dioxin emission factor for each source category is plotted against the chlorine content of the combusted material. The table shows that average dioxin emissions of combustion source categories tend to increase with the average chlorine content.

While a dependence on chlorine content might seem to be a foregone conclusion, there has in fact been doubt on this point since limited data, on test-burns at municipal waste incinerators, for example, have shown no correlation. There are, of course, many variables besides chlorine content, especially the operating conditions of the combustion system, and the application of pollution control technology. Figure 1 shows that favorable operating conditions (open symbols) can lower emissions by as much as two orders of magnitude. But under poorly controlled conditions (closed symbols), there is a clear dependence on chlorine content. Moreover, the relationship is more than proportional since the slope of the log-log plot is somewhere between one and two. Since dioxin molecules contain more than one chlorine atom, a higher order dependence is not unexpected.

The data in Figure 1 are too coarse grained to evaluate differences due to the chemical form of chlorine in the combusted material. In hospital waste, a large fraction of the chlorine may be in the form of polyvinyl chloride, and in transformer fires the chlorine is in the form of polychlorinated biphenyls (PCBs), while in municipal waste a significant fraction of the chlorine may be in the form of sodium chloride, as well as PVC plastics. The figure indicates that, by and large, dioxin emissions are roughly independent of the original form of the chlorine in the combusted material. According to the current understanding of dioxin formation, HCl is the chlorine source for dioxin formation in catalyzed reactions on fly ash, with a maximum at temperatures of about 400°C.[10-13] The HCl is formed during combustion as part of the breakdown process of chlorine containing molecules. Thus the amount of HCl formed might not depend strongly on the type of chlorine compound, although the degree of conversion of chloride salts to HCl is uncertain.

The relationship between chlorine content and dioxin emissions, demonstrated in Figure 1, provides a means to estimate how dioxin emissions are related to the presence of anthropogenic chlorinated compounds in materials that are burned. With municipal and hospital waste combustion being the largest dioxin sources that are affected by anthropogenic chlorinated organic materials (see Table 2), the relationship of total dioxin emissions to anthropogenic chlorinated compounds will depend primarily on how the emission factors for municipal and hospital waste combustion would change in the absence of chlorinated organic compounds. The next largest dioxin sources, forest and agricultural fires, and residential wood burning, are independent of the production of chlorinated organics, while the next largest sources, PCP production and dioxin emissions from copper recycling (attributed to the presence of chlorinated organics mixed in with the copper scrap), would be negligible in the absence of chlorinated organics.

4. DIOXIN EMISSION SOURCES

4.1 Consumer Waste Incineration

Municipal waste incineration: In 1989, about 20 million tons of municipal solid waste (MSW), 15% of the total, were incinerated in the US.[16]

The design of a municipal waste incinerator can significantly affect its dioxin emissions. The main types of incinerators are listed in Table 3, along with the amount of

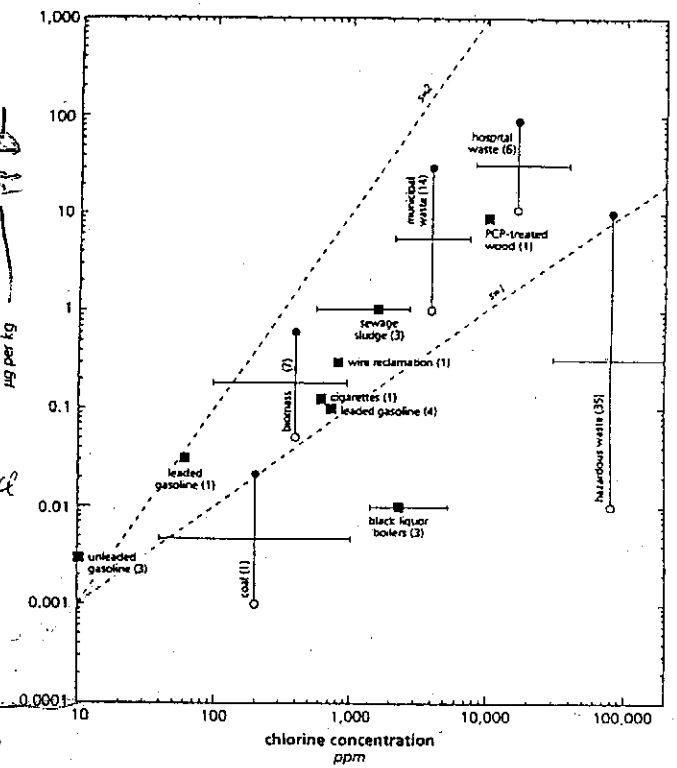

Figure 1. Average PCDD/PCDF emission factors for combustion processes, versus the average chlorine concentration of the combusted material (1989). Where information is available, poorly controlled combustion is indicated by a black dot, and well controlled combustion is indicated by a white dot. In all other cases, the black square indicates the average emission factor. The lines s = 1 and s = 2 have slopes of 1 and 2 respectively.

3. RELATIONSHIP OF DIOXIN EMISSIONS FROM COMBUSTION TO CHLORINE CONTENT

The details of the dioxin emission estimates will be given in section 4, but to show that the data from the different combustion source categories present a coherent and consistent picture of dioxin emissions, we begin with Figure 1, in which the average

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AN ESTIMATION OF DIOXIN EMISSIONS IN THE UNITED STATES

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Total annual US air emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans (PCDD/Fs) from all known sources are estimated to be about 400 kilograms as of 1989, almost entirely from combustion sources. Municipal solid waste incineration is the largest known source of PCDD/Fs, as of 1989. The next largest sources include hospital waste incineration, forest and agricultural fires, and residential wood burning. Anthropogenic emissions of PCDD/Fs are estimated to be an order of magnitude greater than emissions of PCDD/Fs from forest fires. Dioxin emissions are shown to generally increase with the chlorine content of the combusted material, in the absence of effective pollution control systems. Dioxin emissions from 1940 and 1970 are also estimated. The estimates are verified through analysis of the concentrations of dioxin in soil, air, and sediments.

KEY WORDS: Dioxin, furan, PCDD, PCDF, sources, emission inventory, mass balance, dioxin budget, chlorine

1. INTRODUCTION

Chlorinated dioxins and furans, a group of more- and less-toxic chlorinated compounds, are emitted from virtually all combustion processes, and are by-products of some chemical and industrial processes.[1] Increases in cancer incidence have been found among dioxin-exposed workers,[2,3] and effects on reproductive and immune systems of animals have broadened the concern beyond cancer. Controversy remains, however, as to what effects might be expected at the current exposures of the general population.

Public concern about dioxin is high, and fear of dioxin exposure has been focused on emissions from municipal and hazardous waste incinerators, which are known to have a potential for high dioxin emissions. But are these the main sources of dioxin? Are there additional, undiscovered sources of dioxin?

Previous studies, for Canada, the United States, Sweden, and Great Britain, have estimated dioxin emissions, and the latter three tried to verify the emission estimates by comparison with dioxin concentrations in the environment. They all found that the estimated emissions from known dioxin sources were about an order of magnitude less than that expected based on the amount of dioxin found in the environment.[4–6] Much more data is now available, and we have collected a more complete database than has been used in previous studies of dioxin emissions.

Using these data, we have made a new evaluation of dioxin emissions in the United States. We consider the following source categories: consumer waste combustion,

industrial waste combustion, biomass and fossil fuel combustion, and emissions fr dioxin-contaminated chemical products. Based on data from these sources, total curr dioxin emissions are estimated for the United States. This emissions database is also us to examine the effect of chlorine concentration on dioxin emissions from combusti processes.

To verify the estimate of total emissions, data on soil, sediment core, and concentrations of dioxin are compared to those expected from the emission estimat Because dioxin can have an environmental life-time of a decade or more in sor situations, the history of US dioxin emissions is estimated. The historical emissio estimate also provides insight into the causes of changing dioxin emissions, and preindustrial emissions of dioxin.

The data on environmental dioxin concentrations in air, soil and sediments are mutual constraining, in that air concentrations provide information on current emissions, sc concentrations provide information, as a function of the dioxin life-time, on total pa emissions, and sediment cores provide information on the quantity emitted in each year the time reflected in the core. Taken together, the estimates of emissions and loadings a consistent, within the error limits of the data, and do not support the hypothesis of maj unknown dioxin sources.

A recent US EPA study arrived at conclusions that are largely consistent with th analysis, although the details of the ranking of source categories differ somewhat Moreover, although the EPA study evaluates emissions with a "toxic equivalent weighting (TEQ), the total emission estimates are also consistent.

Not addressed here are dioxin emissions to water. Dioxins are emitted from pulp mill using chlorine bleach, and a number of other chemical processes. This represents a essentially separate pathway of dioxin emission and potential exposure than emissions t air and soil. Although in local ecosystems emissions to water can be significant preliminary estimates indicate that total US direct emissions to water are much less tha emissions to air and soil.

The definition used to quantify dioxin is total tetra- through octa- chlorinated dioxin and furans, abbreviated PCDD/F. This is the unit used in the US Clean Air Act for dioxi emissions from municipal waste incinerators. Emissions and emission factors are als given in terms of the I-TEF toxicity-weighted average.[10]

2. SUMMARY OF TOTAL ESTIMATED EMISSIONS

Dioxin emissions from combustion processes, responsible for the bulk of known dioxin emissions, can be highly variable, depending on the completeness of combustion, the combustion system and air pollution control equipment, and the material being burned. While temperatures, oxygen levels, and residence times in a well-operated combustion system are sufficient to destroy PCDD/Fs and their precursors, high emissions can result from poor combustion conditions such as pockets of gas with insufficient oxygen, or of low temperature pathways that allow some of the gases to escape complete combustion, and conditions that allow for the formation of dioxin in the post-combustion zone.

Nevertheless, the data presented in section 4 will show that dioxin emission factors from combustion of similar fuels, with broadly similar combustion systems and pollution control devices, typically vary by less than an order of magnitude. This holds true, for example, for hospital waste incinerators, sewage sludge incinerators, and industrial wood boilers. Thus, for most processes, dioxin emissions can be categorized by the combustion