PCDD/Fs in Soil and Sediment from the Baikal Region

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Introduction

In a previous investigation it was found that biota from Lake Baikal contain elevated levels of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (1). The purpose of this study was to use soil samples from around Lake Baikal and bottom sediment samples from Lake Baikal's shelf zone to evaluate the extent to which atmospheric deposition has contributed to the contamination of the lake.

Experimental Methods.

Soil samples were collected at 34 sites around Lake Baikal, in the remote area to the northeast of Lake Baikal, and in the industrial region Irkutsk Oblast, which extends from the southern end of Lake Baikal towards the northwest (see Figure 1). Whenever possible sites were chosen that were neither forested nor on a flood plain and where the soil was undisturbed. The samples were taken with a 5 cm corer to a depth of 25 cm. Bottom sediment was collected from several sites in Lake Baikal with a scoop to depths of up to 10 cm. The samples were stored in glass jars for transport to the laboratory in Irkutsk where they were dried for one week at room temperature. They were then frozen in glass jars before being transported to the University of Bayreuth. Here they were extracted for 16 h in n-hexane/acetone (1:1), cleaned up using a mixed silica gel column and an alox column, and analysed using HRGC/HRMS at a mass resolution of ~10,000. The homologue sums and the 2,3,7,8-substituted congeners were quantified. The toxicity equivalents (TEQs) were calculated using the NATO-CCMS I-TEFs.

Results and Discussion

The soil concentrations were normalized to the ground area sampled. Since the PCDD/Fs are generally retained in soil close to the surface and in most cases the core included all of the organic soil horizons, these area based concentrations give an estimate of the total amount of PCDD/F beneath a certain piece of ground. If the PCDD/Fs have originated primarily from atmospheric deposition, then the differences in area based concentrations reflect differences in total atmospheric deposition.

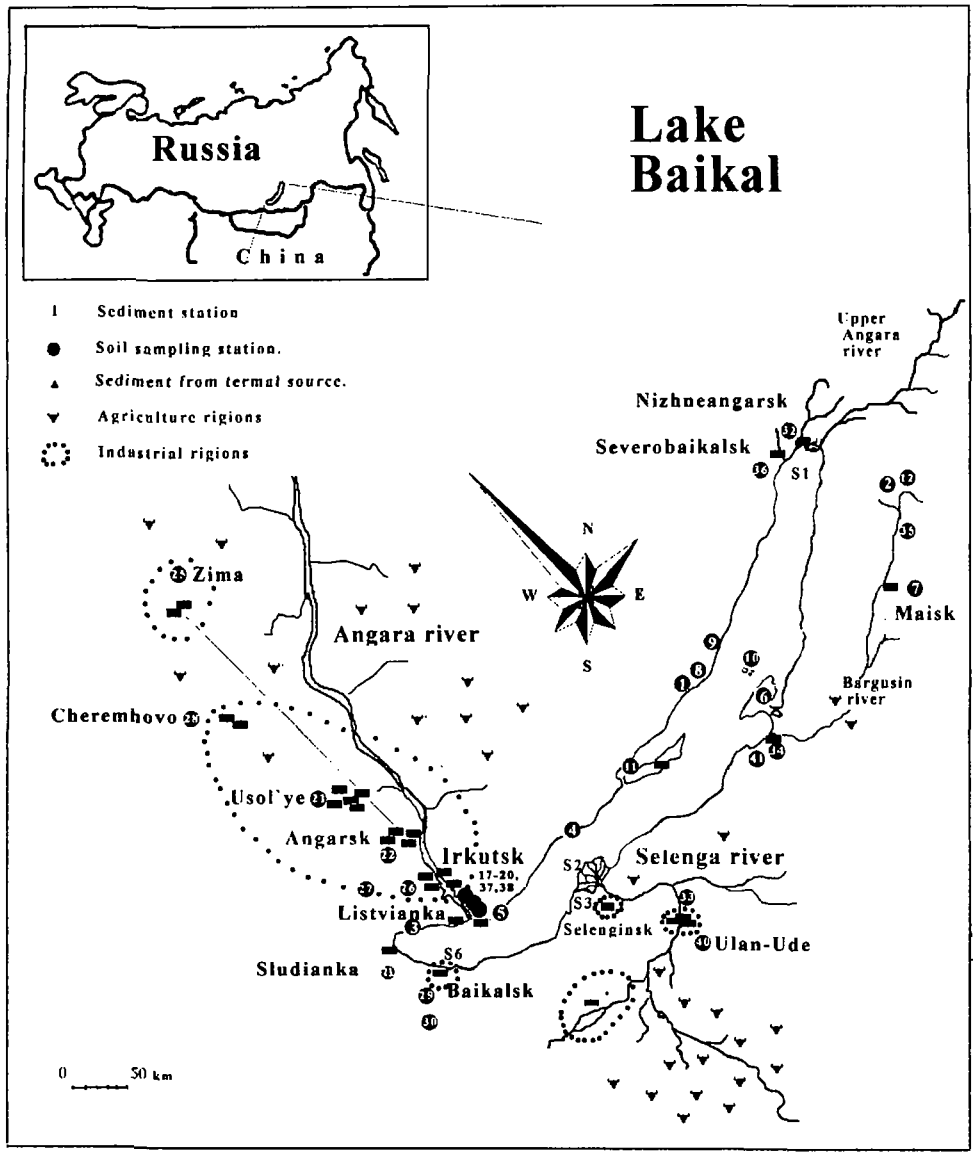

Figure 1: Map of Lake Baikal showing the sampling sites

The area based soil concentrations ranged over three orders of magnitude, from 0.22-0.75 pg TEQ/$(cm)^2$ (0.022-0.10 pg TEQ/g dry weight) in sparcely inhabited places (the areas between

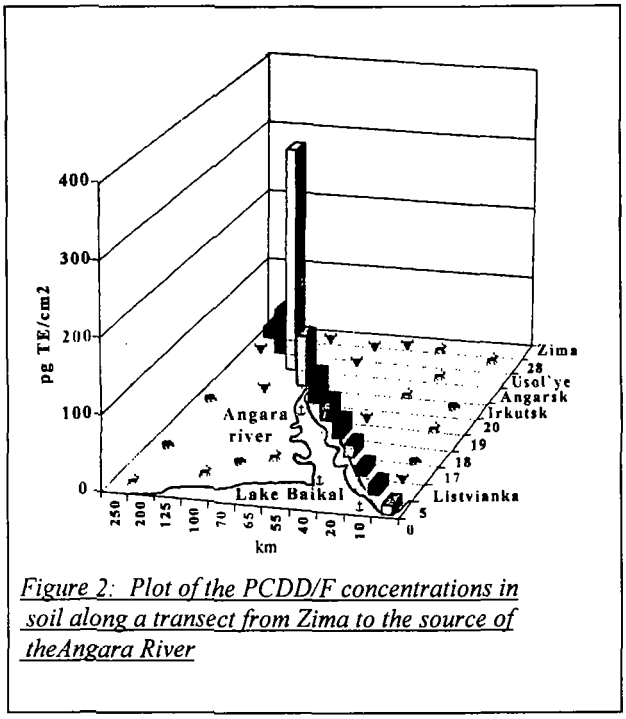

Figure 2: Plot of the PCDD/F concentrations in soil along a transect from Zima to the source of theAngara River

the mouths of the river Barguzine and the town of Severobaikalsk - see Fig. 1) to a maximum of 312 pg TEQ/(cm)^2 (40 pg TEQ/g dry weight) in the heavily industrialised city of Usol'ye to the west of Lake Baikal.

There was a clear spacial trend in the soil concentrations. From the maximum at Usol'ye the concentrations decreased moving up the Angara River valley towards Lake Baikal (the predominant wind direction). The upwind sites towards Zima also showed lower concentrations than in Usol'ye (see Fig. 2). This suggests that there is or was a PCDD/F source close to Usol'ye that has impacted much of the Lake Baikal region.

The congener pattern found in the soil samples indicates the possible nature of this source. The ratio of 1,2,3,4,7,8-Cl_6DF to 2,3,4,6,7,8-Cl_6DF in the Usol'ye soil sample was 13:1. This ratio is typically of the order of 2:1 in combustion related samples and in environmental samples where combustion processes are believed to have been the primary source of PCDD/F contamination. A high ratio of these two congeners such as found here is a marker for PCDD/Fs from technical PCB. The soil sample in Usol'ye showed other characteristics of a PCB source including high levels of the lower chlorinated PCDFs compared to the lower chlorinated PCDDs (see Fig. 3). However, high ratios of the two Cl_6DF isomers have also been reported for industrial/utility coal combustors (2), and, given the wide range of industrial activity in Usol'ye, other sources cannot be ruled out.

Although the concentrations decreased by three orders of magnitude moving downwind from Usol'ye, this characteristic ratio of the two Cl_6DF congeners was in the range of 10 or more in almost all of the soil samples. This indicates that this source has made a dominant contribution to the atmospheric deposition of the lower chlorinated PCDFs throughout this region.

The sediment samples from the shelf zone did not show high concentrations: 0.03 pg TEQ/g in the northern part of Lake Baikal and 0.05 pg TEQ/g in the Selenga delta. One of the tributaries of the Selenga River showed higher levels of up to 1 pg TEQ/g, and sediment collected close to the discharge of waste water from the Baikalsk pulp and paper mill contained 7.7 pg TEQ/g.

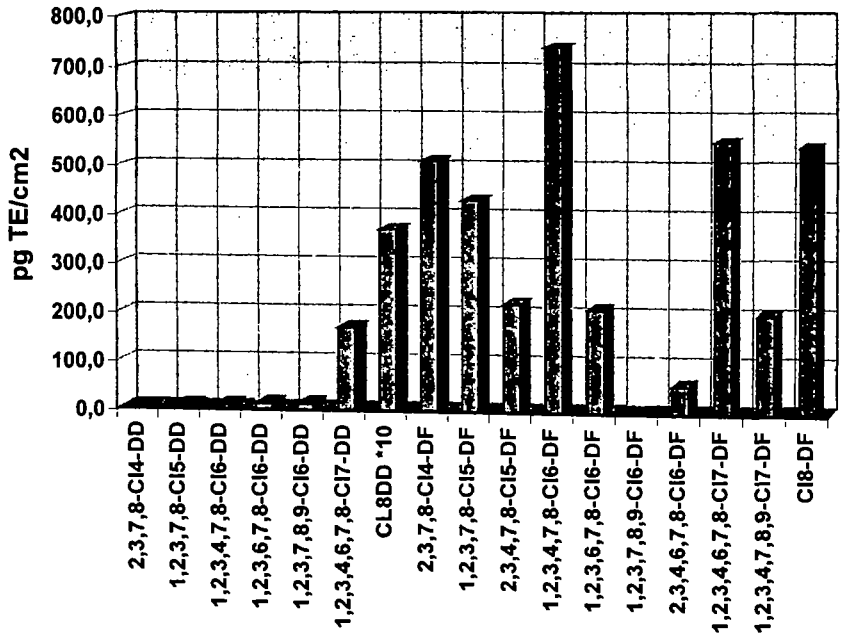

Figure 3: Congener profile for the soil sample from Usol'ye (1,2,3,7,8,9-Cl_6DF was not analysed)

The elevated soil concentrations of 12-14 pg TEQ/$(cm)^2$ found at the source of the Angara River on the shores of Lake Baikal indicate that the PCDD/F source in Usol'ye has resulted in atmospheric deposition of PCDD/Fs to Lake Baikal well above regional background levels. However, more work is needed to clarify the contribution of other potential sources to the lake such as the pulp and paper mills, in particular for the lower chlorinated PCDDs that account for most of the TEQs present in Baikal seals (1).

Acknowledgments

We thank the NGO Baikal Wave and in particular Jennifer Satton for their support in conducting this work, the rangers in Pribaikal and Zabaikal National Parks, Dgergihsky and Barguzinsky Reserves for their support in sampling, and Stefan Will for his assistance in analysing the samples.

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