Toward fire safety without chemical risk

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chondrites. Now that Hayabusa2 has landed on Ryugu, there is the prospect of sampling the planetesimal's material in situ. Luckily, collisions and planetary gravity scattered Ryugu from the main belt of asteroids and made it a near-Earth object, which is much easier to reach, orbiting the sun at approximately the same distance as Earth.

Kitazato *et al.* report on spatially resolved near infrared spectra of the surface of Ryugu. These spectra are sensitive to the minerals composing the asteroid. The spectral data are rich in hydroxyl groups (OH), implying that water was present in the past, and likely lead to an aqueous alteration of what probably were dry minerals before. Some degree of thermal- or shock-induced metamorphosis also can be deduced from the data. This all implies that the asteroid's material might have started cold but was subject to some energy input. This notion is complemented by the imaging of Ryugu's surface by Watanabe *et al.* which implies that the asteroid was not small when it was created. It is thought that after large minor planets initially grew, the Solar System became quite destructive. Small asteroids are presumed to be the rubble piles formed after collisions of larger asteroids, which are often referred to as parent bodies. Watanabe *et al.* confirm this history of Ryugu. To round out the story, Sugita *et al.* report that the surface of the asteroid is rather young on the basis of geomorphological features. For example, the small number of craters identified is indicative of the time interval that its surface was subjected to impacts. In addition, Sugita *et al.* report a very low albedo—that is, the asteroid's surface reflects a small amount of the incoming radiation and absorbs the rest. This finding is consistent with moderate thermal-processed material at the surface, resembling the properties of carbonaceous chondrites.

The remote sensing instruments are not the only instruments on board Hayabusa2. The MASCOT lander was successfully released in October, touching down on the asteroid's surface (*9*). The next step is to bring back a sample from this object, which might now be considered one of the most precious time capsules of the solar system. ■

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CHEMISTRY

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Use of halogenated flame retardants continues despite health and environmental concerns

By **Jacob de Boer**[1] *and* **Heather M. Stapleton**[2]

Halogenated flame retardants are used widely in consumer products such as carpets, textiles, and electronics to reduce the risk of fire. It has been known for more than 20 years that these compounds can leach into the environment, with particularly high concentrations recorded in fish and marine mammals. Concerns have also been raised about carcinogenic and endocrine-disrupting effects in humans. Some brominated flame retardants—in particular, polybrominated diphenyl ether (PBDE) commercial mixtures and hexabromocyclododecane (HBCD)—have been banned or phased out in some jurisdictions, and the possible use of alternative flame retardants has been investigated. Yet, over the past 20 years, global production of flame retardants has continued to rise without a decrease in halogenated flame retardant production. It is time for a critical evaluation of flame retardant use.

In the late 1980s, scientists began to develop analytical methods and gather the first screening data on flame retardants in the environment in Europe, Japan, and North America. Concern among environmental scientists rose when Norén and Meyronité reported rising concentrations of PBDEs in human milk (*1*) and de Boer *et al.* detected PBDEs in sperm whales stranded in the Netherlands (*2*). Soon after, more studies documented increasing PBDE trends in fish, sediment profiles, sewage sludge, aquatic birds, and human tissues (*3*).

Intensive discussions between scientists, regulatory authorities, and the international bromine industry, represented by the Bromine Science and Environmental Forum, followed but did not lead to reductions in the global use of halogenated flame retardants. Instead, repeated regrettable substitutions were made, in which one halogenated flame retardant was phased out and replaced by another halogenated flame retardant, for which less information on exposure pathways and potential environmental and health effects was available (*4*, *5*). All substitutes showed harmful effects, although these effects were sometimes slightly different from those of the compounds they had replaced.

In the meantime, a suite of other halogenated flame retardants was introduced; about 75 different brominated flame retardants are on the market, and many of them have been detected in the environment (*6*). For each of these compounds, scant information was available on their environmental behavior at the time of introduction, because years of research are needed to collect information and support a thorough risk assessment. Such risk assessments have been carried out in the past for single compounds or for well-defined mixtures but are much more difficult to conduct when the effects of multiple substances are cumulative (*7*).

Even after a detailed risk assessment of the flame retardant tris-(1,3-dichloro-2-propyl)phosphate (TDCIPP) found it to present a potential risk for children (*8*), the compound was not taken from the market but only voluntarily removed from children's pajamas. More than three decades later, this same chemical became a popular replacement for pentabromodiphenyl ether (PentaBDE) in U.S. furniture, including baby and juvenile furniture (*9*).

Recent research has drawn attention to human exposure to flame retardants in indoor environments such as homes, with children receiving greater exposure than adults (*6*). Furniture and electronics appear to be substantial sources of flame retardants in indoor dust and air, as well as in cars (*6*). Scientists are now increasingly investigating the importance of dermal absorption and inhalation as primary uptake routes compared with diet.

POLICY AND REGULATIONS

The European Union (EU) issued bans on the production and use of PBDEs and HBCD starting in 2002. More recently, several frameworks and directives have been developed in Europe, including the Registration,

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Evaluation, Authorisation and Restriction of Chemicals (REACH), the Restriction of Hazardous Substances, and the Waste Electrical and Electronic Equipment directives. The current Community Rolling Action Plan of the European Chemicals Agency envisages further possible restrictions on a series of flame retardants, including TDCIPP. These are hopeful signs, but EU frameworks do not yet take account of mixture effects (*7*).

In 2004, the U.S. Environmental Protection Agency (EPA) and the manufacturers reached a voluntary phase-out agreement of PentaBDE and octabromodiphenyl ether (OctaBDE). Several U.S. states prohibited the use of these flame retardants in some products sold in their home states. In 2017, a group of organizations petitioned the U.S. Consumer Product Safety Commission (CPSC) to restrict the use of additive, nonpolymeric, halogenated flame retardants in children's products, furniture, and electronics enclosures on the basis of the Federal Hazardous Substances Act. This approach was unusual in that it requested a ban on an entire class of chemicals. The CPSC must now determine whether it considers halogenated flame retardants to be hazardous as a class. It is currently establishing a Chronic Hazard Advisory panel to make this determination.

Other parts of the world have seen far less regulation of halogenated flame retardants. In January 2018, China added decabromodiphenyl ether (DecaBDE) and HBCD to its list of priority substances, which may imply restrictions in productions or limitations of discharges. Taiwan and Japan have placed restrictions on the use of PBDEs and HBCD. Although India signed the United Nations Stockholm Convention on Persistent Organic Pollutants, in which PBDEs and HBCD are officially labeled as such, no comprehensive legislation for these and other flame retardants exists.

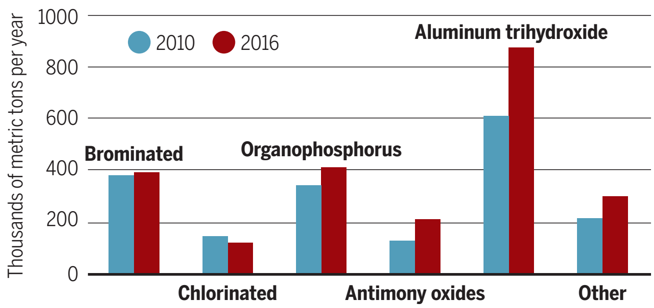
The recent United Nations Global Chemicals Outlook II (*10*) predicts that the volume of chemicals used worldwide will double in the coming decade. It would be prudent to be more selective in the use of flame retardants and to potentially limit this increase. Flame retardants are needed in airplanes, cars, insulation, and electronics, but there are many questions around the need for flame retardants in furniture, children's products, and even products like flags. In the case of residential furniture, the use of flame retardants provides an additional ~30 s to escape from a flashover (the near simultaneous ignition of directly exposed flammable material in an enclosed area); however, this benefit must be considered against the increase of carbon monoxide and smoke produced by some flame retardants (*11*).

PRODUCTION DEVELOPMENTS

The production and sale of flame retardants is a billion-dollar industry. In 2016, the estimated worldwide consumption of flame retardants was 2.3 million metric tons (see the figure) (*12*); the estimated annual growth rate is 3%. Overall production of halogenated flame retardants, excluding chlorinated paraffins used for other purposes, has been stable over the past 20 years at just over 500,000 metric tons (*12*).

Global production of flame retardants

Global flame retardant production increases by around 3% per year. Production of halogenated flame retardants is not decreasing, despite concerns regarding environmental and health impacts. Data from (*12*).



Some changes have occurred over this time. For example, the bromine industry has started production of a brominated polybutadiene-polystyrene flame retardant, which should reduce exposure concerns because it is less likely to leach out of a polymer, compared with small-molecule flame retardants used as additives. The phosphorus industry is hoping to phase out the use of tris-(2-chloroisopropyl) phosphate (TCIPP) in isolating metal panels containing foam cores and to replace TDCIPP with phosphorus-substituted polyols (poly-P-poly-ols) in the automotive industry. However, production of many flame retardants that are harmful to human health and the environment continues.

The European research project ENFIRO has recommended alternatives for persistent, bioaccumulative, and toxic flame retardants (*13*). These alternatives have a better environmental profile and include metal-based compounds, such as zinc stannate, zinc borate, and aluminum diethylphosphinate, as well as melamine polyphosphate. The EPA has used the Design for the Environment program to provide information on alternatives for PentaBDE in polyurethane and DecaBDE in electronics (*14*).

A BETTER WAY FORWARD

The production of potentially hazardous and environmentally unfriendly flame retardants continues even when better alternatives are available. Intense pressure from authorities, and sometimes the general public, can motivate industry to change, but governments have been slow to act. Any regulatory changes will likely raise concerns about impacts on fire-related fatalities and damages. However, environment-friendly alternatives are available and just as safe as the halogenated flame retardants (*13*), and many applications do not require the presence of a flame retardant.

Authorities should ban persistent, bioaccumulative, and toxic flame retardants as soon as safer alternatives become available. It may be even better to only allow flame retardants on the market that have been adequately tested for human toxicity and environmental impacts. Such a focus on the design phase will be required to adhere to requirements for a circular economy, such as readiness of materials for recycling (*13*).

The need for flame retardants in some materials may not be as high as industry lobbyists suggest. The data used to support the implementation of flammability standards, particularly for furniture and televisions, may be flawed or misinterpreted (*15*). No one wants to compromise fire safety, but to protect human and environmental health, it is crucial that the use of flame retardants is critically evaluated to determine where they are needed and where they are not. ■

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