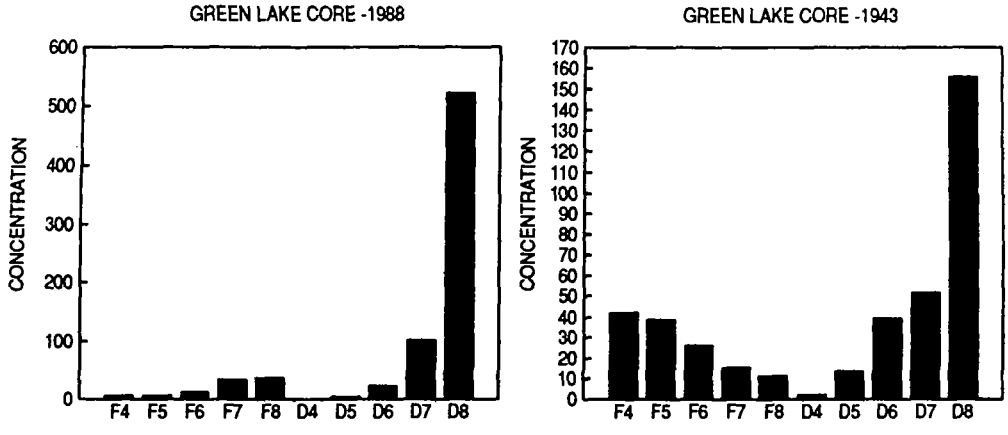

Figure 2: Homolog Distribution Patterns for PCDFs and PCDDs

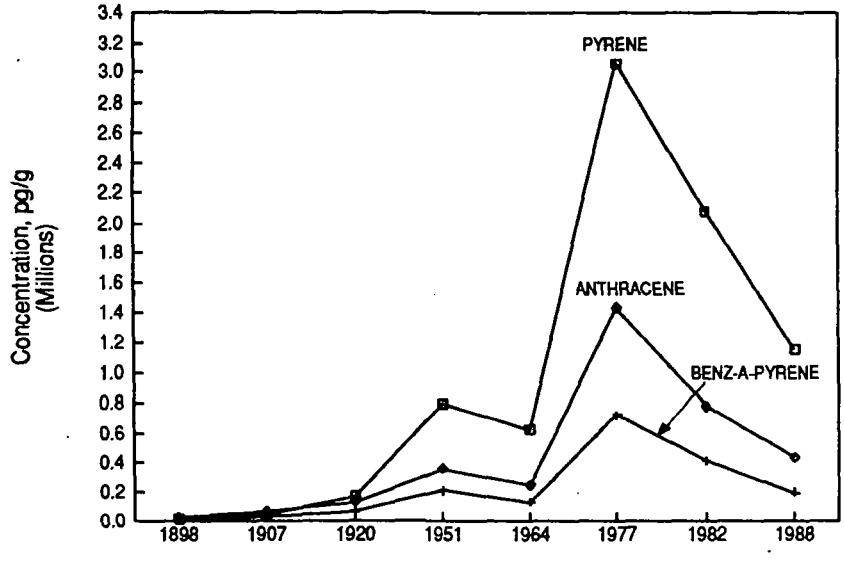

Figure 3: Historical Record of PAHs