DIOXIN -- SCIENTIFIC INFORMATION

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Dioxins are formed in the 200°C (392°F) to 400°C (752°F) range as the exhaust gases and ash are cooling down.[1] What matters most is not the high temperature they reach, but the SPEED at which the exhaust gases and ash drop through that temperature range. This used to be made worse by incinerators that used "hot-side" electrostatic precipitators (ESPs) which allowed the exhaust gases into the ESPs (which are a type of pollution control device) above 400° and which retained the gases in the dioxin formation temperature range longer, massively increasing dioxin emissions.[2] Better incinerators use quench systems to drop the gases through that temperature range more quickly, though this doesn't prevent all dioxin formation... it just reduces it. Most dioxins are formed on the surface of the ash (both the bottom ash and the fly ash particles, some of which escape to the air, some of which are captured in the pollution controls, becoming "fly ash"). I don't think any incinerators try to quench the bottom ash, where most of the dioxin will be present. It's also worth noting that most of the dioxins are formed on the ash because of the presence of metals that serve as dioxin formation catalysts -- most notably copper, iron and zinc.[3]

The assertion that activated carbon injection reduces dioxin emissions is false. It may reduce the emissions to the air, but it increases total dioxin formation by increasing the amount in the fly ash. The dioxin concentration in fly ash with carbon injection is 4-5 times higher than without carbon injection.[4]

Proposals made about massive reductions in dioxins from MSW incinerators are also wrong and misleading. First, most of the reductions of dioxin emissions were from the shut down of so many trash incinerators (thanks to grassroots organizing in many cases). A lot of the reductions are from the closure or upgrading of incinerators that used hot-sided ESPs, like the one in Harrisburg, PA. The reductions don't count any increases due to carbon injection because they don't measure dioxin emissions in the ash. Most importantly, in terms of air emissions, the issue is that they do NOT continuously test for dioxins. By only testing once per year (under best operating conditions), they fail to capture the data on the excessive dioxin emissions during startup, shutdown and malfunction times, when the emissions limits don't tend to apply anyway (even if they were monitoring). Annual stack tests underestimate actual dioxin emissions by 30-50 times.[5] Real-time dioxin emissions monitoring equipment exists and has been tested and verified by EPA,[6] but I only know of one place in the U.S. that requires it so far -- a small local government in Pennsylvania which enacted an air pollution law that they used to stop a crematorium from being built there by subjecting it to continual testing and reporting requirements for mercury and dioxins.[7]

REFERENCES:

[1] 1994 EPA Dioxin Reassessment, Estimating Exposure to Dioxin-Like Compounds, Volume 2, Chapter 3. http://www.cqs.com/epa/exposure/v2chap3.htm (full report available at http://www.cqs.com/epa/exposure/) Some relevant quotes from the chapter

include:

In this investigation, significant increases in total concentration of dioxin TEQ occurred between temperatures of 280-400° C, and concentrations declined at temperatures above 400° C. This is in agreement with the experimental evidence of the temperature range defined as the "window of opportunity" for catalytic formation of CDDs/CDFs on the surfaces of fly ash particles.

Formation kinetics are most favored at temperatures between 200 to 350° C.

Facilities of particular concern are those that use ESPs which operate in a temperature range of 200° - 400° C. As discussed in Section 3.5 these conditions can promote the formation of CDDs/CDFs.

Moreover, formation occurs outside and downstream of the combustion zone of a furnace to a combustion source in regions where the temperature of the combustion offgases has cooled to between 200 and 400° C (Vogg et al., 1987; Bruce et al., 1991; Cleverly et al., 1991; Gullet et al., 1990a; Commoner et al., 1987; Dickson and Karasek, 1987; Dickson et al., 1992).

[2] See http://www.ejnet.org/dioxin/esp.html as well as references to "hot-sided ESPs" in the EPA dioxin reassessment document (http://www.cqs.com/epa/exposure/v2chap3.htm).

[3] "Metals as Catalysts for Dioxin Formation," http://www.ejnet.org/dioxin/catalysts.html. I've compiled and made available several scientific research papers on the topic here.

[4] Chang, M., Lin, J., 2001. Memory effect on the dioxin emissions from municipal waste incinerator in Taiwan. Chemosphere 45: 1151-1157. [see also the separate email I'll forward with the abstract and thread discussing it]

[5] Wevers M. and De Fré R., "Underestimation of dioxin emission inventories," Organohalogen Compounds, Vol. 36, pp. 19-20 (1998). http://www.ejnet.org/toxics/cems/1998_DeFre_OrgComp98_Underest_DIoxin_Em_Inv_Amesa.pdf

"The Amesa system [a long-term dioxin sampler tested and verified by U.S. EPA in 2007] was used for continuous sampling during periods of 15 days. The analysis was carried out in double by 2 laboratories, VITO and GfA. They show that a standard emission measurement according to the European standard method EN 1948 during a period of 6 hours resulted in an emission concentration of 0.25 ng TEQ/Nm3, while the average over 2 weeks in the same period was 8.2 to 12.9 ng TEG/Nm3. This illustrates that the standard measurement underestimated the avereage emission by a factor 30 to 50. [Note: it's actually 33 to 52 times higher.] As a result of these findings doubts have risen over the real emission of the incinerators, and the special commission on incineration has asked from all incinerators in the Flemish region to use the continuous sampling system in order to demonstrate their compliance with the emission limit."

More on continuous emissions monitoring of dioxin here: http://www.ejnet.org/toxics/cems/dioxin.html

[6] Dioxin Emission Monitoring Systems, Environmental Technology Verification Program, U.S. Environmental Protection Agency. http://www.epa.gov/etv/vt-ams.html#dems This page lists the four pieces of dioxin testing equipment that EPA tested and verified in 2006. The Amesa system is one (it's a long-term sampler that can collect a sample of up to 30 days). Others are semi-continuous or actual real-time dioxin emissions monitors. Their "Technology Brief" on Dioxin Emission Monitoring Systems (http://www.epa.gov/etv/pubs/600s07002.pdf) states:

"The four verified technologies fall under one of two categories: automated isokinetic sampling systems of flue gas with laboratory analysis, or semi-continuous laser-based systems that produce ions which are typically detected using a time-of-flight mass spectrometer (TOFMS). Long-term continuous samplers collect samples over time periods up to several weeks to obtain a cumulative record of source emissions and provide evidence of emission levels. Real or semi-real-time continuous monitors, with a frequency of measurement at real time or up to an hour, provide quick feed back to the plant operator by measuring dioxin emission levels on-site."

[7] See http://www.actionpa.org/ordinances/ for the Kulpmont Borough, Pennsylvania ordinance.

March 2012