Are dioxins important carcinogens in thermal processes?

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Abstract
The relative inhalative carcinogenic risk is compared for dioxins and polycyclic aromatic hydrocarbons (PAH) emitted in thermal processes like fires or thermal recycling procedures. The basis for comparison are measured concentrations and toxicological unit risk factors. PAHs are found to clearly determine the carcinogenic potential, whereas dioxins are much less important. This holds for accidental fires of all kind (Düsseldorf Airport fire, fire in an underground railway, fire of chlorinated chemicals, burning cars, forest fires etc.). PAH emissions of all these fires can be of same magnitude. Therefore different types of fires (fires of technical buildings or forests) can create a similar toxic potential mainly determined by PAH. Also in thermal processes with wood and metal PAHs play the dominant role, but measurements are scarce. Up to now there is no indication of any thermal process (including waste incineration or car exhaust) contradicting this.

1. Introduction

Fires or other thermal processes are most important emittors of many environmentally important gases like CO_2 (global warming) or toxins like CO, NO_x, etc. Many carcinogens are also emitted like polyaromatic hydrocarbons (PAH), dioxins etc.. It is not clear, which of these carcinogenic substances is most important from a toxicological point of view or if there are big differences between different fires or thermal processes in this respect.

With the unit risk model we could show that PAHs are much more important by high factors in comparison to dioxins in two fires [1], a fire of a plastic store and the Düsseldorf Airport fire. PAH are dominating the carcinogenic potential of emissions of these fires. Here we show additional data on other fires (underground railway, VCM-train accident, forest fires), of full scale experimental tunnel fires (with cars and railway wagons). Uncomplete data of some thermal recycling processes (steel scrap, wood incineration) are also discussed.

2. Comparing carcinogenic substances.

We concentrate on carcinogenic substances because there are data available regarding inhalative carcinogenic risk of some substances and emission data of these substances in fires and other situations. During and after fires inhalation is the most important route of intake. Due to lack of other data we neglect substances other than dioxins and PAH, such as aromatic amines, nitro-PAH, halogenated organic substances, heavy metals, aza-arenes etc[2]. We do not discuss other areas of toxicology: Acute toxicity of these

substances does not seem to be relevant in a fire situation. Comparative data for different chronic endpoints like teratogenic, imuntoxic or other effects are not available[1].
PAH: Benzo(a)pyrene (BaP) is one of the most important carcinogenic PAH. Other carcino-
genic PAHs can be included by using a method similar to the TEQ-concept for dioxins [2].
Dioxins: 2,3,7,8-TCDD (TCDD) is the most toxic and best examined dioxin. Other dioxins can be included by using the TEQ-concept. International TEQ are used here.
Unit risk concept: The unit risk concept is used to compare the inhalative risk for dioxins and PAH [4]. The unit risk is defined as "risk for cancer by inhalation after constant exposition over 70 years by a concentration of 1 ug of a substance per m^3 in the air". The unit risk of BaP was determined to be 0.07 ($1/(ug/m^3)$) and 1.4 for 2,3,7,8-TCDD; the two values are derived from different epidemiologic (PAH) or animal studies (dioxins) [4].
The inhalative carcinogenic unit risk of TCDD is thus about 20 times higher than that of BaP. It is not discussed here if PAH or dioxins from fires really pose a toxic problem[2].

3. Use of the unit risk concept for dioxins and PAH in thermal processes.
We compare the carcinogenic potential of dioxins and PAH from thermal processes which are mostly adsorbed to soot[3]. Because of this we do not claim a high toxicity of dioxins or PAH adsorbed to soot but compare their relative relevance only. We include other dioxins and PAHs by using TEQ/TEF-concepts: For PAHs we use the TEF-model of Nisbet and LaGoy [5]. The carcinogenity of PAH-mixtures is expressed in form of BaP equivalents (BaP_{eq}). To get the relative "risk" from dioxins or PAHs we multiply TEQ/TEF-concentrations with the unit risk factors[4].

3.1 Accidental fires: Table 1shows all results for fires known to us where dioxins and PAHs have been measured simultaneously and on a comparable basis. A short explanation of these fires:
Düsseldorf Airport Fire, Germany, 11.4.1996: According to the high economical and political importance of this fire intensive measurements both on dioxins, other dioxinlike PCBs and PAH have been published [17]. Inclusion of dioxinlike PCBs and brominated dioxins increased the TEQ by some 25%. This can be regarded as a low contribution knowing that high amounts of PCBs and brominated materials have been burning.
Schönebeck VCM-train fire, Germany, 1.6.1996 [7]. Five railway tanks with VCM (vinylchloride monomer) burned because of a train accident.
Underground railway in Bonn, Germany, 3.8.1996 [8].

Row one in table 1shows dioxin concentrations in soot (TEQ), row two concentration for EPA-PAHs, row 3 for BaP only, row four all carcinogenic PAHs (TEF according to [5]). Row one and four are multiplied with the unit risk factors (dioxins with 1.4, PAH with 0.07) and divided by each other. The resulting factor is shown in table 2 It gives the relative carcinogenic potential of PAHs compared to dioxins. In all fires PAHs are the most significant carcinogenic substances in soot compared to dioxins by a factor between 100 to 500.

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1 Both dioxins and PAH show many of these other effects because of their Ah-receptor coupling
2 This seems not to be the case because in different examinations of fire exposed people no increased dioxin body levels have been detected. Different reasons could explain this: the bioavailabiltiy of these toxins is reduced by adsorption to soot particles; the intake is small compared to normal intake.
3 Due to this adsorption both substances have a heavily reduced bioavailability.
4 In the meantime the german EPA is proceeding in this way also[6].

3.2 Full scale fire experiments in a tunnel with different cars and Railway Cars have been examined for dioxins and PAH in soot [9),10)]. Also here PAH have been emitted in significantly higher concentrations compared to dioxins. Fig. 1 shows relative toxicity factors comparable to table 2. Measurements for different sampling techniques and different distances to the fire are shown.

The next two examples have been partly cited in [1)], they are repeated here to give a better overall view. In these examples like in many others only PAH have been measured.

3.3 BaP in soot from fires of natural materials: Up to 194 mg BaP/kg soot from bush fires have been found [11)].more than 10 mg TEQ dioxins/kg. Such high dioxin concentrations have never been found in soot from fires.

3.4 PAH in soot from a burnt electrical typewriter: 1383 mg PAH/kg soot (77.4 mg BaP/kg and 150 mg/kg BaP_{eq}) have been found [18)]. This equivalates toxicologically some 8 mgTEQ dioxins/kg. Such high dioxin concentrations have never been found in soot from fires.

3.5 Thermal processes with wood and metal recycling: Published data on PAH in such recycling facilities are scarce, dioxin measurments can be found easily.

* **Wood ovens:** Burning of wood is rather important; in many cases there is no gas cleaning system.
* Clean wood: Dioxin values up to 1.2 ngTEQ/m^3 [12),13),14)] can be found. PAH-values have been measured up to some 100 mg/m^3, BaP alone to 20 mg/m^3 [15)].
* Wood mixed with halogen containing material: Dioxin values are found up to 10 ngTEQ/m^3. PAH has not been measured, so we assume similar values as with clean wood. Thus also in wood burning PAH are much more important compared to dioxins, even with wood mixed with halogen containing material.
* **Metal recycling:** Values of PAH are very scarce. In Sweden [16)] PAH-values have been found to be higher by factors around 100 000 compared to dioxin-TEQ. Therefore also in this thermal process PAH seem to be much more important compared to dioxins: We find again a factor of 250 to 500, assuming that as in comparable situations BaP_{TEF}-concentrations can be derived from PAH-values by dividing by 10 to 20.

3.6 Other thermal processes: Municipal waste incinerators without gas cleaning systems, car exhaust gases with leaded or unleaded petrol, etc. should show the same characteristics: Always the inhalative carcinogenic potential of PAH emissions seems to be much more important compared to dioxins. Readers are encouraged to contribute data to all of the above discussed topics.

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Table 1. Fires: Concentrations of dioxins and PAK found in soot *).

Site / Probe	Dioxin TEQ***)	EPA-PAH***)	BaP***)	PAH TEF***)
Düsseldorf**)	51 800	4 986	264	489
Schönebeck	31 900	680	47	56
Bonn U-Bahn	1.5	0.266	0.0104	0.016

*) Dioxin vlaues ar in ng, PAH in mg.
**) Düsseldorf TEQ-values for dioxins contain PCB's and brominated dioxins (see text)).
***) Bonn values are concentrations in soot (i.e. per m^2), Düsseldorf und Schönebeck values are concentrations in soot (i.e. per kg). Dioxins are thus in ngTEQ/m^2, PAH in mg/m^2.

Table 2: Relative carcinogenic potential of dioxins and PAH adsorbed to soot.

Site	PAH-TEF / Dioxins-TEQ
Düsseldorf Airport	470
Schönebeck VC-fire	88
Bonn Underground	533

Fig. 1: Comparison of relativ carcinogenic potential in full scale fire experiments in a tunnel. 3 different samplers have been used.