What are the important carcinogenic substances in soot?

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Introduction:

Accidental fires have an influence on the environment via different types of destruction and by emissions of gases and soot particles. These soot particles have to be removed in most fire events to further use installations not totally damaged. Soot particles are carcinogenic itself. Additionally many toxic substances are adsorbed to them (e.g. polyaromatic hydrocarbons (PAH), dioxins etc.). It is not clear, if these substances are increasing the carcinogenic risk of soot substantially, because absorption reduces the bioavailability significantly. We investigate on basis of the unit risk concept for carcinogenic substances the relative carcinogenic risk of dioxins compared to polyaromatic hydrocarbons (PAH), both absorbed by soot.

We find that PAHs are much more important by factors of 25 to 500 in comparison to dioxins. In some soots from fires (e.g. bush fires) the carcinogenic potential of PAHs is higher than that derived of ever measured dioxin concentrations in soot. Because of this we conclude that if toxicity of soot is really increased substantially by such substances it is not dioxin but other substances like PAHs, which far outweigh the importance of dioxins.

1. Adsorption to soot reduces bioavailability considerably.

Carbon or soot particles have a high tendency to absorb organic substances. This also applies to soot particles from accidental fires: Dioxins, PAH's and other organic substances are readily adsorbed onto them. Due to the high absorbing power of soot the absorbed substances have a low bioavailability. Nevertheless care is necessary in handling soot or even clean carbon particles e.g. in cleaning areas after accidental fires, because such small particles are always toxic if inhalated.

Despite this low bioavailability it was feared that fire fighters for instance, could be endangered by dioxins from fires. During the last years some independant examinations on different populations exposed to fires have been published: In no case have elevated dioxin concentrations been found. Examined were three groups of fire fighters [1,2], one group of people who feared to have been exposed during a huge fire from plastic (Lengerich [1]), one group of people working in a dioxin-contaminated area after a cable fire.

The high absorbing power of soot results in very low degassing of dioxins or PAH from soot and in very low migration to construction material covered by soot. If contaminated soot has been removed surface concentrations of dioxins or PAH are minimal [3] and others. It would be interesting to investigate what happens to such substances in fire conditions with only low quantities of soot in the gas phase; their bioavailability would presumably be much higher.

To recapitulate dioxins and PAH and other carcinogenic substances from fires are readily adsorbed onto soot particles. Their bioavailability is very much reduced. Because of this and other reasons elevated dioxin-concentrations have never been detected in several groups particularly exposed to fires.

2. Carcinogenic substances adsorbed onto soot particles.

Neglecting these facts dioxins are often claimed to convert soot from accidental fires into an especially dangerous and poisoning substance. In this work we discuss whether dioxins really do play such a predominant role or whether other substances are perhaps more important (always bearing in mind that the above mentioned facts refute these claims).

We concentrate on carcinogenic substances because there are data available regarding carcinogenic risk of some substances and concentration of these substances in soot. Due to lack of other data we neglect substances other than dioxins and PAH. Of course other carcinogenic substances are also found in soot, e.g. aromatic amines, nitro-PAH, halogenated organic substances, heavy metals, aza-arenes etc[5]. We neglect other areas of toxicology: Acute toxicity of soot does not seem to be relevant during or after fires. Comparative data for different chronic endpoints like teratogenic, imuntoxic or other effects are not available (it should be remembered that both dioxins and PAH show many of these other effects[4] .

2.1 PAH: Benzo(a)pyrene (BaP) is considered as the most important carcinogenic PAH. BaP is a real carcinogenic substance by some of its metabolites (epoxides). Parallel to this it is binding to the Ah-receptor (Arylhydrocarbonhydroxylase-Rezeptor). From this binding to the Ah-receptor different non-genotoxic chronic endpoints result. Other carcinogenic PAHs can be included by using a method similar to the TEQ-concept of dioxins (discussion of various models in [5]).

2.2 Dioxins: 2,3,7,8-TCDD (TCDD) is the most toxic and best examined dioxin. TCDD is today not regarded as a complete carcinogen because it's mutagenic power seems to be very weak or zero. TCDD is therefore regarded as a tumor promotor. Because of this a concentration threshhold should exist under which TCDD is not toxic. Like BaP it also is binding to the Ah-receptor, thus leading to the same toxic effects as BaP. Other dioxins can be included via the concept of toxicity equivalance factors (TEQ).

The advantages and shortcomings of these concepts and of the toxicological foundations can be found in literature (e.g.[6]).

3. Unit risk concept.

The LAI uses the unit risk concept in it's comparative study on carcinogenic air contaminants [6] . The unit risk is defined in this study 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 as 0.07 ($1/(ug/m^3)$), for 2,3,7,8-TCDD as 1.4; the two values are derived from different studies in literature. It should be remembered, that the unit risk factor for TCDD is a fictitious unit risk (because of a very probable lower threshold for cancer and derived only from animal data), whereas the unit risk of BaP is derived from epidemiological studies on man. This fictitious unit risk for TCDD "is only basis of calculation of a possible carcinogenic risk at concentrations in the air which are lower by a factor of 10^7 to 10^6" [6].

The carcinogenic unit risk of TCDD is thus about 20 times higher than that of BaP. The risk for the population from these substances is derived by multiplying this unit risk with the relevant concentration in the air. The study differentiates between concentrations found in urban or in rural areas. As a result BaP together with soot-particles from Diesel engines are the main contributors to the cancer risk from inhalation (some 80% of the total cancer risk) while TCDD contributes only some 0.001%, either in

urban or rural areas. This result stems from the fact that despite TCDD's 20 times higher unit risk it's environmental concentrations in the air are 10^5 to 10^6 times lower compared to concentrations of BaP.

4. Use of the unit risk concept for dioxins and PAH onto soot.

We compare the carcinogenic potential of dioxins and PAH adsorbed onto soot, remembering that both substances have a heavily reduced bioavailability. Because of this we do not claim a high toxicity of dioxins or PAH adsorbed onto soot but compare their relative relevance only.

In the LAI-study [6] only BaP and 2,3,7,8-TCDD were considered. We include other dioxins and PAHs by using TEF/TEQ-concepts: For dioxins we use the normal TEQs, for PAHs the TEF-model of Nisbet and LaGoy [7] in which the cancerognity of PAH-mixtures is expressed in form of BaP equivalents (BaP_{eq}, discussed in [5]). Table 1 shows the equivalance factors. To get the relative "risk" from dioxins or PAHs absorbed by soot we multiply these TEF/TEQ-concentrations in soot with the unit risk factors. The relative relevance of these "risks" can be more easily understood, if the two numbers are expressed as percentages, 100% being the "risk" of dioxins and PAHs together, and each number giving the percentage of the "risk" of dioxins or PAHs. It should be recalled, that only dioxins and PAH have been included (and not all (nor the most relevant, perhaps) carcinogenic substances) and that the carcinogenic potential is strongly decreased by the adsorption onto soot. The procedure is illustrated by several examples in table 2:

4.1 Soot from an accidental fire (Lengerich, 1 500 t of plastics including 500 t of PVC were burning[2]): Table 2 shows all results for soot where dioxins and PAHs have been measured simultaneously. Row one shows the concentrations in soot in TEQ/TEF for dioxins and PAHs with the BaP-concentration in brackets (ng/m2). Row two is the "risk" as product of concentrations absorbed by soot times the unit risk factor, row three gives numbers of row two in percents. In all cases PAHs are the most significant carcinogenic substances in soot compared to dioxins by a factor between 25 to 500.

4.2 Soot of an accidental fire (Düsseldorf Flughafen, 11.4.1996): Several results on dioxins and one with both dioxins and PAHs have been published [8]. 264 mg BaP/kg soot was found (with 5000 mg/kg EPA-PAHs) versus 42.6 ugTEQ dioxins/kg in a mean probe collected at 10 different places, BaP alone thus being 300 times more important than dioxins (inclusion of other PAHs probably increases this factor to 600 or more). Data from 4.1 and 4.2 can not be compared absolutly because they have different units (ng/m2 or mg/kg); the % values of course can be compared.

Unfortunately both dioxins and PAHs have not often been measured simultaneously and published after an accidental fire. If there is no sign of halogen containing material involved in the fire, mostly only PAHs are measured (if measurements are made at all). We therefore give some results only for PAHs which demonstrate, that PAHs are found in soots of fires in such elevated concentrations which have never been found for dioxins after correction for their different cancer unit risk. Dioxin concentrations in soot from accidental fires have been summarized to reach 0.1 to 110 ug/kg soot for fires with PVC-containing material and pure PVC, and 20 to 2800 ug/kg for fires with PCB containing condensator liquids [9].

4.3 PAH in soot from a burnt electrical typewriter [4]: 1383 mg PAH/kg soot (77.4 mg BaP/kg equivalant to 150 mg BaP_{eq}) have been found corresponding to some 8 mgTEQ dioxins/kg, such high dioxin concentrations have never been found in soot from normal fires .

4.4 BaP in soot from bush fires [10]: In Australia 194 mg BaP/kg soot from bush fires have been found corresponding to more than 10 mg TEQ dioxins/kg, such high dioxin concentrations have never been found in soot from fires (not even after fires with PCBs).

5. Conclusion.

Carcinogenic substances like dioxins or PAHs are strongly adsorbed onto soot particles (from accidental fires) and therefore have a low bioavailability. Partly because of this dioxins have never been found in people influenced by accidental fires in higher concentrations compared to normal population.

Because these facts are often neglected we examined the relative carcinogenic risk of dioxins and PAHs adsorbed onto soot with the unit risk concept. PAHs normally are found to be the determining carcinogenic substances, whereas dioxins play a much less significant (sometimes a negligible) role. Claims that soot from accidental fires are super-toxic exclusively due to their dioxin content or that high cost to remove soot after fires are caused by their high dioxin content have no sound toxicological basis. Up to now it is not clear if toxicity of soot is really significantly increased by these substances.

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Table 1. Toxicity equivalence factors for PAK's according to Nisbet and LaGoy.

Chemical	Abbreviation	BaP_{eq}
Benzo(a)pyrene	BaP	1
Dibenzo(ah)anthracene	DahA	1
Benzo(j+b)fluoranthene	BjbF	0.1
Benzo(k)fluoranthen	BkF	0.1
Indeno(1.2.3-cd)pyrene	IND	0.1
Anthracene	Ant	0.01
Chrysene	Chr	0.01
Benzo(ghi)perylene	BgP	0.01
Acenaphthylene	Aceny	0.001
Acenaphthene	Ace	0.001
Fluorene	Flu	0.001
Phenanthrene	Phen	0.001
Fluoranthene	Fluor	0.001
Pyrene	Pyr	0.001

Table 2: Comparison of carcinogenic risk of dioxins and PAHs absorbed by soot after accidental fires in Lengerich and Düsseldorf Flughafen. BaP-data in square brackets. For explanation see the text. Numbers from Lenge rich and Düsseldorf can not be compared absolutely but only relatively.

	TEFQ ng/m²	Risk=TEFQ * unit risk m/1000	%	Probe	Place
BaP_{eq} [BaP]	2800 [1500]	196	96.2	P01	Lengerich
Dioxins TEQ	5.6	7.84	3.8		
BaP_{eq} [BaP]	4600 [2500]	322	99.8	P02	- " -
Dioxins TEQ	0.4	0.56	0.2		
BaP_{eq} [BaP]	740 [400]	51.8	99.6	P03	- " -
Dioxins TEQ	0.14	0.196	0.4		
BaP_{eq} [BaP]	230 [130]	16.1	99.1	P04	- " -
Dioxins TEQ	0.1	0.14	0.9		
BaP_{eq} [BaP]	240 [140]	16.8	96.	P08	- " -
Dioxins TEQ	0.5	0.7	4.		
	mg/kg	kg/m³ * 1000			
BaP_{eq} [BaP]	[264]	[18.5]	[99.7]		Düsseldorf
Dioxins TEQ	0.043	0.06	[0.3]		

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