

Comment on "Identification of Monochloro-Nonabromodiphenyl Ethers in the Air and Soil samples from South China"

Yu et al.¹ detected three nonabromochlorodiphenyl ethers (NBCDEs) in air and soil samples from Guangzhou China and at an e-waste recycling area. Identifications were made using gas chromatographic retention times of pure reference compounds, as well as matches with full-scan mass spectra data in the electron capture negative ionization mode. Compounds included: 6'-chloro-2, 2', 3,3', 4,4', 5,5', 6-nonabromodiphenyl ether (6'Cl-BDE-206), 5'-chloro-2, 2', 3,3', 4,4', 5,6,6'-nonabromodiphenyl ether (5'Cl-BDE-207) and 4'-chloro-2, 2', 3,3', 4,5,5', 6,6'-nonabromodiphenyl ether (4'Cl-BDE-208). Mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans have been previously detected at sites associated with anthropogenic combustion,² including e-waste dismantling areas.³ Therefore, these novel brominated/chlorinated diphenyl ethers were proposed to be thermolytic transformation products of polybrominated diphenyl ethers (PBDEs) flame-retardants. However, we previously reported two NBCDEs (plus 47 organohalogens including 23 flame-retardants) in land-applied sewage sludge.⁴ In that earlier study, four sludge samples were collected from a Mid-Atlantic U.S. publicly owned wastewater treatment plant (WWTP) between 2002 and 2008. Decabromodiphenyl ether (BDE-209) was the major PBDE detected in each sample, ranging from 23 600 to 38 100 ng g⁻¹, dry weight. This WWTP treats domestic and industrial wastes, including that from an autointerior manufacturer. This facility was a large-scale user of Deca-BDE (primarily BDE-209). Yu et al. also detected in thermoplastics two NBCDEs (4'Cl-BDE-208 and 5'Cl-BDE-207) at 5–8% of that of the BDE-209 contribution. They hypothesized that NBCDEs can also be formed inadvertently during the manufacture of PBDE and chlorine-containing products (e.g., PVC). They also hypothesized that the NBCDEs detected in air and soil samples collected in their study may have also originated from this manufacturing process. This would suggest that waste from our autointerior manufacturer, heavily influenced by residuals derived from flame-retardant treated thermoplastics, should also contain NBCDEs. However, NBCDEs were only detected in the 2008 sludge sample, but not in the earlier (2002–2007) samples, even though they all contained considerable amounts of BDE-209. The ratio of NBCDEs to BDE-209 (unpublished data) in our 2008 sludge sample was also similar to ratios detected in the thermoplastics by Yu et al. We do not believe that autointerior manufacturing processes have changed dramatically over the course of our sample collection period. Hence, an alternative supposition is that NBCDEs were not inadvertently formed during manufacturing, but rather that the composition of the additive flame-retardant has changed. This hypothesis was previously introduced in La Guardia et al.⁴ and supported by details of an Albemarle Corporation Deca-BDE patent.⁵ The patent describes the cofeeding of diphenyl oxide, or partially brominated diphenyl oxide and bromine chloride with bromine or chlorine, into a refluxing reaction mixture of bromine and a Lewis acid bromination catalyst to produce >96% BDE-209 and up to 4% by weight of two NBCDEs.⁵ Similar to previous Deca-BDE formulations, this new product is used to flame-retard macromolecular materials, for example, thermoplastics, thermosets, cellulosic materials, and textile backcoating. Albemarle

Corporation is a global manufacturer and supplier of flame-retardants, located worldwide including Guangzhou China, the location of Yu et al. urban air sampling. PBDEs have been manufactured since the mid-1970, with Deca-BDE formulations contributing nearly one-quarter of the global brominated flame-retardant usage. They thus have had nearly 40 years to undergo thermolytic transformation processes, but NBCDEs have only recently been detected. While NBCDEs could be formed from chlorination of PBDEs through thermolysis, as suggested by Rupp and Metzger⁶ and Yu et al., we believe that a plausible alternative explanation is that they are impurities in the Albemarle Corporation product. The commercial introduction of this process also corresponds temporally with the initial detection of NBCDEs in abiotic matrixes.^{1,4} Between its introduction and 2014, when Deca-BDE U.S. production is scheduled to end,⁷ this "new" production process may thus produce significant volumes of NBCDEs.

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