to estimates of its solar system abundance based on nuclear systematics (*12*, *13*). This overabundance in C1 chondrites is unique because all other volatile elements are present in the predicted amounts.

We have compared the mercury content of our sample to both the observed (*12*) and predicted (*13*) mercury concentrations in C1 meteorites (Table 1 and Fig. 1). For the predicted concentration, 0.3 ppm based on nuclear systematics, our sample is enriched by about a factor of 400 (by 8500 when the data are normalized to nickel). This would make mercury the second most enriched element, exceeded only by antimony. Thus, if C1 meteorites contain only 1 part in 400 (or 1 part in 8500 excluding carbon) of this material, inhomogeneously distributed, this would account for both the excess abundance and the peculiar distribution of mercury. Somewhat smaller amounts of this element in other chondritic material could equally well account for its anomalous abundance there. Since this component is so enriched in mercury, only a small amount is required to account for the total amount of mercury present. At these low concentrations, enrichments or inhomogeneous distributions of only the most strongly enriched elements would be apparent. Interestingly, silver and bromine display considerable variations in C1 meteorites although the same pattern is not exhibited by zinc and antimony (*14*).

If the volatile-rich component present in Abee as well as other meteorites is a primary late condensate from the solar nebula, then it would provide valuable information on the cooling of the solar nebula. Fortunately, the primary nature of this material is not beyond verification. The observed overabundances of chlorine and bromine require that other halogens also be overabundant. The identification of an extinct radionuclide (17×10^6-year ^{129}I) in this material would not only establish the antiquity of this component but also provide chronometric information on the time scale associated with the cooling of the solar nebula. The primary nature of this material would also indicate that efficient accretion of dust and not the dissipation of gas terminated the meteorite parent-body formation.

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Tetrachlorodibenzo-*p*-Dioxin Quantitation in Stack-Collected Coal Fly Ash

Abstract. Gas chromatography–high resolution mass spectrometry has been used to quantitate tetrachlorodibenzo-p-dioxin (TCDD) in fly ash collected from the stack of a typical commercial coal-fired power plant. No TCDD was detected in this fly ash, but minute traces may be present below the detection limit of 1.2 parts per trillion (by weight). This finding indicates that this type of fossil-fueled power plant is not a large source of this compound in environmental samples, in contrast to the conclusions presented in a recent industrial report.*

The projected increase in the combustion of coal for the generation of electric power poses potential adverse environmental and human health problems because of the release of fly ash into the atmosphere. It has been estimated that during 1974 2.4×10^9 kg of fly ash were emitted in the United States as a result of the burning of coal (*1*).

In a recent industrial report (*2*, p. 3) it was concluded that "refuse incinerators and fossil-fueled powerhouses are sources of both airborne and waterborne particulates which contain chlorinated dioxins." The conclusions of this report have been extensively discussed in the popular scientific press (*3*).

Chlorinated dibenzo-*p*-dioxins, particularly the 2,3,7,8-isomer of tetrachlorodibenzo-*p*-dioxin (TCDD), are well recognized as potential hazards to human health. It has been shown that 2,3,7,8-TCDD is fetotoxic in several species, teratogenic in mice, and carcinogenic in rats (*4*) and is toxic at exceedingly low levels in primates (*5*).

The presence of highly toxic materials such as TCDD in airborne particles, if coupled with the potential widespread aerial distribution of particles emitted from power plants, would pose serious hazards to the health of the general public in industrialized nations.

The problem is quantitative and centers on the rate of emission of TCDD on airborne particles. In the industrial study (*2*), the concentration of TCDD was determined on particles collected from the stack of a chemical plant powerhouse burning fuel oil and coal. Various TCDD isomers were found at a concentration of 38 parts per billion (ppb), with a detection limit of 20 ppb; the 2,3,7,8-isomer was not detected at a detection limit of 10 ppb. Concentrations of 2, 4, and 24 ppb of hexa-, hepta-, and octachlorodibenzo-*p*-dioxins, respectively, were also found.

The industrial report includes extensive descriptions of modern analytical techniques that have been used to quantitate chlorinated dibenzo-*p*-dioxins from a variety of samples. These samples include a large number of combustion products, such as refuse incinerator emissions, gasoline-powered automobile exhausts, fireplace soot, charcoal grills, cigarette smoke, and particulate emissions from a chemical plant powerhouse. From these analytical data, it was concluded that measurable amounts of chlorinated dibenzo-*p*-dioxins can be found in the products from many types of combustion, including powerhouses that burn fossil fuels. In order to evaluate the extrapolation to other fossil-fueled power plants, we have quantitated TCDD in stack-collected fly ash from a typical commercial coal combustion facility.

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The fly ash was collected downstream from the electrostatic precipitator located in the smokestack breeching of a large modern power plant burning low-sulfur, high-ash coal (*6*). The particles were collected in four size fractions (F1 through F4) which have been extensively characterized in terms of their aerodynamic behavior (*7, 8*), morphology (*9, 10*), and elemental composition (*10, 11*). In addition, the cyclohexane-, saline-, and serum-soluble surface components of these fractions have been shown to be mutagenic in the Ames *Salmonella* bacterial assay (*1, 12*). The extraction, separation, and analysis for TCDD were undertaken on a 10-g sample of fly ash fraction F2, to which was added 5.50 ng of an internal standard, 2,3,7,8-TCDD fully labeled with the ^{37}Cl isotope (^{37}Cl$_4$-TCDD). Two procedural control samples were processed in parallel. One (sample 2) contained no fly ash but was spiked with 5.50 ng of ^{37}Cl$_4$-TCDD; the other control, an empty container (sample 3), contained neither fly ash nor the internal standard. The three samples were extracted with a mixture of hexane and acetone, and, after cleanup and fractionation procedures, the extracts were analyzed by packed column gas chromatography–high resolution mass spectrometry (*13*). The ions monitored had the elemental compositions $C_{12}H_4O_2{}^{37}Cl_4$ (mass-to-charge ratio m/z = 327.8848, the molecular ion for the internal standard, ^{37}Cl$_4$-TCDD) and $C_{12}H_4O_2{}^{35}Cl_3{}^{37}Cl$ (m/z = 321.8936, the most abundant molecular ion from TCDD having natural isotopic abundances and comprising 42 percent of the total molecular ion abundances).

The peak profiles averaged throughout the elution of TCDD (2,3,7,8-TCDD and other isomers that elute at the same time) from the gas chromatographic column are shown in Fig. 1. Figure 1A shows the profiles for 470 pg of the internal standard (left) and an authentic sample, 47 pg, of TCDD of natural isotopic abundance (right). Figure 1, B and C, show the profiles obtained from two analyses of sample 1, the fly ash extract and the internal standard. A small quantity of an ion of composition $C_{12}H_3{}^{35}Cl_5$ (m/z = 321.8677) could be detected at high gain settings (Fig. 1C) and was assigned as an ion derived from a polychlorinated biphenyl (PCB) which may originate from the solvents (levels of this magnitude and greater have frequently been observed in solvent blanks). However, no TCDD with natural isotopic abundance could be detected; using a signal-to-noise criterion of 2.5 (*13*), the detection limit was calculated to be 0.6 parts per trillion (ppt) of F2 fly ash. From relative response factors calculated from calibration curves, the recovery of the internal standard was calculated to be 75 ± 10 percent from each of two analyses (Fig. 1, B and C). The peak profiles obtained in the same manner for sample 2 (internal standard only) are shown in Fig. 1D; the recovery of the internal standard was calculated to be 80 ± 10 percent, and no TCDD of natural isotopic abundance was detected. The peak profiles for sample 3 (no fly ash, no internal standard; profiles not shown in Fig. 1) obtained under similar conditions showed neither ^{37}Cl$_4$-TCDD nor unlabeled TCDD. These data demonstrate that TCDD, if present in fraction F2 of coal fly ash, comprises less than 0.6 ppt (by weight) of this size fraction.

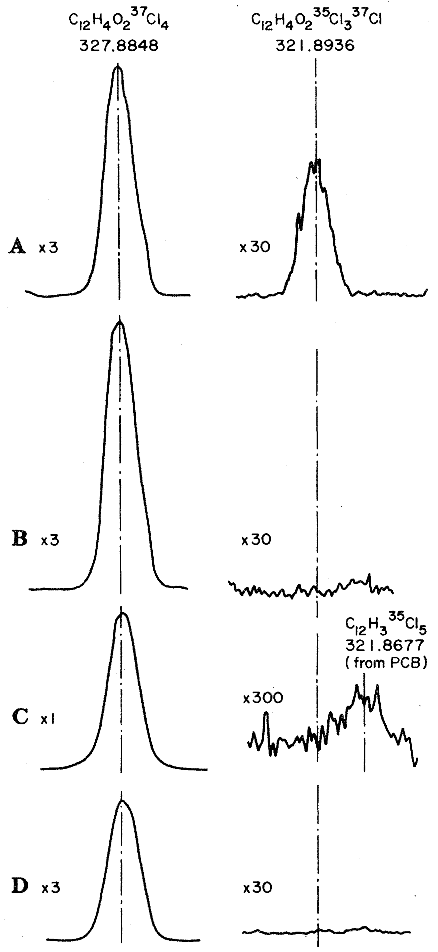

Fig. 1. High resolution mass spectral peak profiles from the analysis of TCDD in fraction F2 of coal fly ash. Shown on the left are the signals for the internal standard, ^{37}Cl$_4$-TCDD ($C_{12}H_4O_2{}^{37}Cl_4$; m/z = 327.8848). On the right are the signals for the elemental composition $C_{12}H_4O_2{}^{35}Cl_3{}^{37}Cl$, which corresponds to the most abundant molecular ion from TCDD having natural isotopic abundances (m/z = 321.8936). (A) Profile from 470 pg of ^{37}Cl$_4$-TCDD (left) and 47 pg of an authentic standard of TCDD. The relative signal averager attenuation is 0.5 with amplifier gains of ×3 and ×30. (B) Profiles from 32 percent of the final extract of sample 1 (fraction F2 fly ash and internal standard). The relative signal averager attenuation is 1.0 with amplifier gains of ×3 and ×30. (C) Profiles from 28 percent of the final extract of sample 1. The relative signal averager attenuation is 0.5 with amplifier gains of ×1 and ×300. (D) Profiles from 30 percent of the final extract of sample 2 (procedural control including the internal standard). The relative signal averager attenuation is 2.0 with amplifier gains of ×3 and ×30.

Having determined this upper limit for the F2 size fraction of coal fly ash, we can now calculate the upper concentration limit for TCDD on the total emitted particles and then estimate a maximum daily output of TCDD for a typical commercial coal-fired power plant. In order to extrapolate the TCDD concentration for the F2 fraction to that for an isokinetic (representative) sample of the same fly ash, it is necessary to assume that the concentration of TCDD on fly ash particles is proportional to the surface area of these particles (*14*). On the basis of surface area measurements for the four size fractions and particle size analyses for an isokinetic sample (*15*) of the same fly ash collected during the 30-day sampling period (*12*), we have calculated that the surface area of an isokinetic sample is approximately twice the surface area of the F2 fraction used in this study. Therefore, the total concentration of TCDD, if emitted on coal fly ash particles, is less than 2 × 0.6 = 1.2 ppt by weight of fly ash.

A representative 750-MW (electric) power plant burns about 200 tons (1 ton = 909 kg) of coal per hour, of which about 10 percent is fly ash. With an electrostatic precipitator (ESP) as the control device and assuming 95 percent efficiency of collection, the total released fly ash can be calculated to be 24 ton/day. From our analyses for TCDD, the upper limit of 1.2 ppt thus corresponds to an upper limit of 26 μg of TCDD per day emitted on all fly ash particles.

The chlorine content of the input coal used in the power plant from which the four fractions of the fly ash were derived has been determined to be 48 ± 17 μg/g (*8*) or about 50 parts per million (ppm); this corresponds to a total chlorine input of 0.24 ton/day or 218 kg/day. The efficiency of conversion of chlorine in the input coal to TCDD on emitted particles is, therefore, extremely low. The above calculations will, of course, change in proportion to the rate of coal combustion, the percentages of ash and chlorine in the input coal, the type and efficiency of the control devices, and the surface area properties of the released particles.

The detection limit of TCDD found in this study is lower by at least a factor of

32,000 than that found in the emissions from the industrial powerhouse burning coal and fuel oil. One explanation for the large difference in TCDD concentration may be the nature of the fuel sources (including the total chlorine content). For the same reason, the findings of significant amounts of chlorinated dibenzo-*p*-dioxins in emissions from refuse and chemical waste incinerators (*2*, *16*) should not be used to infer that these compounds are also significant products of fossil-fueled power plants. In fact, we find that a commercial coal-fired power plant will emit less than 1 μg of TCDD per hour on fly ash particles from the combustion of 200 tons of coal. As this result is many times less than the amount found in the emissions from the chemical plant powerhouse, we believe it is invalid to extrapolate the latter result to the conclusion that ". . . fossil-fueled powerhouses are sources of both airborne and waterborne particulates which contain chlorinated dioxins."

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13. Sample 1 contained 10.022 g of fly ash; the internal standard was 22 μl of a 0.25 ng/μl solution of $^{37}\mathrm{Cl}_4$-TCDD in benzene. Each sample was extracted four times with 20 ml of a mixture of hexane and acetone (equal volumes) and then centrifuged, and the supernatants were filtered. The solvent extracts were washed with aqueous KOH, water, concentrated H_2SO_4, water, and aqueous Na_2CO_3; the resulting hexane solutions were dried with anhydrous Na_2CO_3, concentrated under a stream of N_2, and fractionated on alumina columns. The TCDD fractions were evaporated to dryness, dissolved in 60 μl of toluene, and sealed under vacuum in a glass tube until analyzed by gas chromatography–high resolution mass spectrometry (Perkin-Elmer Sigma II and Kratos MS-50). The gas chromatographic column (180 cm by 2 mm inside diameter, glass) contained 0.60 percent OV-17 + 0.40 percent Poly S-179 coated on 100 percent methyl silicone bonded to 80/100 mesh Chromosorb W-AW and was operated with a helium flow rate of 15 ml/min. The temperature was held at 250°C for 1.5 minutes and then increased linearly to 300°C at a rate of 10°C per minute. The entire effluent from the gas chromatographic column was admitted to the mass spectrometer ion source and ionized with 70-eV electrons. The source temperature was 250°C, the accelerating voltage 8 kV, and the mass spectral resolution 10,000 (10 percent valley definition). The 2,3,7,8-TCDD and other isomers that elute at the same time (between 3.3 and 4.4 minutes) were quantitated by dual ion monitoring using peak matching. One channel was centered at *m/z* 327.8848 ($^{37}\mathrm{Cl}_4$-TCDD, the internal standard) and the other at *m/z* 321.8936 (the most abundant molecular ion of TCDD having natural isotopic elemental abundances). The complete peak profiles were acquired by scanning at a frequency of 2 Hz, corresponding in each case to a mass range of 300 ppm (0.096 atomic mass unit). The output was accumulated with a signal averager (Nicolet model 1170), and the resulting signals were submitted to a three-point smoothing routine prior to printout (Fig. 1). The concentration of TCDD was calculated using the ratio of the intensities (maximum peak heights) at *m/z* 327.8848 and 321.8936; if no signal was observed, the detection limit was set at 2.5 times the noise amplitude [a 2.5 : 1 signal-to-noise criterion as described in (*2*)].
14. This assumption is consistent with the vapor condensation model proposed by D. F. S. Natusch [*Environ. Health Perspect.* **22**, 79 (1978)]. The model is substantiated by the measured concentrations of volatile trace elements [G. L. Fisher and C. E. Chrisp, in *Application of Short-term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures*, M. D. Waters, S. Nesnow, J. L. Huisingh, S. S. Sandhu, L. Claxton, Eds. (Publication EPA-600/9-78-027, Health Effects Research Laboratory, Environmental Protection Agency, Research Triangle Park, N.C., September 1978), p. 441] and by the relative mutagenic activities (*12*) that are enhanced for the smallest-sized particles because these are surface-associated parameters.
15. The measurements of surface area (in square meters per gram) for each of the fractions and the fractional weight contributions to an isokinetic sample were provided by A. R. Biermann (personal communication).
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Vertical Distribution and Isotopic Composition of Living Planktonic Foraminifera in the Western North Atlantic

Abstract. *Thirteen species of planktonic foraminifera collected with vertically stratified zooplankton tows in the slope water, Gulf Stream cold core ring, and northern Sargasso Sea show significant differences in their vertical distributions in the upper 200 meters of these different hydrographic regimes. Gulf Stream cold core rings may be responsible for a southern displacement of the faunal boundary associated with the Gulf Stream when reconstructed from the deep-sea sediment record. Oxygen isotope analyses of seven species reveal that nonspinose species (algal symbiont–barren) apparently calcify in oxygen isotope equilibrium, whereas spinose species usually calcify out of oxygen isotope equilibrium by approximately −0.3 to −0.4 per mil in* $\delta^{18}O$ *values. The isotope data indicate that foraminifera shells calcify in depth zones that are significantly narrower than the overall vertical distribution of a species would imply.*

The interpretation of species-specific differences in the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in the calcite ($CaCO_3$) shells of planktonic foraminifera samples from deep-sea cores is still a fundamental question in marine geology (*1*). The oxygen isotopic composition of calcite that is precipitated in equilibrium with seawater has been predicted theoretically and verified experimentally (*2*). Although there is a general consensus that planktonic foraminifera do not deposit their calcite shells in carbon isotopic equilibrium, conflicting evidence exists concerning equilibrium versus nonequilibrium precipitation of oxygen isotopes measured in living planktonic foraminifera (*3*).

Answers to questions concerning species-specific isotopic differences are further complicated when they are derived from individuals taken from Holocene core-top sediments, which are a composite of species whose abundances in the overlying water are seasonally and vertically distributed in unknown proportions. Although the surface (upper 1 m) distribution and seasonal succession of planktonic foraminifera at particular localities have been determined (*4*), very

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