Relation of chlorine, copper and sulphur to dioxin emission factors

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Abstract

Dioxin emission factors for different combustion categories range over five orders of magnitude. Both chlorine (Cl_2) and transition metals, including copper (Cu) have been suggested to promote the formation of dioxin in incinerators, and sulphur (S) has been suggested to inhibit dioxin formation. We show that dioxin (PCDD and PCDF) emission factors from 17 different combustion categories are approximately linearly correlated with the average copper or chlorine content of the combusted material, and inverse linearly correlated with the average sulphur content of the material. Copper and chlorine are correlated and, thus cannot be distinguished. The analysis suggests that the wide range of dioxin emission factors could be explained by the content of sulphur and transition metals or chlorine in combusted materials.
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1. Introduction

The amount of dioxin emitted by combustion of different types of materials ranges over five orders of magnitude, from 0.03 ng/kg I-TEQ for Kraft paper recovery boilers to nearly 2000 ng/kg I-TEQ for uncontrolled medical waste incinerators [1]. Some of this range can be explained by the details of the combustion systems, and pollution control. But these factors do not explain the entire five orders of magnitude range. For example, combustion of wood produces about two orders of magnitude less dioxin than combustion of the same amount of municipal solid waste, even though municipal waste combustion typically is better controlled than wood combustion.

Here, we investigate the extent to which dioxin emissions could be explained by the elemental composition of the material combusted, through examination of the correlation with chlorine (Cl), copper (Cu), and sulphur (S).

Because dioxin contains chlorine, it is clear that a source of chlorine is needed to produce dioxin. Both organic chlorine, such as polyvinyl chloride (PVC), and inorganic chlorine, such as sodium chloride (NaCl), have been shown to be chlorine sources for the production of dioxin in combustion processes [2,3].

But what is not clear is the extent to which changes in the amount of chlorine will affect the amount of dioxin produced. A number of laboratory and combustor-scale studies have shown that the addition of chlorine compounds increases the production of dioxin [3,4]. In 1995, one of us published a paper showing that average dioxin emission factors are correlated with the average chlorine content of the combusted material [5]. At about the same time, Rigo et al. published an analysis concluding that there is no statistical relationship between dioxin emissions and feed stream chlorine content [6,7].

Other elements are also thought to influence dioxin production. A number of studies have suggested that the principal mechanism of dioxin formation is solid-phase formation catalysed by copper on fly ash surfaces through a Deacon-type process.

$$Cu + 1/2\,O_2 = CuO$$
$$CuO + 2\,HCl = Cu + H_2O + Cl_2 \qquad (1)$$
$$2\,HCl + 1/2\,O_2 = H_2O + Cl_2$$
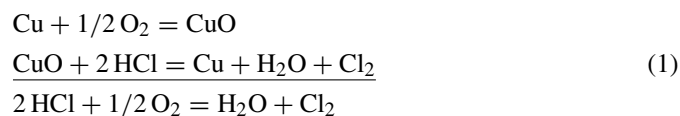
The Cl_2 produced subsequently chlorinates the aromatic ring structures through substitution reactions. Other transition

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metals, especially iron, have been suggested to play a similar catalytic role [8–10].

In addition, sulphur has been identified as an inhibitor of dioxin formation. The addition of relatively high sulphur coal reduces dioxin emissions from the combustion of municipal waste, refuse-derived fuel, and natural gas [11,12]. Several mechanisms have been proposed to explain this inhibitory effect. Sulphur may deplete Cl_2 levels through the gas-phase reaction.

$$Cl_2 + SO_2 + H_2O = 2HCl + SO_3 \qquad (2)$$
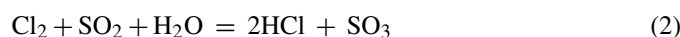
Sulphur may also hinder the copper-catalyst surface already existing on fly ash particles.

$$CuO + SO_2 + 1/2O_2 = CuSO_4 \qquad (3)$$

2. Data

2.1. Dioxin emission factors

Numerous publications provide information on the dioxin emission factors. To make our analysis transparent, we base our analysis entirely on the dioxin emission factors developed by the US EPA in its US dioxin emissions inventory [1]. This data set is used because the emission factors have been peer-reviewed several times, and are based on data from a broad range of sources. These data are largely consistent with emission factors reported by the United Nations Environment Programme for other coun-

tries [13]. Table 1 shows the US EPA's dioxin emission factors for the years 1987 and 2000. For some source categories, the emission factors are the same for both years. But for municipal solid waste, and some other categories, the emission factors are generally lower for 2000 because of improvements in combustion systems, and emission controls. In the calculations that follow, the 1987 values will be used because they better represent typical emissions in the absence of state-of-the-art pollution control.

The US EPA did not quantitatively define the uncertainties in the emission factors, and instead assigned qualitative confidence ratings of medium or low to the emission factors (none were assigned high confidence). These assignments are shown in Table 1. In the figures and in the analysis, those emission factors with medium confidence are assigned an uncertainty of a factor of four, and those emission factors with low confidence ratings are assigned an uncertainty of an order of magnitude. These assignments do affect the statistical analysis, and this issue will be discussed in Section 3.

The term "dioxin" as used here, refers to the tetra-through octa-chlorinated dibenzo-*p*-dioxins and -furans. The emission factors are expressed as a toxicity-weighted sum of the tetra- through octa-chlorinated dioxins and furans, denoted as TEQ. The specific toxicity-weighting schemed used is the international scheme adopted by the US EPA in 1989, denoted I-TEQ. The nomenclature also uses subscripts to indicate which family of compounds has been included in the emission factor calculations. The subscript

Table 1
US EPA estimates of dioxin emission factors (data from [1])

Emission source	Dioxin emission factor (ng/kg I-TEQ$_{DF}$)		Confidence rating
	2000	1987	
Waste incineration			
Municipal waste incineration	2.82	570	m
Hazardous waste incineration	2.12	3.8	m
Boilers/industrial furnaces	1.21	0.64	l
Medical waste/pathol incineration	630	1700	l
Sewage sludge incineration	6.65	6.9	m
Tire combustion	0.28	0.28	l
Backyard barrel burning	72.8	72.8	l
Power/energy generation			
Vehicle fuel combustion[a]			
Leaded (45 pg/km driven)	0.56	0.56	l
Unleaded (1.5 pg/km driven)	0.02	0.2	l
Diesel (172 pg/km driven)	1.2	1.2	l
Wood combustion			
Residential	0.5	2	l
Industrial	0.56–13.2	0.56–13.2	m
Coal combustion - industrial/utility	0.079	0.079	m
Oil combustion - industrial/utility	0.2	0.2	l
Other high temperature sources			
Cement kilns burning hazardous waste	1.44	1–29	l
Cement kilns not burning hazardous waste	0.27	0.27	l
Cigarette combustion (0.00043–0.0029 ng/cig)[b]	0.54–3.6	0.54–3.6	l
Kraft recovery boilers	0.029	0.029	l

[a] For vehicles using leaded and unleaded gasoline, EPA assumes a fuel combustion rate of 10 km/L. For diesel fuel vehicles, EPA assumes a fuel consumption rate of 5.5 km/L. The emission factors are calculated assuming an average density of gasoline of 0.8 kg/L.

[b] An average cigarette weighs 0.8 g, which implies an average emission factor of 13 ng/kg.

Table 2
Chlorine content of combusted materials

Emission source	Average chlorine (ppm)	Range (ppm)	References
Waste incineration			
Municipal waste	5000	2500–8900	[1,3,18]
Hazardous waste	50000	10000–100000	[1,5,18]
Boilers/industrial furnaces (combusting hazardous waste)	50000	3000–100000	[19]
Medical/pathological waste	40000		[20]
Sewage sludge	1600	600–3000	[21,22]
Tire-derived fuel	1000	600–1500	[23,24]
Power/energy generation			
Leaded vehicle fuel	60	50–150	[5]
Unleaded vehicle fuel	10		[5]
Diesel vehicle fuel	10		[25]
Residential wood	100	10–600	[5]
Industrial wood	100	10–2000	[1]
Industrial/utility coal	500	200–1000	[26]
Industrial/utility oil	20		[27]
Other high temperature sources			
Cement kilns combusting hazardous waste	30000	5000–80000	[5]
Cement kilns not combusting hazardous waste (coal-fired)	500	200–1000	[26,28]
Cigarettes	700	500–800	[29]
Black liquor (kraft recovery boilers)	20000	5000–40000	[30]

D refers to dioxins and F refers to furans. Thus, the designating I-TEQ$_{DF}$ in Table 1 indicates that both dioxins and furans, but not PCBs, have been included in the calculation [1].

2.2. Elemental composition of combusted materials

Tables 2–4 show data on the chlorine, copper, and sulphur content of the combustion categories corresponding to Table 1. There is relatively little data on the distribution of these values about the mean. In addition to showing the average value reported in the literature, the tables show the ranges of values found for individual samples. In the figures that follow, the average values are assigned an uncertainty of a factor of four. It is important to note that the values shown in Tables 2–4 are measures of the total Cl, Cu, and S content, and may overestimate the amounts available to contribute to the dioxin formation.

3. Calculation

Figs. 1–3 show the dioxin emission factors from Table 1 versus the average content of copper, chlorine and sulphur from

Table 3
Copper content of combusted materials

Emission source	Average copper (ppm)	Range (ppm)	References
Waste incineration			
Municipal waste	350	80–900	[31]
Hazardous waste	200	50–500	[32,33]
Boilers/industrial furnaces (combusting hazardous waste)	200	50–500	[32,33]
Medical/pathological waste	500		[20]
Sewage sludge	900	80–1300	[22,33]
Tire-derived fuel	140	100–180	[24]
Power/energy generation			
Leaded vehicle fuel	2		[27,33]
Unleaded vehicle fuel	2		[a]
Diesel vehicle fuel	2		[a]
Residential wood	4	1–14	[33,34]
Industrial wood	4	1–14	[33,34]
Industrial/utility coal	20	0.3–40	[33,26]
Industrial/utility oil	12		[27,35]
Other high temperature sources			
Cement kilns combusting hazardous waste	200	50–500	[32,33]
Cement kilns not combusting hazardous waste (coal-fired)	20	0.3–40	[26,33]
Cigarettes	13	10–16	[29]
Black liquor (kraft recovery boilers)[b]	40		[36]

[a] Unleaded vehicle fuel and diesel vehicle fuel were assumed to have the same Cu content as leaded vehicle fuel, in the absence of specific data for these fuels.

[b] Black liquor was assumed to have a Cu content an order of magnitude higher than the original wood, based on comments in the reference.

Table 4
Sulphur content of combusted materials

Emission source	Average sulphur (ppm)	Range (ppm)	References
Waste incineration			
Municipal waste	2000	1500–3000	[33]
Hazardous waste	5000	100–25000	[18,32]
Boilers/industrial furnaces (combusting hazardous waste)	5000	100–25000	[18,32]
Medical/pathological waste	1700		[18]
Sewage sludge	10000	8000–11000	[22]
Tire-derived fuel	14000	12000–16700	[23,24,37]
Power/energy generation			
Leaded vehicle fuel	335		[27]
Unleaded vehicle fuel	340		[38]
Diesel vehicle fuel	500		[39]
Residential wood	600	200–1000	[18]
Industrial wood	600	200–1000	
Industrial/utility coal	30000	6000–50000	[18,26]
Industrial/utility oil	8000		[40]
Other high temperature sources			
Cement kilns combusting hazardous waste	5000	100–25000	[18,32]
Cement kilns not combusting hazardous waste (coal-fired)	30000	6000–50000	[18,26]
Cigarettes	4000	2100–5400	[29]
Black liquor (kraft recovery boilers)	50000		[41,42]

Tables 2–4, respectively. Because the quantities range over several orders of magnitude, the data are shown as log–log plots.

Here, we will be considering linear fits of the form

$$\log\ EF = A + B\ \log\ X \qquad (4)$$

where X is the concentration of Cu, Cl, or S. The best-fit line is calculated by minimizing the χ^2 function

$$\chi^2(A, B) = \sum\nolimits_{i=1}^{N} \left(\frac{\log\ EF_i - A - B \log\ X_i}{\sigma_i} \right)^2 \qquad (5)$$
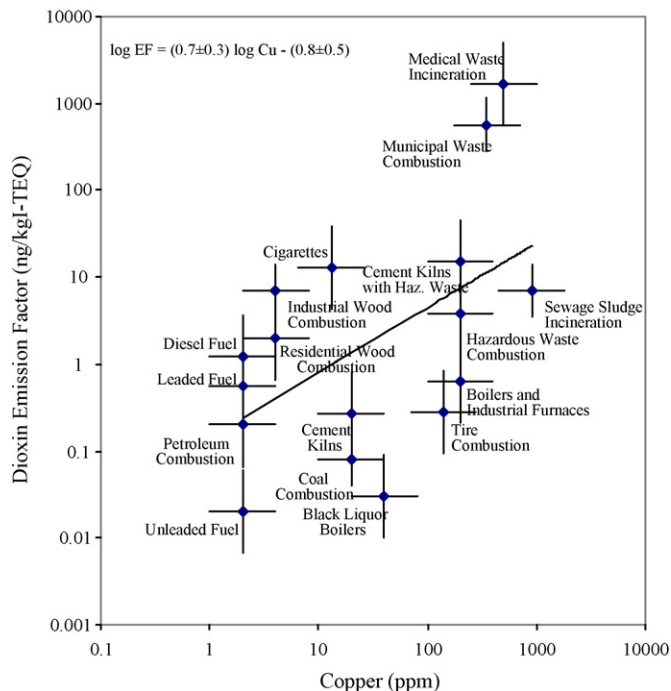

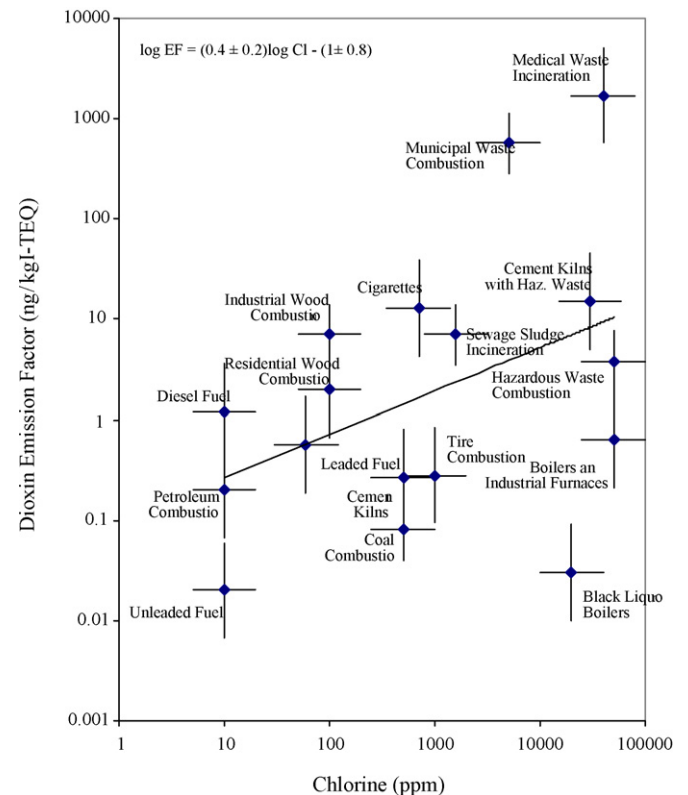Fig. 1. Dioxin emission factors vs average copper content of combusted material.

Fig. 2. Dioxin emission factors vs average chlorine content of combusted material.
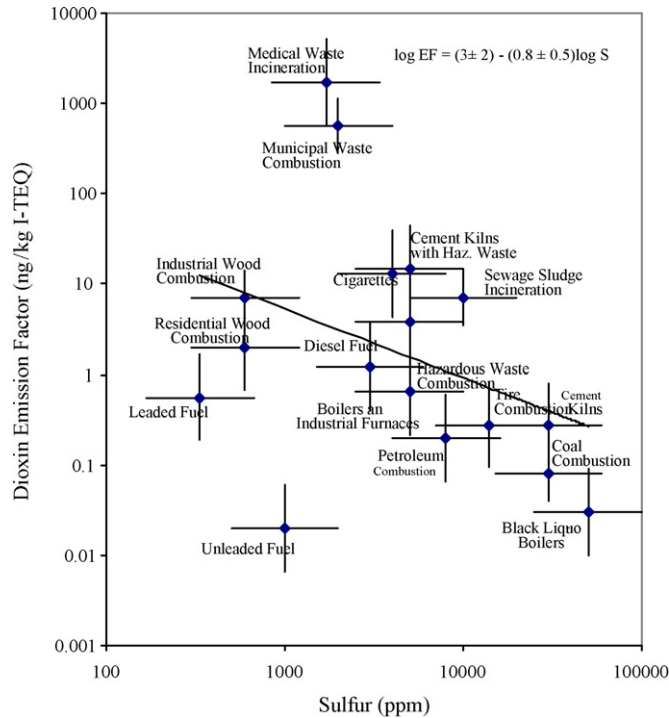
Fig. 3. Dioxin emission factors vs average sulphur content of combusted material.

where A and B are as defined in Eq. (4) [14]. Note that the value of χ^2 depends on the values of σ for each data point. As was mentioned previously, the uncertainties in the data are not well quantified. Thus, the magnitude of χ^2 is not well quantified, but it remains a useful measure of the relative merit of different models.

For these data, the uncertainty in the X values is nearly as large as the uncertainty in the emission factors, and thus, both uncertainties need to be included in σ [15]. The indirect contribution of the uncertainty in X to the uncertainty in the emission factor EF can be expressed as

$$\sigma_{I,i} = \sigma_{X,i} \frac{d \log EF_i}{d \log X_i} \qquad (6)$$

and the square of the combined total uncertainty is

$$\sigma_i^2 = \sigma_{I,i}^2 + \sigma_{EF,i}^2 \qquad (7)$$

where $\sigma_{EF,i}$ is the uncertainty in the ith emission factor.

4. Results

4.1. Copper and chlorine

Municipal waste and medical waste have high copper content, and high dioxin emissions; vehicle fuels have low copper content, and low dioxin emissions. Fig 1 shows that there is a positive correlation between the emission factors and copper content, and the best fit is

$$\log EF = (0.7 \pm 0.3) \log Cu - 0.8 \pm 0.5 \qquad (8)$$

The error-weighted χ^2 for this fit, from Eq. (5), is 100.

Fig 2 shows that there is also a positive correlation between the emission factors, and chlorine content. The best fit is

$$\log EF = (0.4 \pm 0.2) \log Cl - (1 \pm 0.8) \qquad (9)$$

with an error-weighted χ^2 of 100.

However, before attributing any physical meaning to the correlation with copper or chlorine, it is important to note that chlorine and copper are strongly correlated, with an R^2 of 0.75 for the regression of the logarithms. This means that the correlation of the dioxin emission factors with chlorine is much the same as the correlation of the dioxin emission factors with copper, and that the regression analysis cannot distinguish copper from chlorine. Moreover, it is possible that other elements also are correlated with the copper and chlorine concentrations, and it is possible that elements not included in this analysis are important. Iron, for example, has also been suggested to catalyse dioxin formation [10].

4.2. Sulphur

Fig 3 shows that there is a weak negative correlation between the emission factors and sulphur content. The low dioxin emission factors of black liquor boilers, coal combustion, cement kilns, and tire combustion are consistent with their relatively high sulphur content.

Sulphur content is not correlated with copper ($R^2 = 0.02$) or chlorine ($R^2 = 0.003$). The best fit of the emission factors with respect to sulphur is

$$\log EF = (3 \pm 2) - (0.8 \pm 0.5) \log S \qquad (10)$$

4.3. Sulphur and copper or chlorine together

To examine the relation of sulphur to dioxin emission factors separate from the relation with copper or chlorine, Fig. 4 shows the residual from the copper regression, that is, the difference between the actual emission factors and the emission factors predicted by the copper regression of Eq. (8). The residual (Fig. 4) shows a considerably stronger correlation with sulphur than does the original data (Fig. 3).

Because chlorine and copper cannot be statistically distinguished in this analysis, we will define a new variable $\log C = (\log Cu + 0.6 \log Cl)/2$, where the scaling is derived from a linear combination of Eqs. (8) and (9) [16]. The best fit of the emission factors with respect to sulphur and the combined copper and chlorine variable C is

$$\log EF = (1.0 \pm 0.3) \log C - (1.3 \pm 0.4) \log S + (3.1 \pm 1.4) \qquad (11)$$

This regression provides a considerably better fit than regression with Cu, Cl, or S alone. The error-weighted, residual χ^2 is reduced from 100 for the Cu or Cl regression to 40 when S is added. In simplified form, and to one significant figure, this expression can be written as
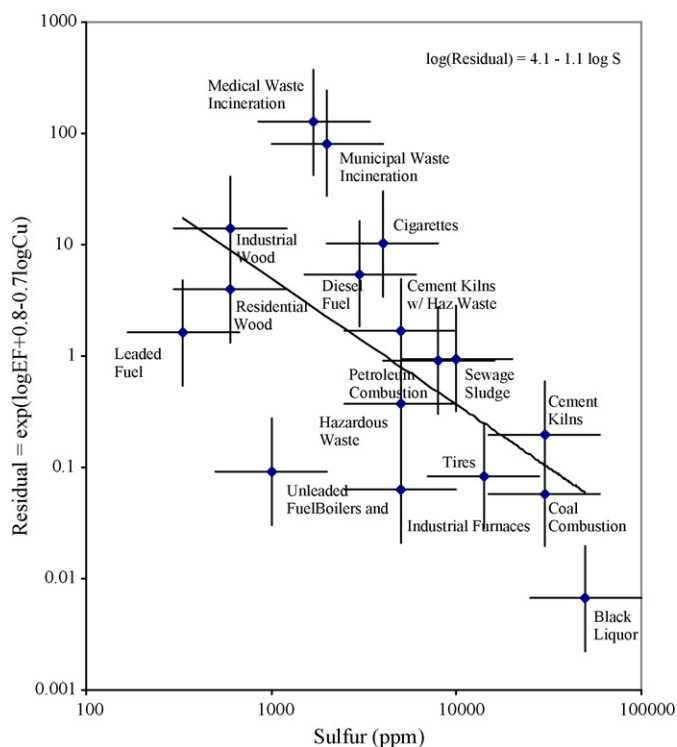
$$\log EF = \log (C/S) + (3 \pm 1) \qquad (12)$$

Fig. 4. Dioxin emission factors residual vs average sulphur content of combusted material. The dioxin emission factor residual is calculated from the regression shown in Fig. 1, and is the actual emission factor minus the best-fit predicted by copper concentration (Eq. (8)).

5. Discussion

The dependence of the dioxin emission factors on chlorine and copper is approximately linear, and the dependence on sulphur is approximately inverse linear. These relations are consistent with the results of Addink and Altwicker [17], who found that dioxin formation increases with the addition of both copper and chlorine. The results are also consistent with those of Raghunathan and Gullett [12]; who found that dioxin formation decreases as the ratio of sulphur to chlorine increases.

A key question is whether the correlations described here are causal. The validity of Eq. (12) could be determined experimentally by, for example, examining the impact of copper and other transition metals on dioxin emissions from biomass- or municipal-waste combustion [12]. While the reduction of dioxin emissions by addition of sulphur has been demonstrated [11], the potential to reduce dioxin emissions by reducing the content of transition metals has yet to be fully explored experimentally.

6. Conclusion

Taken together, sulphur and either copper or chlorine can provide a simple and approximate model for dioxin emission factors from uncontrolled combustion that holds over more than two orders of magnitude in chlorine, copper, and sulphur concentrations, and five orders of magnitude in dioxin emission factors.

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