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Review

Memory effect driven emissions of persistent organic pollutants from industrial thermal processes, their implications and management: A review

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ABSTRACT

Memory effect is delayed emission of certain persistent organic pollutants (POPs). Many of the POP compounds viz. polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) get trapped in the particulate phase deposited in the flue transfer lines and air pollution control systems (equivalent to storage in the memory of a system) and released subsequently. Memory effect driven emission is a combination of *real time* emission and emission of stored compounds and so is not a true measure of actual *real time* emission. Memory effect is now realized to have existed for a long time but was not identified and understood until recently. Memory effect has several serious implications e.g. it wrongly depicts emission patterns of POPs; it makes compliance to stipulated emission standards difficult; it could lead to wrong calculations of emission factors and emission inventory estimates of a plant and leads to misinterpretation of efficacy of processes and air pollution control systems. Further, new PCDD/Fs may be formed in the trapped particulate phase via *de novo* synthesis and the new compounds may be emitted, thereby increasing total PCDD/F emissions, apart from altering the homologue pattern of PCDD/Fs in emissions. Memory effect could be minimized by judicious operational and management (O&M) procedures like optimizing combustion, minimizing unnecessary halts in operations, periodical cleaning of flue transfer lines, application of inhibitors etc.

1. Introduction

Memory effect is delayed emissions of certain persistent organic pollutants (POPs), primarily associated with the particulate phase that gets trapped by impaction, interception or gravity settling on the inner walls of flue gas transfer lines and air pollution control systems or any other post combustion system attached to certain industrial thermal operations. The trapped particles might remain exposed for long time within a certain temperature range at which significant desorption of already adsorbed PCDD/Fs or new PCDD/F formation take place, elevating PCDD/F concentration in the emissions. Memory effect has been found to play a role in the emissions of some specific pollutants, notably persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs) and poly chlorinated dibenzo-*p*-dioxins/polychlorinated dibenzo furans ((PCDD/Fs) (Zimmermann et al., 2001). POPs tend to show memory effect as they are resistant to degradation through chemical or biological processes, making them persist in the trapped particulate phase (Wikstrom et al., 2004; Zimmermann et al., 2001).

Emissions of PAHs and PCDD/Fs can be classified under two regimes: (i) Direct emission phase (ii) Memory emission phase. After malfunctions in post combustion system, memory effect is observed to occur for several species of PAHs (Zimmermann et al., 2001). The observed memory effect in POP emissions is reported to be associated with notable shifts in the homologue pattern of, in particular, PCDD/Fs and mono chlorinated phenol (MCPh). During memory emission phase under some malfunction, some POPs showed no change in concentration such as PCBs while low-chlorinated PCDD/Fs increased between 1 order of magnitude (e.g. monochlorinated dibenzofurans) and 2 orders of magnitude (dichlorinated homologues). Higher chlorinated homologues decreased in concentration and reduction was larger for homologues with a high degree of chlorination (Zimmermann et al., 2001).

We review and analyse the reported cases of memory effect driven emissions and instances where memory effect is now suspected to have played a role in modifying PAH and PCDD/F emissions from stationary sources. The ramifications of memory effect driven emissions and scope of minimizing memory effect have also been discussed.

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2. Memory effect: an insight

Memory effect must have existed since industrial thermal processes began but it was never identified until recently. The cause of low PCDD/Fs removal during the preliminary stages of Activated Carbon Injection (ACI) was found to be due to memory effect (Van De Kleut and Van De Akker, 1998; Wevers and De Fre, 1998). Further, during stable combustion and efficient air pollution control operations, municipal solid waste incinerators (MSWI) emitted more than expected PCDD/F emissions after breakdown or transient pause in the process, revealing emissions of stored (in the memory) contaminants under the previous worse operating condition (Li et al., 2011). The manifestation of memory effect in incinerators is depicted in Fig. 1.

Emissions of PCDD/Fs have exhibited a significant time lag in relation to changes in operational conditions in incineration plants, with higher than expected emissions for prolonged periods after implementation of changes or incomplete combustion (Chang and Lin, 2001; Weber et al., 2002; Zimmermann et al., 2001). Memory effect most commonly manifests itself during start up periods of thermal processes or after periods of incomplete combustion. During unstable combustion, high emissions of PAH and PCDD/Fs (gaseous and particulate phase combined) were observed for several hours even though the actual combustion conditions were stabilized again (Zimmermann et al., 2001; Wikstrom et al., 2004). Gullett et al. (2006) showed that average PCDD/F concentration along with PCDD:PCDF changed during process start up. The elevation in PCDD/F concentration was substantial, about 8 folds, during start up but only marginal (only about 1.5 times) during shut down over a steady state condition. After only a few hours of start up, PCDD/F concentrations started to decline to get close to the steady state concentrations, indicating the transient nature of memory effect (Table 1). Li et al. (2011) have reported that the period under influence of memory effect for PCDD/Fs in aged filter bags was about 96 and 34 days in two different electric arc furnaces (EAFs). Some recent studies on memory effect were conducted on boilers, where periods of poor combustion or start-ups led to fouling of inner walls of the boiler with soot and/or fly ash deposits, which acted as sink of PCDD/Fs and became enriched. A link between soot formation and higher PCDD/F levels has been demonstrated through both laboratory experiments (Lee et al., 1998; Wikstrom et al., 2003) and field measurements (Zimmermann et al., 2001), providing an explanation for unpredictably high and temporally persistent PCDD/Fs yields in waste incinerators (Gullett et al., 2000a,b; Zimmermann et al., 2001). Tejima et al. (2007) also showed that PCDD/F and dioxin-like PCB emissions from boiler outlets and stack outlets were maximum during start up (Table 2). The concentration of PCDD/Fs increased by a whopping >500 times in bottom ash and 1.6 times in fly ash during start up over the steady state condition in the studied boiler. Significantly, the elevation of PCDD/Fs in fly ash released to air was not as high as that in bottom ash. During shut down, however, the elevation of PCDD/F in bottom ash was marginal and there was an appreciable reduction of concentration in fly ash over steady state condition. Blumenstock et al. (2000) found an elevation in PCDD/Fs after a period of bad operating conditions in a pilot scale incinerator.

Table 1
Changes in PCDD/F concentration and ratio during different operating condition.

Condition/state	ng TEQ/dscm	PCDD/PCDF ratio
Steady state	25.5	0.18
During high CO, followed by shut down	39.9	0.37
Shut down	39.6	0.56
Start up (1 h after shut down)	198.9	0.45
Late start up (2–3 h after start up)	40.4	0.28

CO: carbon monoxide; TEQ: toxic equivalency; dscm: dry standard cubic meter; PCDD/PCDF: polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans.
Source: Gullett et al. (2006).

Memory effect of POPs are triggered by two basic phenomena viz. (i) adsorptive memory effect – desorption of previously formed PCDD/Fs which were adsorbed on particulates impacted on to inner linings of flue transfer lines or (ii) *de novo* memory effect – increased emission due to newly formed PCDD/Fs via *de novo* synthesis with the aid of carbonaceous matter and other elements including catalysts generated from the products of incomplete combustion (PIC) during the malfunctioning of the thermal process (Weber et al., 2002). Fig. 2 schematically explains adsorptive and *de novo* memory effect.

In adsorptive memory effect, fly-ash/soot deposited on the inner walls of transfer lines or air pollution control systems act as an adsorption matrix for PCDD/Fs and PAHs and these compounds are desorbed into the flue gas stream subsequently, showing memory

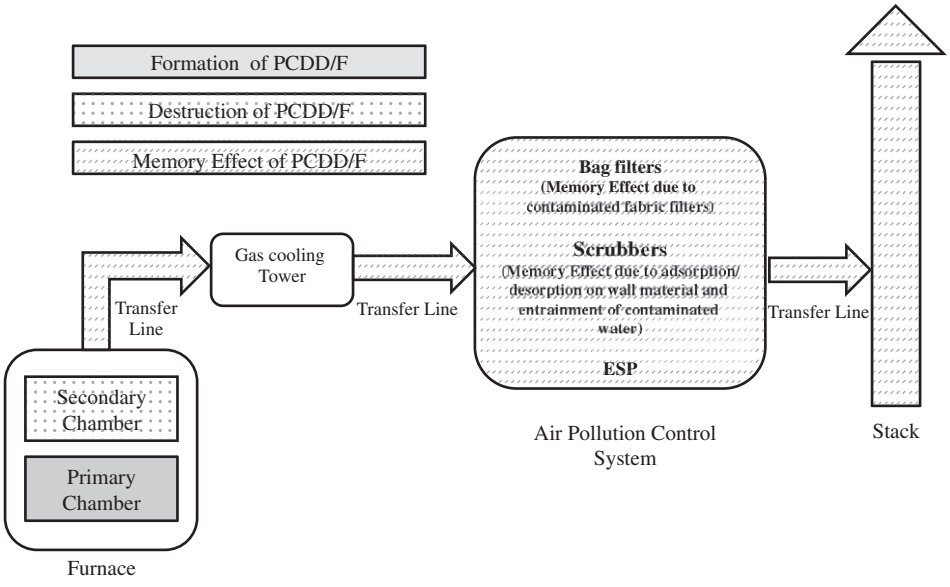

Fig. 1. Possible places for memory effect, formation and destruction of PCDD/PCDF in a thermal incinerator.