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Research Article

EPFRs Formation/Emission from Waste Burning

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Abstract

Thermal treatment of wastes and e-wastes is associated with the formation of toxic products of incomplete combustion. One of the most feared by the public pollutant from such processes are polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs).In this manuscript we have shown, that other pollutants should be also considered more due to their large emission factors. Our recent discoveries of the Environmentally Persistent Free Radicals (EPFRs) as key intermediates of PCDD/F formation route have indicated, precursor model to be the most important path to PCDD/F formation. At the same time, EPFRs can be emitted independently from PCDD/F associated with the particulate matter matrix. Current studies were concentrated on the EPFRs emission from combustion sources depending on the presence of their precursors in the combustion fuel where experiments were designed to mimic the backyard trash burning. It was found, that incineration of waste materials containing chlorinated organics doubles the level of EPFRs on the (particulate matter) PM, and such EPFRs have a longer lifetime in the ambient atmosphere. Since the health impacts of EPFRs indicate a potential health hazard, their emission can define the health impacts of the emitted PM. The primary fuel components have been found to be a driver of EPFRs emission.

Keywords: Environmentally Persistent Free Radicals (EPFRs); Dioxins and furans; Waste incineration

Introduction

One of the most common methods of waste disposal is incineration. Though in the past waste incineration has gained a bad reputation due to the poor air pollution control, with technological advances in APCDs it is making a comeback. One of the biggest concerns associated with waste incineration is the formation and emission of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans PCDD/Fs. In recent years, great strives have been made in understanding the mechanism of the PCDD/F formation. Currently, it is believed that all PCDD/Fs that are emitted from combustion processes are formed in the cool zone of the exhaust systems, within the temperature range of 500-150°C [1,2]. Lomnicki and Dellinger [3,4] have shown that the mechanism of the surface assisted formation of PCDD/Fs is based on the fly ash propensity to generate surface – bound radicals, which are the intermediates in the condensation process to form PCDD/Fs molecules. In essence it is these surface radicals that determine the emission of PCDD/Fs and other toxic combustion by-products. Stabilization of the radicals on the surface will result in the increased propensity for the formation of PCDD/Fs, while their fast decomposition will lead to the degradation and oxidation of the adsorbed organics. Studies have shown that surface bound radicals can be form within the entire cool zone temperature range. Oxides of many metals present in fly ashes such as: Cu, Fe, Ni, Zn, Al and probably many others are catalytically active in their formation [5-9]. Interestingly, a temperature shift is observed between the maximum formation of dioxins and highest radical yields: 280-400°C and ~200-250°C, respectively [3,4,10-12]. These points to the changing reactivity of EPFRs towards different products at different temperatures: at the inlet to the cool zone where the temperatures are the highest EPFRs undergo fast degradation and oxidation. With decreasing temperature of the cool zone a condensation reaction becomes important, which leads to the formation of PCDD/Fs. Finally at the lowest temperature, surface radicals became stable and long lived (thus their name Environmentally Persistent Free Radicals EPFRs). This results in their emission with the Particulate Matter (PM) Figure 1.

Development of EPFRs theory has advanced the understanding of many processes within the cool zone of combustion systems. An important implication of these discoveries is interpretation of PCDD/F analysis of solids (both PM and ashes) as they are prone to misidentification of EPFRs as PCDD/Fs, due to the condensation process during solvent extraction [13]. The studies of EPFRs have focus so far on the mechanism of their formation. There is no data on how the composition of the combustion feed affects EPFRs speciation and yield. These are important aspects of environmental impact: emitted with PM EPFRs, has been linked to various health effects [14-19] and associated with PM exposure related diseases might be in fact

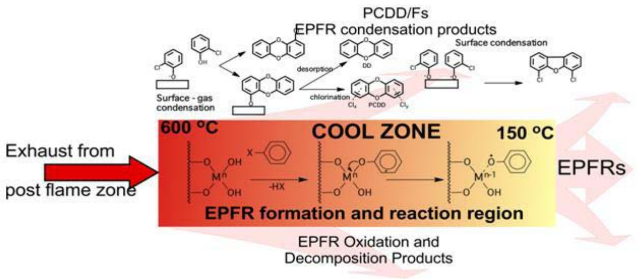

Figure 1: Schematic diagram of some important surface reactions in the cool zone of incinerators.

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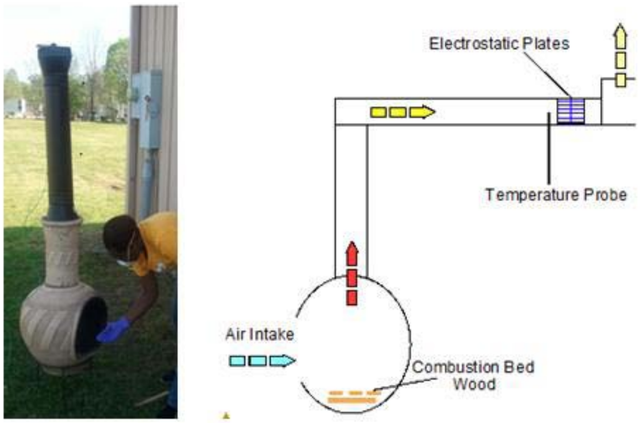

Figure 2: Experimental setup of combustion chamber.

associated with EPFRs bioactivity. Indeed, experiments have shown that EPFRs induce hydroxyl radical generation *in vivo* and *in vitro* [20,21], So far, a model systems composed of silica matrix and active metal oxide phase with adsorbed radical precursor has been used for EPFR studies. Turning towards environmental exposure evaluation it is important to establish the correlation between the combustion feed composition, radical yield and speciation. This manuscript is a first step towards these goals and provides information of weather small addition of halogenated aromatic compounds to the feed, affects the yield of EPFRs formation. We have designed a simple experimental system emulating a pit/barrel-burning of biomass material (pine wood stakes) with and without the addition of chlorinated aromatic precursor. We have selected 2-monochlorophenol for a precursor compound as it was studied before on model systems and its chemistry of EPFR formation is well understood. It also represents a large group of contaminants that can be present within the waste streams.

Experimental

Sample generation

Experiments were performed on the soot/fly-ash particles and bottom ashes from the combustion of Piny on Pine wood stakes. 2 types of wood samples were used: virgin samples combusted as is and wood samples impregnated with 2-MonoChloroPhenol (2-MCP), where 2-MCP load was 25g/500g of wood. Overall, spiked with 2-MCP wood contained 1.3% chlorine based on empirical calculations. All samples were combusted in the clay combustion chamber equipped with 3m long exhaust extension Figure 2. This system can represent a simple combustion devise used commonly to incinerate backyard trash. Combustion conditions were based on the natural air draft. At the exhaust exit electrostatic plates were mounted to collect soot/fly-ash samples. Temperature at the collection plate ranged between 80-100°C. Soot/fly-ash samples were later retrieved from plates by gentle scraping. Bottom ash was collected after finishing the burn and cooling down for 24hr. Each experiment was performed in triplicate and the data represent the experimental average. The variation of the radical concentration was within 10% range.

Radical analysis

All EPR (Electron Paramagnetic Resonance Spectroscopy) measurement were performed using a Bruker EMX-20/2.7 EPR spectrometer (Bruker Instruments, Billerica, MA) with dual cavities, X-band, 100kHz and microwave frequency 9.53 GHz. The spectra were obtained at room temperature. The typical parameters were: microwave power of 1mW, modulation amplitude 4G, sweep width 200G, and time constant 40.960 ms.

Radical concentration is calculated based on the comparison to a stable radical standard DPPH (2,2-diphenyl-1-picrylhydrazyl) and expressed

For the studies of EPFRs lifetime, samples were exposed to air and spectrum was measured after different time intervals to obtain the radical concentration *vs.* air exposure time correlation. The radical lifetime ($t_{1/e}$) is defined as the time the original concentration of EPFRs to decay 1⁄e of the original concentration $R_t = 1/e\, R_0$, thus

$$1/e\, R_0 = R_0\, e^{-kt}$$

$$t_{1/e} = 1/k$$

For the sample re-exposure with radical precursors, samples (virgin fly ash/soot) were placed in exposure reactor as described in [6]. Briefly, the reactor containing the particles was evacuated to 10^{-1} torr, and the particles were stored under vacuum with the main vacuum valve and the adsorption port valve closed until the adsorbate was introduced. Vapors of the adsorbate molecules were introduced into the equilibration chamber at the desired pressure (10 torr), and the dosing tube valve was opened to expose the particles to the adsorbate vapors at the desired temperature for 5 min. Exposures were performed at 230°C. Once the exposure was completed, the port and dosing tube were evacuated for 1 hr at the dosing temperature and 10^{-2} torr pressure to remove any residual physisorbed dosant. The reactor was then sealed under vacuum with a vacuum tight PFE stop-cock and the sample was cooled to room temperature. The prepared sample was then detached from the port and ready for EPR measurement.

Results and Discussion

Combustion of waste results in the formation of particulates that are emitted to the atmosphere which can be a significant risk for the exposed population. Recent discoveries have pointed to the EPFRs as one of the factors that are major health risk agent associated with particulates. The formation of EPFRs is associated with the adsorption of aromatic products of incomplete combustion on the metal centers of PM [5-9].

Introduction of chlorinated aromatics into the biomass material had a significant impact on the radical concentration on both fly ash/soot particles collected in the exhaust duct and in the bottom ash samples (Table 1). All collected samples have shown the presence of narrow (<10 Gauss), paramagnetic signal in the magnetic centerfield of ~3540 Gauss, which typical for the organic radical species. The speciation of the radical can be recognized based on the value of g factor. The g factor of the spectrum is an indication of "chemical shift" associated with the electron promotion to a higher spin level, and it is dependent on the local environment [22]. Unlike radicals in the solution, surface bound radicals are typically characterized by the singlet line, due to the limited degrees of freedom. The 2-MCP spiked wood (Wood-MCP) has produced fly ash/soot particles with over 2 time's higher radical concentration compare to virgin wood (No-

Table 1: Parameters of the EPR spectra for the experimental samples.

	Sample	g-factor	ΔH_{p-p} (G)	(Spins/g)
Fly ash/Soot	No-MCP	2.0037	5.0	2.26×10^{19}
	Wood-MCP	2.0035	6.7	5.37×10^{19}
	Dosed-MCP	2.0031	2.0	9.3×10^{19}
Bottom Ash	No-MCP	2.0034	3.1	1.7×10^{18}
	Wood-MCP	2.0036	4.9	1.50×10^{19}
	Dosed-MCP	2.0039	4.8	5.3×10^{19}

MCP). At the same time the width of the peak (measured as peak-to peak value ΔHp-p) has increased from 5 to 6.7 Gauss and overall g-value of EPR spectrum has decreased from 2.0037 to 2.0035.

In general, combustion of woody biomass produces quite large amounts of hydroxylated aromatic species [23, 24]. Such species are potential precursors for the formation of surface bound radicals down the exhaust stream. Current data are in line with those observations: the observed g value of 2.0037 for no-MCP fly ash/soot particles indicates presence surface bound oxygen centered radicals. Typically, 3 major groups of EPFRs can be distinguished: those with a g value <2.003 characteristic for mostly carbon centered radicals (such as in graphite or polyaromatic carbon sheets), 2.003>g>2.0042 characteristic for phenoxyl type radicals and g >2.0042 typical to semiquinone type radicals. One radical type will result in a sharp and very narrow (~2-3 gauss) spectral line, while broadening of the spectral line is indicative of the presence of more than 1 type of radical species. Broadening and convolution of multiple spectral lines also affects the g factor [6]. Thus it is concluded that g value of non-MCP wood PM indicate the presence of both semiquinone and phenoxyl radicals.

Addition of 2-MCP to wood resulted in a lower g-value of PM associated EPR signature (2.0037 to 2.0035). This indicates change in the radical speciation compared to virgin wood material. It has been shown before, that 2-MCP forms predominantly chlorophenoxyl radicals, and the shifts towards the lower g values combined with the broadening of the EPR signal for MCP-treated wood indicates increase in phenoxyl type radicals for MCP-doped wood PM, compared to virgin wood PM, Contrary to the fly ash/soot samples, bottom ash samples of no-MCP showed the formation of radicals with a relatively narrow signal in EPR Table 1 and lower g value, indicating primarily phenoxyl radicals being formed. Addition of 2-MCP to wood have increased both g-value and peak width to produce similar species as those in wood-MCP fly ash samples.

Further support for the radical assignment was provided by the exposure experiments of no-MCP fly ash/soot to 2-MCP vapors at 230°C (cf. Figure 3 and Dosed-MCP in Table 1). The experiment resulted in doubling the number of EPFRs. The EPR signature of such samples was characterized by a narrow signal width (ΔHp-p of 2 Gauss), which indicates dominance by single species with g value of 2.0031. Such signals can be attributed to, phenoxyl radicals. To summarized, phenoxyl radical species on those samples create a paramagnetic signal at g = 2.0031 confirming the g value shift in the samples PM from Wood-MCP should be attributed to increased formation of phenoxyl radicals.

One of the most important implications of the formation of radicals on the particulates is their persistency in the environment; Persistency of the surface bound radicals is tested by their exposure to ambient air and analysis of the radical decay profile over time. Figure 4 presents the radical decay profiles of both no-MCP and wood-MCP fly ash/soot samples. For No-MCP fly-ash/soot samples at least 2 type of radical decay kinetics can be observed: fast, with a lifetime $t_{1/e}$ = 2.9 days and slow with $t_{1/e}$ = 27 days. Such behavior is associated with the presence of different EPFR species, each with a distinct decay profiles or association radicals of with different metal sites that are determining their stability [25]. Fine [23,24] has shown, that zinc is usually a dominant metal in the particulates emitted from wood burning. In fact, observed here decay profile is similar to that observed on zinc oxide and resulting from a mixture of phenoxyl and ortho-semiquinone radicals [25]. Introduction of chlorinated aromatics to the wood samples resulted in EPFRs with much longer lifetime (50 days, cf. Figure 4, right), and such lifetimes are also consistent with the radicals formed on model particulates containing zinc oxide [25].

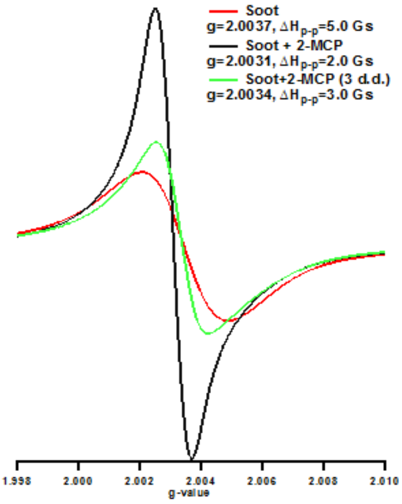

Figure 3: EPR spectra of no-MCP fly ash/soot before and after exposure to 2-MCP vapours.

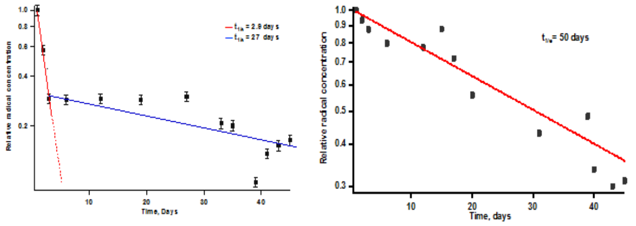

Figure 4: Decay studies of fly ash/soot radicals for no-MCP (left) and wood-MCP samples (right).

Current studies

Clearly have shown that the presence of chlorinated aromatics in the combustion feed increases the concentration of EPFRs. This implies that the composition of feed fuel has a direct impact on the speciation of the EPFRs. In fact, it is not only the combustion by-products formed during the combustion process that result in EPFRs. Undestroyed fraction of fuel or POHC (parent organic hydrocarbon compounds) can drive the concentration and speciation of EPFRs.

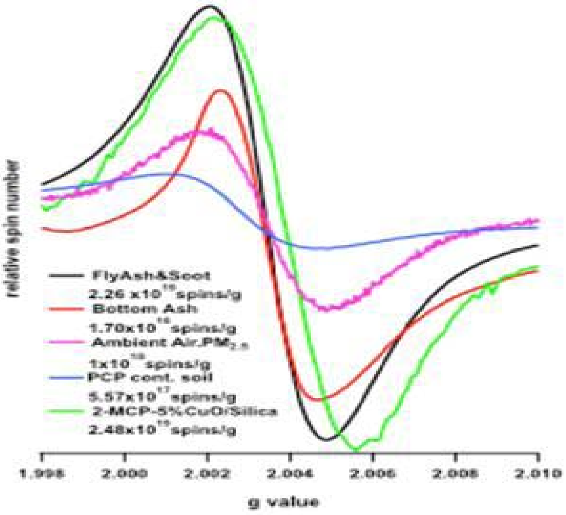

Figure 5: Comparison of EPR spectra of different environmental EPFR samples.

Once formed and emitted with PM, EPFRs have a long lifetime and will remain on the particle surface long after the release from the source. It is also important to emphasize that the potential emission of PCDD/Fs from combustion of wastes that include chlorinated organic is not the only concern, and much higher yields of EPFRs should be taken into the account as a potential hazard. Figure 5 presents the comparison of the radical species present in different environmental samples, including ambient air PM, fly ash/soot samples, contaminated soils and model PM samples used for the laboratory studies. Based on the characteristic EPFR signature, it can be assumed with high certainty that EPFRs in PM samples are of combustion origin and are associated with combustion borne fraction of ambient air PM. Indeed the average concentration of EPFRs on PM is at the level of 1x1018 spins/g [26], which is an order of magnitude lower compared to fly ash/soot samples, a drop resulting from both environmental decay and PM dilution in air by non-combustion PM. Since fly ash/soot particles from sources containing chlorinated organics significantly increase the concentration of EPFRs, one can anticipate a same level of EPFR increase in ambient air PM samples in areas prone to the PM emission from waste combustion.

Conclusion

Our studies have confirmed the correlation between the certain components of waste fuels and the formation and emission of EPFRs. The composition of fuel in waste combustion defines not only the formation of products of incomplete combustion but also the concentration and speciation of EPFRs. In particular, chlorinated aromatics are prone to form large quantities of EPFRs. A simple backyard waste burning simulation produces large quantities of EPFRs per unit mass of PM. Though PM emitted from combustion are subject to large dilution factors in the ambient air, long lifetime EPFRs results in ubiquitous presence of those radicals in ambient air PM samples.

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