

HBCD: Facts and insinuations

The Hexabromocyclododecane (HBCD) Industry Working Group—producers and users of the flame retardant HBCD—disagrees with some fundamental statements in a July 1, 2005, *ES&T* feature article by Law et al. (1). The article is a comprehensive and helpful review of recent work on HBCD from academic research groups. Unfortunately, the relevant information is prejudiced by some flawed facts and unsubstantiated conclusions. The following examples of these are not intended as a comprehensive list but aim to provide the reader with the scientific background to draw better-informed conclusions.

The article insinuates that HBCD is persistent or similar to a persistent organic pollutant, without providing a solid assessment. For instance, the authors write: “As with many other halogenated persistent organic pollutants (POPs), HBCD has been analyzed via GC/MS . . .” (1). This casual assertion of persistency is supported by neither the authors’ own data (2) nor other work (3–4). All three studies demonstrate a rapid degradation in the relevant compartments for all three diastereomers of the technical product. A thorough discussion of the available evidence would be more helpful for supporting a sound decision by regulators rather than an attempt to foreclose their conclusion.

The article also states: “HBCD has been detected . . . at very remote sites . . . suggesting . . . long-range atmospheric transport. This has been confirmed by the detection of HBCD, after atmospheric transport from Western Europe and Eastern North America, in polar bears from Greenland and Svalbard in the Arctic Ocean” (1). However, the original, referenced publication states: “There are large regional variations in concentrations in top predators with highest . . . HBCD in biota from regions influenced by atmospheric

transport from Western Europe and eastern North America. . . . Results for [polydiphenyl ethers] indicated that there are local sources . . . in the arctic. Further work is needed to evaluate the relevance of local sources” (5). A thorough assessment of the long-range transport potential of HBCD commissioned by industry concludes that HBCD has a very low potential to reach remote areas (6).

The HBCD Industry Working Group is concerned about monitoring data reporting HBCD in biota living in urban and remote areas. We are committed to elucidating the causes for the pattern, and an extensive monitoring program is under development. However, we will only be effective in our counteraction if we work closely along the lines of facts.

Another example is the constructed link between HBCD and hexachlorocyclohexane (HCH). Both substances, together with well over 300 others of the ~75,000 organic substances in the Syracuse database, are halogenated cycloaliphatics; an intrinsic property of an aliphatic compound is that it exists as diastereomers. Enantioselectivity is characteristic of biological processes, but it does not contribute to “clear parallels” between the two substances. In fact, there are essential discrepancies: HBCD is used mainly as a flame retardant in polystyrene insulation boards and the back coating of upholstery fabric, whereas HCH, an agricultural insecticide, has been used widely and at volumes that are an order of magnitude higher than HBCD production volumes. The authors claim that the production volume for HCH is 10,000 t/yr, whereas the International Agency for Research on Cancer reports 53,000 t/yr for the U.S. (1951); 54,500 t/yr for France, West Germany, and Spain (1973); 18,000 t/yr for the USSR (no year); and additional undisclosed volumes in Italy, Poland, Yugoslavia, Romania, and the former East Germany (7).

The article claims that according to Darnerud, (8) the “toxicological database for HBCD lacks relevant, high-quality studies”. The authors refer to conference presentations on results generated with nonvalidated methods, uncertain reliability, and doubtful relevance. However, relevant and high-quality studies on HBCD are in the public domain. Industry has volunteered to have HBCD evaluated in the frame of the U.S. EPA’s High Production Volume Challenge Program. Study summaries are publicly available (9), and the data have been reviewed by EPA (10). In the meantime, a revised study summary that includes more recent studies has been submitted (11). The reported exposures of fish and mammals are within the preliminarily predicted no-effect levels derived from these data for the respective species (12). All of these studies have been performed with the technical product. We disagree with the authors that these data do not sufficiently reflect “internal exposure”, which “may be dominated by other isomers” (1). Enantioselectivity is expected to also occur in tested animals, and the diastereomer selectivity has been confirmed in a series of studies (9).

In parallel to continuous emission control, the HBCD Industry Working Group prioritizes the understanding of both the environmental fate of HBCD and its degradation products and the contribution of potential emission sources in the life cycle of HBCD. A similar approach of conclusions and actions based on facts would have better served the original article.

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References for this letter are available as Supporting Information at <http://pubs.acs.org/est>.

Response

We appreciate the comments from Drohmann. Our article (1) was, of necessity, focused on the stereochemistry of HBCD and its implications for environmental analysis and assessment. It was not intended to be a comprehensive review of all aspects of the environmental chemistry and toxicology of HBCD. We are grateful, therefore, for the opportunity to present additional information on these aspects.

Drohmann argues that our statements regarding the persistence of HBCD are supported “by neither the authors’ own data nor other work.” In the Supporting Information for this letter (available on the web), Table S1 presents the available information on the degradability of HBCD. As Drohmann states, it is apparent that HBCD degrades much faster under anaerobic conditions than the persistence criteria currently in use, but under aerobic conditions degradation is much slower. In aerobic soils, one study found only 10% degradation over 112 days, whereas in another study the half-life was 63 days. However, in the latter study, activated sludge was mixed with the soil sample in order to “simulate conditions in which sludge is added to agricultural fields” (2). Such an addition makes this study inappropriate for drawing general conclusions about degradability in soils, and we regard the first study as more conclusive.

Usually a half-life of >6 months in soil is regarded as the cut-off point for rapid degradability, and so, on the basis of these data, HBCD is persistent. Further, the rapporteur of the draft EU risk assessment document, from KEMI (the Swedish Chemicals Inspectorate), argues that HBCD meets “the P-criterion [for persistence] due to slow transformation (sequential debromination) leading to an end-product (cyclododecatene), which itself is a PBT [persistent, bioaccumulative, and toxic] candidate. The ubiquitous presence of HBCD in the environment further supports the conclusion of HBCD being a P-substance” (3).

More data on the persistence and fate of the individual stereoisomers are needed. However, the fact that α -HBCD has been detected in the blubber of porpoises at concentra-

tions up to 9000 $\mu\text{g}/\text{kg}$ lipid weight argues very strongly for the persistence of this isomer, reflecting that in this case it has transferred from the source of discharge and bioaccumulated through an entire food chain to a marine top predator without degrading (4).

Drohmann’s letter also questions HBCD’s potential for long-range transport, concluding that a thorough assessment undertaken by industry finds that the compounds have “a very low potential to reach remote areas.” Although such modeling activities provide useful information, they are no substitute for real environmental measurements. We suggested that HBCD undergoes long-range atmospheric transport because of its detection in air samples from very remote sites in northern Sweden and Finland as well as the discovery of HBCD in polar bears from Greenland and Svalbard in the Arctic Ocean. Although there may be some local sources, the human population levels in these areas are probably too small to explain the environmental levels observed. In addition, HBCD has been detected in other remote areas (see Table S2). Amongst these, local sources can be entirely ruled out for the HBCD detected in fish from Swiss mountain lakes. It is clear from these studies that long-range transport of HBCD via the atmosphere occurs, but its importance relative to other sources and transport routes remains to be established.

Drohmann’s letter also tries to take the comparison of HBCD and HCH far beyond our original intentions. Our point was that both are or were high-production-volume chemicals, with a clear parallel in their stereochemistry. The differing behavior of HCH stereoisomers was found to contribute to their environmental occurrence and significance, and we were keen to ensure that this aspect was not neglected in studies on HBCD. For this reason, we urged “all environmental scientists to use LC/MS in all applicable studies and to adopt a diastereoisomer- and enantiomer-specific approach to HBCD analysis” (1).

Drohmann also says that “relevant and high-quality studies on [the toxicity of] HBCD are in the public domain,” whereas our article indicated that the “toxicological database for HBCD lacks relevant,

high-quality studies,” citing a paper by Darnerud (5). In fact, Darnerud stated that “there is a lack of relevant studies of high quality that could form a basis for risk assessment of this compound” (5).

In our view, this lack is manifested in two ways. First, all studies to date have focused on the technical product, which is dominated by the γ -HBCD isomer, whereas in biota the dominant congener (often >90% of the total) is the α -HBCD isomer. Moreover, studies to date have been primarily focused on acute toxicity; hence, the database on non-lethal effects is incomplete.

The major concern of the industry working group seems to be the possible future consideration of HBCD as a potential Persistent Organic Pollutant (POP). From the information currently available, we consider that it is clear that HBCD is a persistent organic pollutant (all in lowercase), but it remains to be seen whether it will be categorized as a POP within the more restrictive definitions of the relevant conventions.

As requirements for a comprehensive risk assessment of the continued use of HBCD, we should highlight the need for more information on neurotoxicology, developmental toxicity, and the potential for endocrine disruption. We are pleased that the industry group is committed to further elucidating the environmental fate of all HBCD diastereoisomers, and we look forward to working in parallel with them toward the goal of an effective assessment of the risks associated with the continued production and use of HBCD.

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