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Chemical Alternatives Assessment:

The Case of Flame Retardants

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Abstract

Decisions on chemical substitution are made rapidly and by many stakeholders; these decisions may have a direct impact on consumer exposures, and, when a hazard exists, to consumer risks. Flame retardants (FRs) represent particular challenges with very high volumes, designed-in persistence, and often direct consumer exposure. Newer FR products, as with other industrial chemicals, typically lack data on hazard and exposure, and in many cases even basic information on structure and use in products is unknown. Chemical Alternatives Assessment (CAA) provides a hazard-focused approach to distinguishing between possible substitutions; variations on this process are used by several government and numerous corporate entities. By grouping chemicals according to functional use, some information on exposure potential can be inferred, allowing for decisions based on those hazard properties that are most distinguishing. This approach can help prevent the “regrettable substitution” of one chemical with another of equal, or even higher, risk.

Keywords

alternatives assessment

hazard assessment

chemical substitution

flame retardants

TB117

1. Introduction

Chemical Alternatives Assessment (CAA) is one application of the broader process of alternatives assessment. The CAA approach is being used by the United States Environmental Protection Agency to inform safer substitution decisions, and other government entities (including the European Union) are beginning to require similar processes. Several companies and trade organizations use CAA to inform their own internal chemical substitution decisions. This paper will describe the CAA methodology, demonstrating its utility for the specific case of flame retardants, and highlighting some of the differences between alternatives assessment and risk assessment frameworks. In particular, the preference for an alternatives assessment or a risk assessment approach may derive in part from a stakeholder's views about the efficacy of exposure controls in managing risk.

1.1 Flame Retardants

Flame retardants (FRs) pose numerous risk management challenges. FRs belong to several classes of chemistry and structure; are produced in very high volumes; and, out of functional necessity, are typically designed to be persistent. In many applications, including home furnishings and consumer electronics, consumers have direct exposure to FRs in the product itself or as the FRs migrate out of the product. Many FRs, notably the polybrominated diphenyl ethers (PBDEs), have been found in environmental and biological monitoring, making them of interest to nongovernmental health and environment organizations (NGOs) as well as to regulators. The largest set of data is available for PBDEs, due to their relatively early

identification and very widespread use; but in recent years, replacement FRs are reaching the levels of ubiquitous exposure that first raised flags for PBDEs a decade ago. If these substitutions have lower hazard, they may be expected to pose less risk to consumers. Most replacements, however—with a few exceptions like tris(1,3-dichloro-2-propyl) phosphate (TCDPP)—are of more recent origin and hence much less studied; indeed, most newer industrial chemicals are unlikely to be studied for toxicity in any rigorous way (Grandjean and Landrigan 2006). Information on exposure may be even less common. Egeghy et al (2012) report that only 20% of chemicals for which hazard data exists have any exposure information at all—and in most of these cases, available exposure information consists of very basic descriptors like production volume.

The use of pentabrominated diphenyl ether (pentaBDE) in foam furnishings has been largely driven by California's Technical Bulletin 117 (1975), which requires small (candle-sized) open flame testing of uncovered foam samples, necessitating the use of flame retardants (BHF 2000). Because manufacturers prefer not to reformulate products for separate markets, TB117 appears to have become a *de facto* national standard (Stapleton et al 2012). (In November 2013, California approved revisions to the TB117 standard. The new standard replaces the flame test with a smolder test, which will allow, but not compel, manufacturers to reduce FR loads in furniture foam; see BHFTI 2013.) PentaBDE was phased out voluntarily by the only US manufacturer, Great Lakes (now Chemtura), under pressure from EPA and environmental NGOs, at the end of 2004 (USEPA 2012). Shortly thereafter, EPA published a Significant New Use Rule to prevent future use of pentaBDE in this market segment (although the rule does not restrict import of products containing pentaBDE).

This phase-out appears to have been effective in reducing consumer exposure to pentaBDE, according to measurements in house dust (Dodson et al 2012) and in samples taken from furniture (Stapleton et al 2012). The most commonly used alternatives have been TDCPP, which had seen widespread use in concert with pentaBDE before the phase-out, and Firemaster 550 (FM550), a blend of two brominated and two phosphate-based FRs (Stapleton et al 2012).

As part of EPA's action on pentaBDE, EPA's Design for the Environment (DfE) branch convened the Furniture Flame Retardancy Partnership (FFRP) in 2003 to assess alternatives to pentaBDE for use in furniture foam (USEPA 2005). This project was an early attempt to use alternatives assessment to provide important hazard information on all known available alternatives, including TDCPP and FM550.

2. Discussion

2.1 Chemicals Alternatives Assessment

“Alternatives assessment” encompasses a wide-range of decision-making tools and has been described elsewhere (O'Brien 2000). More specifically, chemical alternatives assessment (CAA), as described by Lavoie et al (2010), applies a hazard framework to inform decision-making around chemical substitution; this definition will be used here. There are a number of variations on alternatives assessment processes, but they share some key features.

- The key aim of CAA is to avoid “regrettable substitution”, that is, the unwitting selection of an alternative that poses equal or higher risk.
- CAAs compare numerous options at once, whereas risk assessment typically treats chemicals singly (often in greater depth).
- CAAs are intended to be quicker and simpler than risk assessments, generally by focusing on hazard evaluation, avoiding the complexities of exposure assessment (although the addition of information on exposure and persistence may help prioritize alternatives).
- CAAs, and AAs in general, are intended to lower risks by encouraging selection of chemicals and processes with the lowest available hazard profiles. This contrasts with a more traditional risk assessment approach of keeping risks below a threshold by managing exposures.

Most descriptions of alternatives assessment processes also stress the importance of process transparency, the value of stakeholder participation, and the goal of continuous improvement (Rossi et al 2006).

Alternatives assessment can be seen as an overarching approach to decision making, within which specific tools like hazard-oriented CAA and life-cycle assessment are applied to evaluate alternatives along endpoints of interest (Elizabeth Sommer, USEPA Design for the Environment, personal communication). AAs performed by different users with different needs might address

any of a diverse set of endpoints ranging from physical and chemical hazards, to fate and transport in the environment, to lifecycle impacts. Given the range of endpoints, and of tools used to distinguish among them, AA is not an easily defined process, but varies in depth and complexity. Even within the realm of hazard, often considered to be the principal concern of AA, there are a large number of human health and environmental endpoints that might be considered. Tools applied to assess an endpoint might range from a comparison with various “red lists” of chemicals of concern, to a literature-based hazard screen, or even to a comprehensive evaluation of risk. Regardless of this variety, however, and fundamental to the idea of alternatives assessment, any AA should first start with an assessment of the need for the chemical function under study: For example, assessing whether FRs added to products are effective in improving fire safety characteristics or in increasing escape times.

The DfE Alternatives Assessment process is an example of a hazard-oriented CAA process for informing chemical substitution decisions; this approach is primarily concerned with human health and environmental toxicity endpoints over the entire lifecycle. The DfE process examines endpoints for human and environmental toxicity as well as persistence and bioaccumulation (see Table 1). DfE’s goal is to provide information to support decision-making by other stakeholders, especially manufacturers; its assessments focus on describing alternatives to chemicals which have been identified by other actors, whether within EPA or internationally, for possible regulation or substitution. (EPA does not use the CAA methodology to make regulatory decisions.) For example, hexabromocyclododecane (HBCD), for which DfE published a draft alternatives assessment in the fall of 2013, is not yet the subject of regulation in the US, but has been listed by the EU as a Substance of Very High Concern (SVHC), requiring US

manufacturers to find an alternative to stay competitive in the global market. DfE's CAAs do not make recommendations about specific choices, in part because considerations of performance, efficacy, and cost fall outside the branch's expertise, and are best left to manufacturers. However, DfE's process does include extensive consultation with chemical and product manufacturers to ensure, as far as possible, that all appropriate chemicals are assessed, and that those chemicals assessed are appropriate to the functional use class in terms of efficacy and practicality. In this sense, the scoping of the DfE CAA incorporates basic information about performance and feasibility.

Within the category of flame retardants, DfE has published, or is in the process of writing, assessments of alternatives to pentaBDE in furniture foam; to HBCD in expanded and extruded polystyrene foam; to tetrabromobisphenol A (TBBPA) in circuit boards; and to decabrominated diphenyl ether (decaBDE) in a variety of uses. In each case, as manufacturers seek substitutes for chemicals being phased out or otherwise under pressure, the goal is to avoid "regrettable substitution". In this sense, DfE's goals may be seen as aligned with those of industry, since both would prefer a choice of substitute that would preclude the need for later regulation.

2.2 Hazard Assessment and Risk Assessment

Risk is usually defined as a function of both hazard and exposure. While risk assessment cannot change the hazard properties of a chemical, it can identify risk levels expected to be associated with different exposure scenarios, and those risks can sometimes be mitigated via exposure

controls. By contrast, the emphasis of CAA is that risk can be more effectively lowered by reducing hazard. The hazard-oriented approach aligns with several of the principles of green chemistry: That chemical products should have minimal toxicity; that their synthesis should involve as little toxicity as possible; and that prevention is better than cleanup (Anastas and Warner 2000).

These approaches reflect different philosophies about exposure. Cordner (2013) describes the different perspectives of government and industry about exposures:

For the chemical industry, defining exposure includes exposure potential, documented exposure, and the integration of this information with hazard data to determine whether the dose reaches level of concern.

... in contrast ... EPA researchers and regulators argued that exposure is difficult to manage. An axiomatic position for some at EPA is, “exposure controls can, do, and will fail.” This echoes Perrow’s (1984) classic argument about ‘normal accidents.’ If problems are not identified ahead of time, exposure controls are useless once widespread exposure exists.

The views described here, while not necessarily shared by all EPA employees, represent several common concerns about exposure. First, assessment of real-world exposures is famously difficult, and variability and unknowns in exposure assessment are major sources of uncertainty in risk assessment. The second point expressed in Cordner’s interviews, that exposure controls

will sometimes fail, needs no demonstration. This category includes exposures ranging from ill-fitting personal protective equipment, to “routine” accidental releases reported under the EPA’s Toxics Release Inventory program, to the 2012 railway accident that plunged four rail cars into Mantua Creek, New Jersey, releasing 87,000 L of vinyl chloride (NOAA undated).

An additional critique of exposure controls is the idea that unanticipated exposure scenarios may prove to be important. Carignan et al (2013) vividly demonstrate an example of this problem with a recent study of female gymnasts, who practice routines in pits filled with foam “pit blocks”. The study found that the pit blocks, presumably manufactured to meet the TB117 standard, contained high loads of FRs including pentaBDE, FM550 (identified by its brominated components), and TDCPP. Concentrations of these FRs in gym dust samples were elevated compared to Boston residences, and gymnasts had serum levels of PBDE congeners significantly higher than background levels in the US population, in some cases comparable to levels in workers occupationally exposed to foam. These unforeseen exposures to girls and young women in sensitive developmental stages highlight the difficulties of a comprehensive exposure assessment.

In short, a risk assessment perspective sees exposures as controllable; a hazard-oriented view anticipates that some exposure is likely to occur, and that reducing hazard is a more effective way to reduce risk. While the EPA relies on risk assessment for regulatory decisions, DfE’s CAAs are important in highlighting hazard differences between substitutable chemicals.

2.3 Comparisons by Functional Use

When comparing a number of alternatives, “the most valuable end points are those that reveal significant variation in toxicity among alternatives; these end points are ‘distinguishing’ and make it possible to differentiate ‘safer’ from ‘less safe’” (Lavoie et al 2010). Which characteristics are “distinguishing” depends on many factors. Among potent chelating agents, for example, algal toxicity is a concern due to the effectiveness of some chelating agents in sequestering nutrients (Schowanek 1996), but that concern can be mitigated by rapid degradation, which is therefore a distinguishing characteristic. In the case of FRs, persistence is not a distinguishing characteristic, since virtually all FR chemicals are designed to be persistent to provide protection over the lifetime of a product; in these cases human and ecological toxicity can be distinguishing. While evaluations are made for all endpoints, the emphasis is on those endpoints for which hazard rankings differ. In this way, the CAA provides information directly relevant to decision-making among chemicals which provide the same functional role in a product.

The idea that lowering hazard lowers risk entails the assumption that exposure stays constant (or decreases). Lavoie cites an assumption that exposures within a functional use class are roughly constant. The functional use class is typically defined based on the chemical being substituted out. For example, additive discrete (non-polymeric) flame retardants used in flexible polyurethane furniture foam, replacing pentaBDE, constitute a functional use class. Chemicals within the class are expected to have similar patterns of use, consumer contact, and disposal; in the case of furniture foam FRs, this involves high (~ several percent) loadings of FRs in

furnishings, migration out of the product and into the home microenvironment, and consequent exposure to consumers. Similar patterns of use and consumer contact can be expected of any additive discrete FR successfully substituted in these products.

If, in addition to similar patterns of use, chemicals being compared have similar physical properties and chemical structures, the exposure potential (i.e., fate, transport, bioavailability, bioaccumulation) would be similar across the class, and a risk assessment would simplify to a hazard assessment. In some cases, this is a reasonable assumption. For example, many new FRs consist of very similar molecules: triphenyl phosphate (TPP), isopropylated, methylated, and other alkylated TPP derivatives have all been identified in furniture foam (Stapleton et al 2012; USEPA 2013b). These related FRs are likely to have very similar exposure characteristics.

Within the broad category of furniture foam FRs, however, DfE assesses halogenated organics, non-halogenated phosphate-based organics, metal- and metal-oxide-based inorganics, polymeric FRs, and some very different chemistries like intumescent expandable graphite (USEPA 2013b). These groups represent a very wide variety of fate and transport parameters. The problem of comparing exposures is mitigated to some extent by the fact that the most desirable alternatives, from the perspective of the foam manufacturer, are the drop-in chemical substitutes. In polyurethane foam manufacturing, a drop-in substitute must have viscosity and size within a narrow range: polymeric FRs, with their very different viscosity, or expandable graphite flakes, too large to fit through spray nozzles, cannot be used with current foam production techniques. These products do not lend themselves to drop-in substitution, nor to an exposure analogy with

pentaBDE; therefore, at least from the manufacturer perspective, they may be seen as falling outside the functional use class.

The closer an alternative is to a drop-in solution, the better an exposure analog it is likely to be; in these cases exposure potential itself is not a distinguishing characteristic, and chemicals in the class can be considered as exposure analogs, in the same way that risk assessors choose a hazard analog in assessing toxicity endpoints for which no data is available. A CAA can then focus on hazard differences. Some drop-in substitutes will be so closely related as to have similar hazard properties, but this is not necessarily the case, as drop-in functionality is often driven by bulk properties like viscosity rather than by structure. Even when drop-in substitutes are structurally similar, there may be distinguishing hazard endpoints: For example, methylated TPP mixtures may contain *ortho*-substitutions including tri-*o*-cresyl, a structurally-specific and potent cause of organophosphorus ester-induced delayed neurotoxicity (Weiner and Jortner 1999).

The choice of a lower hazard alternative with lower exposure potential—e.g., less migration from foam—should generally, although not necessarily, result in lower risk. Choice of a lower hazard alternative with increased exposure potential, however, might not result in a reduced risk. There is also the related problem of performance: A lower-hazard substitute with lower efficacy in its functional performance may require use of more chemical (e.g. a higher load of FR in the product), possibly leading to higher exposure.

2.4 Challenges of Chemical Alternatives Assessment

The most substantial difficulties with hazard assessment, as with risk assessment, derive from a lack of data.

2.4.1 Lack of information about chemical identities

The structure of a flame retardant product, particularly newer products, is often proprietary information. For example, the components of FM550, a major pentaBDE replacement, were unknown until the brominated components were identified by Stapleton et al (2008), and the isopropylated triphenylphosphate components several years later (Klosterhaus et al 2010). Such identification is necessarily made after the product has seen widespread introduction, until which time these chemicals cannot be studied by independent and academic researchers. This may be one reason for the “Matthew Effect” described by Grandjean et al (2011), whereby researchers focus on prominent known chemicals despite the need for information on newer or less well known exposures.

Because all chemicals must be identified to EPA via the Premanufacture Notice (PMN) program before commercial production, EPA’s DfE program is uniquely suited to perform alternatives assessments on proprietary products. DfE’s approach is to evaluate proprietary ingredients, reporting hazard data without revealing structural information. Unfortunately, this means that nongovernmental actors must depend on EPA’s ability and willingness to assess hazards of proprietary products, and have limited ability to act independently.

This protection of structural information pervades the complex supply chain; in particular, chemical manufacturers with novel products have strong motivation to protect their intellectual property (IP) from off-label producers. Conversations with DfE stakeholders indicate that FR manufacturers are typically unwilling to supply details about their products, restricting available data to basic physical/chemical properties and MSDS sheets, a problem that has been described before (GC3 2011). Counterexamples exist, however. Dow Chemical's alternative to HBCD, a block copolymer of polystyrene and brominated polybutadiene, has been fully disclosed, and its manufacture licensed to Great Lakes, ICL Industrial Products, and Albermarle under various trade names (USEPA 2013c). As analytical techniques continue to improve, protection of IP by nondisclosure—an approach derided as “security through obscurity” in the field of computer security—may become untenable, leading manufacturers to rely instead on legal means of IP protection and on continual innovation. Such a shift would be a boon to transparency of information through the supply chain, as well as to consumers and nongovernmental evaluators, and would likely benefit most the suppliers with the most innovative and least hazardous products.

2.4.2 Lack of hazard data

Even when structures are known, little data on either hazard or exposure is available for the majority of chemicals; most of the alternatives studied by DfE are extremely data-poor. EPA's *Chemistry Assistance Manual for Premanufacture Notification Submitters* reports that between 1979-1985, 41% of non-polymer PMN submissions, and 70% of polymer PMN submissions,

contained no test data at all; the report asserts that “Current [i.e., 1997] trends in test data submissions are similar” (USEPA 1997). In many cases, data submitted consists of confidential studies, available (as with other forms of proprietary data) to EPA but not to external stakeholders. As with other limitations of hazard assessment, of course, this lack of data applies equally to risk assessment. DfE fills data gaps with models, with data from structural analogies to known chemicals, and with information about specific structural alerts based on known moieties; many of the tools used by DfE were developed by the EPA’s New Chemicals Program for the evaluation of chemicals regulated under the Toxic Substances Control Act. (For more details about the DfE process, see Lavoie et al 2010.)

2.4.3 Lack of data on exposure and on chemical use in products

While few chemicals have any substantial exposure data available (Egeghy et al 2012), there is an even more significant lack of data on the product level, since there is no required reporting of chemicals used in most consumer products (exceptions exist, including California’s Proposition 65, California’s Safe Cosmetics program, and labeling requirements set by the U.S. Food and Drug Administration for many personal care products). For information about what chemicals are used to supply a given function, DfE relies on voluntary disclosure by manufacturers, on reports from other agencies (e.g., the Consumer Product Safety Commission), and on academic researchers who have sampled products and reported their results. Without detailed voluntary disclosure, these inventories are likely to miss up-and-coming substitutions, and in many cases information on chemical uses in products is simply unavailable, especially to stakeholders

outside EPA. For example, although much media and regulatory attention has recently been given to FRs in home furnishings, very little attention has been dedicated to furniture in public spaces like offices or schools. Recent sampling has identified decaBDE and HBCD in textile backcoatings in furniture sampled from colleges and universities (Heather Stapleton, personal communication). Without this type of detailed knowledge of sources, any attempt at exposure assessment will remain incomplete.

2.4.4 Exposure considerations within a hazard-based approach

Hazard is only one aspect of risk. While the assessment of chemicals within a functional use class gives a first estimate of exposure, a more nuanced approach will often be necessary. For example, some hazards are limited by route of exposure. A recent study of aloe vera found significant intestinal irritation in rats and mice, and cancer in rats, at high doses (Boudreau 2013). If borne out, such results might earn aloe vera a hazard ranking that would eliminate it from products under any strict standard intended to eliminate carcinogens; but it is not clear that applying an intestinal carcinogenicity finding to topical uses would be an appropriately protective decision, given the context of complex but often positive data for aloe vera's dermal properties. While there is value in reducing the use of hazardous chemicals, there is also room for practical considerations, such as differential toxicity via route of exposure, that would allow for reasonable and nuanced decision-making.

3. Conclusion

Decisions on chemical substitution and use made by stakeholders throughout the value chain have a direct impact on consumer exposures, and, when a hazard exists, to consumer risks; in addition, governmental and nongovernmental actors make decisions that influence chemical use. Especially in the case of chemicals with extremely large production volumes and direct consumer exposure, like flame retardants, rapid and accurate tools are needed to support decision-making by stakeholders of all types.

Decisions on substitutions can often be made very quickly, driving a need for assessment tools than can be implemented more quickly than a risk assessment. California added TDCPP to its Proposition 65 list in October 2012, citing concerns of carcinogenicity (Cal/EPA 2012); the following month, ICL Industrial Products announced that it would discontinue TDCPP sales for upholstered home furnishings as of the beginning of 2013 (PR Newswire 2012). The ingredients of ICL-IP's replacement products for upholstered polyurethane foam are proprietary.

CAA can be a valuable way to inform decisions on chemical substitution. Alternatives grouped by functional use are likely to have similar patterns of exposure to consumers, although their fate and transport properties may result in divergent risks. In the case of structurally similar drop-in substitutions, exposure itself is unlikely to be a “distinguishing characteristic”, in which case decisions based on hazard (or on intrinsic exposure properties like persistence) can be an effective way to reduce risk. A well-defined functional use class provides insight into exposure

potential, and comparing hazard information within the class allows for the selection of those options with the lowest risk, rather than simply meeting a risk threshold. In the many cases where no hazard data exists, estimation methods must be used to characterize potential hazard, with uncertainties clearly described.

While CAA emphasizes the evaluation of hazard, some consideration must also be given to exposure routes, fate and transport, and other exposure-related parameters, as well as to practical factors like performance, efficacy, and benefit. The European Union's REACH program provides one example of such an approach. The designation of a chemical as an SVHC is largely based on hazard endpoints (carcinogenicity, PBT, vPvB). SVHCs can then be moved to Annex XIV, a list of chemicals requiring authorization for use after a specified sunset date. A manufacturer requesting authorization for continued use of an Annex XIV chemical must submit an assessment of alternatives, including their likelihood of reducing overall risks and their technical feasibility. This approach is designed to reduce use of chemicals with higher intrinsic hazards, while potentially allowing for continued use of an SVHC in cases where the benefit-risk tradeoff is substantial (ECHA undated).

Hazard assessment is only one approach to the broader process of alternatives assessment. The endpoints evaluated in an AA may vary widely for different stakeholders depending on their needs and interests. For example, carbon footprint might be the primary endpoint of interest in an energy-oriented AA process. The tendency of some authors to conflate the terms "alternatives assessment" and "chemical substitution" should be resisted, keeping in mind the much broader scope of alternatives assessment. A broad approach to AA requires first an

evaluation of the need for the function under study; for example, assessing the utility and efficacy of FRs. (In the case of flame retardants in furniture, such an assessment has essentially been rendered moot by California's TB117, which, until 2014, effectively required FRs for furniture foam.) A full AA would also require consideration of alternative methods for meeting the functional need. The Consumer Product Safety Commission has shown some interest in this approach in its 2008 proposal for a national furniture flame retardancy standard (CPSC 2008), which could have been met by FRs in foam, by internal fire barriers, or by backcoating the upholstery. (Since the CPSC standard is performance-based, however, it would not preclude increased loading of FRs in foam as an approach to meet a flammability test.) DfE's assessments, while emphasizing hazard-focused chemical substitution, do typically give a brief description of alternative means of providing the same function. However, the hazards that might be associated with different construction techniques—e.g., that might be due to an internal fire barrier—are not easily comparable to those due to additive chemical FRs in foam; these represent very different functional use classes.

Is hazard assessment effective? Processes like the one described here have been used by a wide range of stakeholders. The GreenScreen benchmarking system, which builds on DfE's CAA methodology, has been incorporated into the latest Leadership in Energy and Environmental Design (LEED v4) green building standard (USGBC 2013). The Outdoor Industry Association, a trade association in the outdoor recreation industry, promotes chemical hazard assessment as a key component of an overarching Chemicals Management Framework (OIA 2013).

Manufacturers like Hewlett-Packard use CAA to inform selection of chemical uses in products, both to meet narrow regulatory requirements as well as to select environmentally preferable

materials, “ensuring their long-term freedom from chasing chemical after chemical for elimination” (Lavoie et al 2010). In principle, the views of manufacturers and government on regrettable substitution are aligned: Both would prefer to prefer selection of a chemical that will not require future regulation. In practice, industry’s motivation to use drop-in substitutes is likely to be driven by substantial investment in a particular process (e.g., slabstock polyurethane foam manufacturing); substitutes requiring new investment may be more difficult to implement. This emphasis on drop-in substitution does, however, lend itself to CAA, since these are the chemicals for which exposure potential is most likely to be similar.

While CAA can help inform decision-making, the process—like risk assessment—suffers from an extreme paucity of data, whether on the identity of possible substitutes, on their use in products, or on their human and environmental toxicity. In the USA, this gives EPA a special and critical role in hazard assessment, since structural information and confidential toxicity data is available to assessors within the agency. A shift by chemical manufacturers to a more open approach would benefit everyone with a need to evaluate chemicals, and would favor the most innovative, lowest-hazard alternatives.

Many chemical decision-making processes are designed to move users away from negative outcomes, risks, or liabilities. “Red lists” of chemicals of concern emphasize the deselection of known bad actors; risk assessment is based on the mitigation of anticipated negative outcomes. But decision-making based simply on running away from bad choices without evaluation of the alternatives puts us at risk of regrettable substitution, and “treating all unrestricted substances as equally viable greatly increases the risk of unintended consequences” (Lavoie et al 2010).

Alternatives assessment, along with the principles of green chemistry, points us in a different direction. Rather than running away from the bad, we need to identify, and move towards, the better: Chemicals with low intrinsic hazard and greatly reduced risk.

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References

Anastas PT, Warner JC. 2000. Green Chemistry: Theory and Practice. New York: Oxford University Press. ISBN-13: 978-0198506980

BHF (Bureau of Home Furnishings, Department of Consumer Affairs, State of California).

2000. Technical Bulletin 117: Requirements, test procedure and apparatus for testing the flame retardance of resilient filling materials used in upholstered furniture.

<http://www.bhfti.ca.gov/industry/117.pdf>

- BHFTI (Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation, Department of Consumer Affairs, State of California). 2013. Technical Bulletin 117-2013. http://www.bearhfti.ca.gov/about_us/tb117_2013.pdf
- Boudreau MD, Mellick PW, Olson GR, Felton RP, Thorn BT, Beland FA. 2013. Clear evidence of carcinogenic activity by a whole-leaf extract of *Aloe barbadensis* miller (aloe vera) in F344/N rats. *Toxicol Sci.* 131:26-39. doi:10.1093/toxsci/kfs275.
- Cal/EPA (California Environmental Protection Agency). 2012. Amendment to Section 25705(B) No Significant Risk Level (NSRL) for tris(1,3-dichloro-2-propyl) phosphate (TDCPP). Office of Environmental Health Hazard Assessment. <http://oehha.ca.gov/prop65/law/100912tdcpp.html>
- Carignan CC, Heiger-Bernays W, McClean MD, Roberts SC, Stapleton H, Sjödin A, Webster TF. 2013. Flame retardant exposure among collegiate United States gymnasts. *Environ Sci Technol* 47:13848-56. [dx.doi.org/10.1021/es4037868](https://doi.org/10.1021/es4037868)
- Cordner A. 2013. Defining and Defending Risk. In *Risk, Power and Policy in Environmental Health Controversies: The Social Implications of Flame Retardant Chemicals*, unpublished PhD dissertation. Department of Sociology, Brown University, Providence, RI.
- CPSC (Consumer Product Safety Commission). 2008. 16 CFR Part 1634: Standard for the Flammability of Residential Upholstered Furniture; Proposed Rule. <http://www.cpsc.gov/PageFiles/96693/furnflamm.pdf>
- Dodson RE, Perovich LJ, Covaci A, Van den Eede N, Ionas AC, Dirtu AC, Brody JG, Rudel RA. 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house

dust samples from California. *Environ Sci Technol.* 46:13056-66.

doi:10.1021/es303879n.

ECHA (European Chemicals Agency). Undated. Authorization.

<http://echa.europa.eu/regulations/reach/authorisation>

Egeghy PP, Judson R, Gangwal S, Mosher S, Smith D, Vail J, Cohen Hubal EA. The exposure data landscape for manufactured chemicals. 2012. *Sci Total Environ.* 414:159-66. doi: 10.1016/j.scitotenv.2011.10.046. Epub 2011 Nov 21.

GC3 (Green Chemistry and Commerce Council). 2011. Meeting customers' needs for chemical data.

http://www.greenchemistryandcommerce.org/downloads/GC3_guidance_final_031011.pdf

Grandjean P, Eriksen ML, Ellegaard O, Wallin JA. 2011. The Matthew effect in environmental science publication: a bibliometric analysis of chemical substances in journal articles.

Environ Health. 10:96. doi:10.1186/1476-069X-10-96.

Grandjean P, Landrigan PJ. 2006. Developmental neurotoxicity of industrial chemicals.

Lancet. 368:2167-78. doi:10.1016/S0140-6736(06)69665-7

Klosterhaus S, Stapleton HM, La Guardia M, Davis E, Eagle S, Blum A. 2010. Recent studies on the identification and occurrence of pentaBDE replacement chemicals in indoor and outdoor environments. Fifth International Symposium On Flame Retardants, April 7-9 2010, Kyoto.

Lavoie ET, Heine LG, Holder H, Rossi MS, Lee RE, Connor EA, Vrabel MA, Difiore DM, Davies CL. 2010. Chemical alternatives assessment: Enabling substitution to safer chemicals. *Environ Sci Technol.* 44:9244-9. doi:10.1021/es1015789.

NOAA (National Oceanic and Atmospheric Administration). 2012. A train derails in Paulsboro, NJ, releasing 23,000 gallons of toxic vinyl chloride gas. Office of Response and Restoration. <http://response.restoration.noaa.gov/about/media/train-derails-paulsboro-nj-releasing-23000-gallons-toxic-vinyl-chloride-gas.html>

O'Brien M. 2000. *Making Better Environmental Decisions: An Alternative to Risk Assessment.* Cambridge, Mass: The MIT Press. ISBN-13: 978-0262650533.

OIA (Outdoor Industry Association). 2013. Chemicals Management Framework Pilot. April 22, 2013. <http://www.outdoorindustry.org/responsibility/chemicals/cmpilot.html>

PR Newswire. 2012. ICL to increase production of polymeric flame retardant at West Virginia facility. November 13, 2012. <http://www.prnewswire.com/news-releases/179095971.html>

Rossi M, Tickner J, and Geiser K. 2006. *Alternatives Assessment Framework, Version 1.0.* Lowell Center for Sustainable Production, University of Massachusetts Lowell. <http://www.chemicalspolicy.org/alternativesassessment.lowellcenter.php>

Schowanek D, McAvoy D, Versteeg D, Hanstveit A. 1996. Effects of nutrient trace metal speciation on algal growth in the presence of the chelator [S,S]-EDDS. *Aquatic Toxicology* 36:253-275.

- Stapleton HM, Sharma S, Getzinger G, Ferguson PL, Gabriel M, Webster TF, Blum A. 2012. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. *Environ Sci Technol.* 46:13432-9. doi:10.1021/es303471d.
- USEPA (United States Environmental Protection Agency). 2005. Chemistry assistance manual for Premanufacture Notification submitters. Office of Pollution Prevention & Toxics, New Chemicals Program. <http://www.epa.gov/oppt/newchemicals/pubs/chem-pmn/>
- USEPA. 2005. Environmental profiles of chemical flame-retardant alternatives for low-density polyurethane foam. Office of Pollution Prevention & Toxics, Design for the Environment. <http://www.epa.gov/dfe/pubs/flameret/altrep-v1/altrepv1-f1c.pdf>
- USEPA. 2011. Design for the Environment Program alternatives assessment criteria for hazard evaluation, Version 2.0. Office of Pollution Prevention & Toxics, Design for the Environment. http://www.epa.gov/dfe/alternatives_assessment_criteria_for_hazard_eval.pdf
- USEPA. 2012. Polybrominated diphenylethers (PBDEs) Significant New Use Rules (SNUR). Office of Pollution Prevention & Toxics, Design for the Environment. <http://www.epa.gov/oppt/existingchemicals/pubs/qanda.html>
- USEPA. 2013a. TSCA Work Plan Chemicals. Office of Pollution Prevention & Toxics. <http://www.epa.gov/oppt/existingchemicals/pubs/workplans.html>
- USEPA. 2013b. Flame retardants to be evaluated in the DfE Furniture Flame Retardancy update. Office of Pollution Prevention & Toxics, Design for the Environment. <http://www.epa.gov/dfe/pubs/flameret/ffr-alt.htm>

USEPA. 2013c. Flame retardant alternatives for hexabromocyclododecane (HBCD). Office of Pollution Prevention & Toxics, Design for the Environment.

<http://www.epa.gov/dfe/pubs/projects/hbcd/hbcd-draft-full-report.pdf>

USGBC (U.S. Green Building Council). 2013. LEED v4. <http://www.usgbc.org/leed/v4>

Weiner ML, Jortner BS. 1999. Organophosphate-induced delayed neurotoxicity of triarylphosphates. *Neurotoxicology*. 20(4):653-73.

<http://www.ncbi.nlm.nih.gov/pubmed/10499364>

Table 1. Human and environment endpoints evaluated by DfE (USEPA 2011; USEPA 2013c). (While DfE sometimes considers additional endpoints, specific criteria are available for those listed here.)

<p>Human health effects</p> <ul style="list-style-type: none">• Acute mammalian toxicity• Carcinogenicity• Mutagenicity/genotoxicity• Reproductive• Developmental toxicity (including developmental neurotoxicity)• Neurotoxicity• Repeated-dose toxicity• Respiratory sensitization• Skin sensitization• Eye irritation/corrosivity• Skin irritation/corrosivity• Endocrine activity <p>Environmental toxicity and fate</p> <ul style="list-style-type: none">• Aquatic toxicity: Acute• Aquatic toxicity: Chronic• Environmental persistence• Bioaccumulation <p>Additional endpoints</p> <ul style="list-style-type: none">• Physical hazards• Other forms of ecotoxicity: Avian, bees
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