pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 137 May 2022

EU CHEMICALS POLICY

EcoDesign proposal and chemicals

The proposed update of EU EcoDesign could have wide impacts on chemicals used in consumer products. EU EcoDesign enables definition of obligatory energy and sustainability criteria for products. The overall Ecodesign Regulation, to replace the existing Ecodesign Directive, will fix the framework for these criteria, under the EU Green Deal sustainable products initiative (see pinfa Newsletters 121 and 125). The draft new Ecodesign for Sustainable Products Regulation was published 30th March 2022 (as part of the Circular Economy Action Plan) and will be submitted to European Parliament and Member States (Council). Criteria for different product groups will then be adopted by the European Commission as "delegated acts", within this framework. The Commission has stated that this new Regulation "*will be able to take action to restrict the presence of chemicals in products for reasons linked to improving the product's environmental performance along its life cycle*", that is independently and beyond EU chemicals regulations.

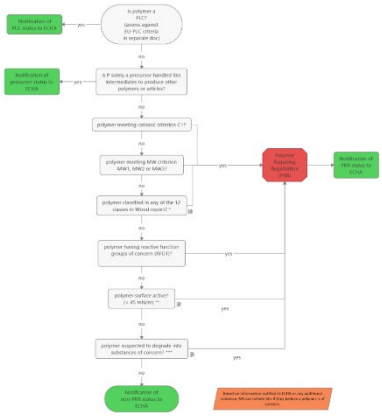
The new Ecodesign for Sustainable Products Regulation proposed text suggests (preamble 22) that criteria can limit chemicals for reasons other than chemical safety, and would require extensive information on chemicals in consumer products (preamble 25) and tracking of "substances of concern" throughout the product life cycle (art.7).The proposed text suggests a new definition of "substances of concern" which includes both a wide list of environmental and health hazard classifications and also potentially any chemical which "*negatively affects the re-use and recycling of materials in the product*". This is the logic by which, already in 2019, the European Commission banned all halogenated flame retardants in TV and monitor cases under Ecodesign criteria, as validated recently by the European Court (see pinfa Newsletter n°136).

Commission communication on "On making sustainable products the norm", COM(2022)140, 30th March 2022
https://ec.europa.eu/environment/publications/communication-making-sustainable-products-norm_en

Graphic source: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52022DC0140&qid=1649112555090

EU "Sustainable product policy and ecodesign" page
https://ec.europa.eu/growth/industry/sustainability/sustainable-product-policy-ecodesign_en

"Proposal for Ecodesign for Sustainable Products Regulation" – "Proposal for a Regulation establishing a framework for setting ecodesign requirements for sustainable products and repealing Directive 2009/125/EC 30th March 2022"
https://ec.europa.eu/environment/publications/proposal-ecodesign-sustainable-products-regulation_en



FRs and REACH registration of polymers

The proposals to require REACH registration or "notification" of polymers should take into account reactive flame retardants. As part of the new EU Chemicals Strategy for Sustainability, the European Commission is proposing to require REACH registration of polymers "of concern" and possibly "The obligation to NOTIFY … ALL polymers … from the threshold of 1 tpa." (DG ENV – ECHA 1 April 2022).

Recent Commission proposals 30th March 2022) no longer include the obligation of registration for polymers containing > 0.2% w/w lithium, boron, phosphorus, titanium, manganese, iron, nickel, copper, zinc, tin or zirconium, which would have directly impacted some polymeric PIN flame retardants (Wood 2020 proposals).

pinfa underlines however that the proposed requirement of "**notification**" of "all" polymers needs to be clarified concerning reactive flame retardants and other plastics additives. It would be unworkable for the industry value chain if, every time an FR reacts with a polymer during compounding or textile finishing, the result is considered to be a "new polymer" requiring a "new notification", which would have to be made by the compounder or the textile processor.

The European Commission proposals for polymer REACH registration are based on the Wood report, June 2020, doc. ref. 40867-WOOD-XX-XX-RP-OP-0002_S3_P03.5

Development of the Commission's proposals can be followed on the publicly accessible CIRCABC website of the Commission's CARACAL group (Competent Authorities for REACH and CLP), sub-group CASG-06 Polymers https://circabc.europa.eu/ui/group/a0b483a2-4c05-4058-addf-2a4de71b9a98/library/806e87e4-1236-4b2b-a768-de1ac2ba15c4

European Commission

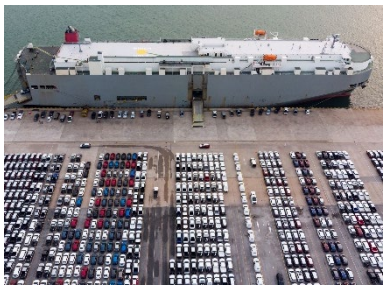
Have your say

EU consultations underway

Proposed regulatory text for update of **Construction Products Regulation**. **To 1st June.**

Call for Evidence on restriction of the use of hazardous substances in electronics **(RoHS Directive). To 2nd June 2022.**

FIRE SAFETY



Shipper concerned about EV fire risks

After the Felicity Ace car ship fire, leading car carrier Hyundai Glovis is increasing safety because of EV fire concerns. The Felicity Ace, carrying some 4 000 Volkswagen – Audi - Porsche – Lamborghini cars, estimated at over 400 million € value, sank near the Azores on 1st March 2022 after burning for a week. The cause of the fire is unknown, but many electric vehicles were involved. One of the largest car carrier operators, Hyundai Glovis (90 ships), has now announced new measures to increase fire safety on its ships, including training protocols to address the specific fire risks related to electric vehicles. Hyundai Glovis transported a quarter of a million EVs already in 2021. In particular, car fire covers will be deployed. These can be spread over a burning vehicle to prevent oxygen inflow and block heat and smoke, with the aim of preventing fire spreading to adjacent vehicles.

"Hyundai Glovis Enhances Fire Safety for Car Carriers Addressing EVs", 1st April 2022 https://www.maritime-executive.com/article/hyundai-glovis-enhances-fire-safety-for-car-carriers-addressing-evs

Kiss Nightclub fire

Report says appropriate building materials could have prevented the Kiss Nightclub's 242 fire deaths, Brazil Jan. 2013. The fire started when a firework lit by one of band playing on stage ignited sound insulation foam on the ceiling. Fire deaths resulted from a combination of causes, including absence of fire extinguishers, only two emergency exits and poor emergency signage (see court judgements summarised in pinfa Newsletter n°133). This research report assesses to what extent use of appropriate ceiling materials and emergency exits according to current Brazil fire regulations could have saved lives. Modelling concludes that existence of appropriate emergency exits would not have prevented all deaths with the polyurethane foam present on the nightclub ceiling. The official fire report states that the nightclub was practically filled with smoke from this foam in less than two minutes. If the foam had respected current Brazil standards (PET foam is modelled), instead of the polyurethane foam used in the nightclub, with adequate safety exits, all deaths would have been prevented.

"Investigation on the causes and consequences of Kiss nightclub fire in Brazil", G. Hennemann et al., Architecture, Structures and Construction 2022 https://doi.org/10.1007/s44150-022-00032-1

Ten die in Egypt tourist coach crash fire

Ten people died and fourteen more were injured when a tourist coach burst into flames after a collision near Luxor, Egypt. The coach apparently burst into flames after hitting a truck. Reports show the coach covered in flames and indicate that some victims were killed by the fire. Casualties include nationals of Egypt, France and Belgium.

"Egypt: Bus carrying tourists collides with truck, 10 killed", Aljazeera 13th April 2022 https://www.aljazeera.com/news/2022/4/13/at-least-10-killed-in-egypt-bus-crash-says-governor

Compressed Natural Gas (CNG) bus fire

Nobody was injured in this spectacular natural gas powered bus fire, near Perugia, Italy, 16th April. Only the driver was on board. The columns of fire result from automatic vending of natural gas, intended to keep the fire away from the vehicle to give time for escape. In this case this caused the fire to spread to roadside woodland, where it was successfully extinguished.

"CNG fuels spectacular bus fire in Italy" https://www.autoblog.com/2022/04/21/cng-bus-fire-explosion-italy-natural-gas/?guccounter=1

US IBC Code and combustible cladding

Proposal to ban combustible cladding in renovations of high-rise buildings, unless sprinklers are fitted. The IEBC Technical Committee (International Building Code) has approved proposal EB33 to create a new section 309.2.1 to ban the use of "combustible" materials in wall coverings in renovations of high-rise buildings (except if < 15% of wall area per façade) unless the building is "protected throughout with an automated sprinkler system". Combustibility is here defined by ASTM E136, a very demanding test, which even some mineral insulation materials will fail depending on the amount of organic binders present. The Code already requires sprinklers in new high-rise buildings, but does not require to retrofit in existing buildings. Sprinklers inside the building will not impact fire spread in cladding, and the change seems to be an indirect way to pressure building owners to retrofit sprinklers. The proposed change is currently out for comment **until 20th June 2022**, Comments must be submitted via the ICC website.

For more information, see GBH International "Fire Safety & Technology Bulletin" April 2022, vol. 17, n°4 https://www.gbhint.com/fire-safety-and-technology-bulletin/

*Comments can be submitted **to 20th June 2022** at https://www.cdpaccess.com/login/ - register – then click "Current Cycle -> Proposals" then enter "EB33" in the search Agenda Number box*

SUSTAINABILITY ASSESSMENTS

NIST review on LCAs of plastics

This NIST review analyses current knowledge on life cycle and environmental assessments of plastics, based on over 150 publications. It is noted that "FRs are usually ignored in plastics LCA studies". Only six publications relevant to FRs are cited: Broeren 2016, Samani 2020, Deng 2016 (these are summarised in pinfa Newsletter n°118), Jonkers ENFIRO 2016 (pinfa Newsletter 58) and Andersson and Simonson fire-LCA studies (2002, 2004). One study (Broeren) suggests that FRs can contribute up to 40% of plastics GHG emissions, but this is based on bio-based plastics. One study (Jonkers) concludes that brominated FRs have worse environmental impacts, caused mainly at product end-of-life. The two fire-LCA studies conclude that, because of environmental and greenhouse impacts of "avoided" fires, FR containing (plastic) products have an overall preferable LCA.

"Life Cycle Environmental Impacts of Plastics: A Review", P. Rikhter et al., 2022 NIST GCR 22-032
https://nvlpubs.nist.gov/nistpubs/gcr/2022/NIST.GCR.22-032.pdf

Apple, Google & ChemFORWARD

Independent chemical assessments for safer flame retardants for electronics targets PIN FRs. The Science-based NGO ChemFORWARD has announced that it is now working with Apple and Google to implement its SAFER™ (*) value-chain chemical hazard repository for PIN flame retardants in electronics. ChemFORWARD's SAFER system requires an analysis by an accredited independent assessor, taking into account all intentionally added chemicals and impurities > 100 ppm. Chemicals are assessed based on GHS Classification, national chemical databases and other screening lists, and thus allocated to SAFER categories A, B, C F or U. Category A ("Low hazard and low risk") is indicated to be equivalent to GreenScreen Benchmark 4, SAFER B ("Some moderate hazards but low risk") is equivalent to Greenscreen 3 and SAFER C to Greenscreen 2. The aim is to collect full information from the product value-chain, then make the final assessment report available to stakeholders. ChemFORWARD states that, with Apple and Google, a "comprehensive set of chemical hazard assessments" for PIN flame retardants used in electronics is being generated, with more than 20 PIN FRs assessed to date

"Apple, Google and ChemFORWARD join forces to drive support for safer flame retardants in-the Electronics Sector", 6th April 2022

ChemFORWARD SAFER Program Overview, January 2022
https://www.chemforward.org/s/ChemFORWARD-SAFER-Program-Overview-JAN-2022.pdf

** ChemFORWARD's system called SAFER is not to be confused with ICL's company methodology for assessing flame retardant risks, see pinfa Newsletter n°79.*

RESEARCH AND INNOVATION

PIN FR engineering thermoplastic

pinfa member Asahi Kasei's PIN FR mPPE shows application success in automotive, electronics, photovoltaics, and water installations. mPPE (modified polyphenylene ether) is a combination of polyphenylene ether with polystyrene, polyamide, polypropylene, polyphenylene sulfide or other polymers. These blends allow for non-halogenated UL 94 HB or V-0 flammability, electrical and mechanical properties, hydrolysis resistance and chemical resistance. Application success stories include drinking water and swimming pool applications (water certifications: KTW, ACS, W270, WRAS, NSF). Automotive applications include EV battery casing parts, under-the-hood parts such as relay boxes, heat-exchanger cover, body parts such as panels, wheel caps, and door handles. In the field of renewable energies it is a suitable material for PV connectors and inverter covers.

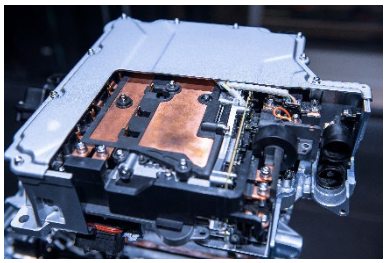
Asahi Kasei https://www.asahi-kasei-plastics.com/en/products/xyron/ see "Application cases"

PIN FR labels for fire-safe electronics

Polyonics continues to improve its non-halogen flame-resistant labels for miniature, high-power electronics. Component and material labels in electronic equipment and batteries are essential to enable component and material identification, quality control, commercial traceability, maintenance and dismantling – recycling. They must resist high temperature, demanding conditions over time, without contributing to fire risk. Polyonics proprietary label systems combine polyimide and polyester (PET), with specific pressure-sensitive adhesive and printable coating formulations. Heat transfer and release of flammable gas in case of fire is limited by generation of char layers, achieving UL94 VTM-0, FAR 25.853, BSS 7238/7239 or DOT FMVSS302 fire, smoke and toxicity standards. The latest line of barcode labels and tags is designed for tracing hot metals through processing and is rated up to 700°C using specific non-yellowing PIN FR polymer, coating and adhesive system.

"Flame Retardant Label Materials Prevent the Propagation of Fire in Electrical Assemblies", 19 August 2020
https://polyonics.com/news/materials-prevent-fire-propagation-aug2020.php#

"New Polyonics HIGHdegree Tag and Label Materials Help Metal Processing Facilities Avoid Costly Expense of Recalls", 13 January 2021
https://polyonics.com/news/highdegree-jan2021.php



HFFR polyphthalamide (PPA) for e-vehicles

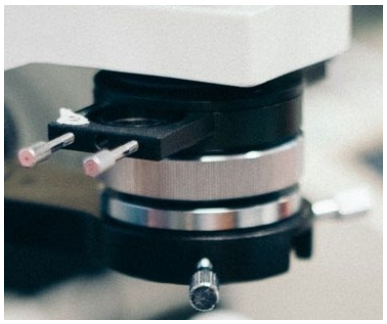
Solvay's new halogen-free flame retarded PPA offers electrical, heat resistance and dimensional performance for EV drives. UL 94 V-0 (@ 0.4 mm) fire performance is achieved, CTI > 600 volts and heat resistance > 120°C, adapted for demanding conditions in electric vehicle motors, power electronics and transmission systems. Mechanical and processing performance enable design of highly miniaturised components. The non-halogenated formulation ensures minimal risk of electronics corrosion. The non-halogen PPA grades are part of a wider range for various applications and requirements.

"Solvay launches new Amodel® Supreme and Bios grades to support further sustainable innovation in e-mobility", 18th November 2021 https://rfindy.com/solvay-launches-new-amodel-supreme-and-bios-grades-to-support-further-sustainable-innovation-in-e-mobility/

PCL's PIN FR performance polymers range

Polymer Compounders offers a range of non-halogenated FR PC/ABS, FR PC/ASA and polycarbonate blends for demanding customer applications. Polymer Compounders Ltd (PCL) has been developing high performance engineering thermoplastics since 1993. The company now uses polymeric phosphorus based FRs to supply applications such as electronics, battery casings and medical devices using FR PC/ABS, FR PC/ASA and polycarbonate blends. The non-halogenated (PIN) flame retardant Notoxicom® range offers UL 94 V0 performance (down to 0.8mm), glow wire flammability at 960°C and very low smoke toxicity. In addition, these compounds can provide excellent levels of heat resistance and impact performance, achieved with a non-migratory polymeric PIN flame retardant. Injection moulding and extrusion grades are both available.

"Notoxicom® Flame Retardant Plastic" https://polymer-compounders.com/en/product/notoxicom/ *and "Introducing the Notoxicom® Product Family" 8 October 2021* https://polymer-compounders.com/en/notoxicom-product-family/



Nitrogen – phosphorus – mineral synergy

A combination of allylamine polyphosphate (20%) and clay (2%) achieved UL-94 V0 (3.2 mm) in polypropylene, showing better fire performance than only APP (ammonium polyphosphate), APP + clay or only allylamine polyphosphate (AAPP). LOI was increased from below 18 (pure PP) to >29. The authors note that literature shows that clay synergist can improve fire performance of PP with ammonium polyphosphate, because the clay reduces melt-dripping and heat release, but that this is limited because of char instability and incompatibility between clay and APP. With allylamine polyphosphate plus 2% clay, there is exfoliation of clay platelets, and formation of dense, continuous, honeycomb structure char. Peak

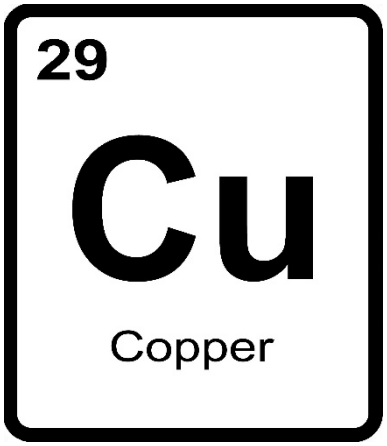
smoke release was around 50% lower than for neat PP, total smoke release was 55% lower, and smoke toxicity (peak carbon monoxide release) was around one third lower.

"Highly efficient flame retardant and smoke suppression mechanism of polypropylene nanocomposites based on clay and allylamine polyphosphate", D. Xiao et al., J Appl Polym Sci. 2022;139:e52311
https://doi.org/10.1002/app.52311

Intumescent + clay for PIN SLS 3D-printing

Triazinyl 22% with organo-clay 3% achieved UL 94 V-0 (1.6 mm) in SLS-printed TPU (thermoplastic polyurethane). TPU with 25% aluminium diethyl phosphonate (AlPi) was also tested (but not AlPi plus clay). The FRs were mixed with TPU powder using a high-speed mixer then ball milling, then 1.6 mm thick samples were SLS (Selective Laser Sintering) printed using a Hunan Farsoon HT 252P printer. SLS printed samples using neat TPU showed LOI of 17. AlPi 25% raised LOI to 27 for the SLS sample, achieving UL 94 V-2. Triazinyl macromolecule (an intumescent containing 45% nitrogen) raised LOI to 30. The addition of % organically modified montmorillonite (with 22% triazinyl) achieved UL 94 V-0 despite reducing the LOI slightly, because flaming dripping was prevented. The authors note that the organo-clay limits dripping and shortens self-extinguishing times, with better effect than sodium clay being probably the result of better polymer compatibility so better dispersion. AlPi was not tested with the organo-clay. LOIs for compression molded samples were slightly higher, both for the neat TPU and for the different PIN FR combinations, and in one case the UL 94 classification was also better, probably due to pores in the SLS sample because pressure is not applied.

"The synergism effect of montmorillonite on the intumescent flame retardant thermoplastic polyurethane composites prepared by selective laser sintering", J. Li et al., Polymer Composites. 2022;1–14
https://doi.org/10.1002/pc.26621



Wastewater copper removed recycled as FR

A complex, magnetic iron – zinc compound was lab tested to adsorb copper ions then tested as an FR coating for PU foam. An iron – zinc – ammonium compound (FeO-ZIF8) was synthetised from magnetic Fe_3O_4 nanoparticles, zinc nitrate and 2-methylimidazole. This compound showed to be effective in adsorbing copper from (pure) solution, and it is suggested it could therefore be used for water treatment (interference of other ions in wastewaters was not tested). The copper loaded FeO-ZIF8 was then coated onto polyurethane foam using silicone rubber adhesive then fire performance tested. The silicone adhesive coating alone reduced heat release rate by 25% whereas coating with FeO-ZIF68 led to a 69% reduction. Release of toxic carbon monoxide is also reduced. This paper provides a demonstration of concept, but further work would be needed to verify the effectiveness of copper removal in real wastewater, the durability of the foam coating and

the possible implications for PU recycling of the copper or other elements from wastewater.

"Magnetic Fe_3O_4 Nanoparticle/ZIF-8 Composites for Contaminant Removal from Water and Enhanced Flame Retardancy of Flexible Polyurethane Foams", Z. Xi et al., ACS Appl. Nano Mater. 2022, 5, 3491−3501 https://doi.org/10.1021/acsanm.1c04115

Chitosan - DOPO PIN FR for epoxy

The bio-polymer chitosan, modified with nitrogen, was used with the PIN FR DOPO, achieving UL 94 V-0 (3.2 mm) in epoxy. Chitosan is the second most abundant bio-polymer, after cellulose, and the most abundant organic compound containing nitrogen, and can be sourced e.g. from seafood wastes. Chitosan was reacted in methanol with nitrobenzaldehyde ($C_7H_5NO_3$) to introduce NO_2. The modified chitosan (CSN) was then cured into epoxy with DOPO (a standard PIN flame retardant, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). With a total CSN + DOPO loading of 5% (both with 1/3 CSN, 2/3 DOPO and with the converse), UL 94 V-0 was achieved (3.2 mm) and LOI was increased from 22 (neat epoxy) to 32 – 34. Total smoke production and smoke production rate were reduced by more than two thirds. Tensile strength, flexural strength and transparency of the epoxy were maintained. The authors suggest that the fire performance is related to char production (supported by the carbon and nitrogen in the CSN) whilst hydroxyl and amine groups contribute to retaining epoxy mechanical properties.

"Epoxy resin modified with chitosan derivatives and DOPO: Improved flame retardancy, mechanical properties and transparency", C. Zhou et al., Polymer Degradation and Stability 199 (2022) 109931 https://doi.org/10.1016/j.polymdegradstab.2022.109931

Liquid chitosan – P FR for natural fibres

Chitosan reacted with phosphoric acid was tested as a liquid PIN FR for natural fibres used to reinforce vinyl ester resin. Chitosan solution, prepared using acetic acid, was phosphorus-loaded by reacting with phosphoric acid. The natural fibres (wool, mulberry silk) were treated with sodium hydroxide, soaked in the liquid P-chitosan solution, then dried, resulting in c. 7% w/w PIN FR uptake.. Finally fibres were set into vinyl ester (VE) resin at c. 30% fibre loading. All three VE-fibre composites after treatment achieved UL 94 V-0 (3 mm) and showed peak heat release rate reduced by 2 - 4 x. The authors suggest that the flame retardant effect is the result of release of phosphoric acid and ammonia, generating dense, protective char, and release of non-combustible gases (water, CO_2, ammonia and for silk SO_2). They suggest that this could be a cost-effective, bio-based solution for fire protection of natural fibres in polymer composites.

"Preparation of a novel bio-flame-retardant liquid for flame retardancy of natural fibers and their composites", L. Maksym et al., J. Industrial textiles, 2022 https://doi.org/10.1177/15280837221079273

OTHER NEWS

Impacts of aryl phosphate PIN FRs on PC/ABS smoke emission. Neat PC/ABS, polymer + anti-dripping agent PTFE, polymer + PTFE + 10% loading of six different aryl phosphate PIN FRs (TPP, CDP, RDP, BTPP, BTP, Sol-DP) were tested for fire performance, smoke emission and smoke toxicity as per EN 45545-2. Neat PC/ABS emitted toxic smoke, with hydrogen cyanide and carbon monoxide. The aryl phosphates had varying impacts on maximum smoke density (Ss_{max}), from -2% to +36%. All of the aryl phosphates significantly increased emissions of CO and HCN (up to +60% and +40% respectively). The aryl phosphates were effective in reducing the fire hazard by preventing flame spread, reducing heat emission and increasing time to ignition. The authors conclude that the varying effects of the different aryl phosphate PIN FRs on smoke and toxic gas emission depends on the balance between solid phase (char formation) and gas phase effects.

"Effect of aryl phosphates on toxicity of combustion gases of flame-retardant polycarbonate/acrylonitrile butadiene styrene blends according to EN 45545 railway standard", A. Sánchez, S. Villanueva, Fire and Materials. 2022;1–11, https://dx.doi.org/10.1002/fam.3062

Review concludes 'conflicting conclusions' on long-term environmental risks of organophosphate esters (OPEs). Analysis of over 100 studies and publications covers 18 OPEs, which are used as plasticisers and/or flame retardants. Conclusions are that OPEs are widespread in oceans and in the atmosphere, both in coastal waters near industrial regions, and also in remote oceans and polar regions. Total levels of OPEs are increasing and today exceed those of brominated flame retardants in some oceans, as these are phased out. Total OPE concentrations in the ng/litre range are found in polar oceans, both in water and in sediments. Transport is both in air and in water. OPEs are however often non-detectable or at very low levels in animals and birds, but data is limited, and comes mainly from industrialised regions. OPEs undergo degradation or attach to particles and sink in the water column, so providing in the long-term the nutrient phosphorus to ocean ecosystems. The authors conclude that there is "conflicting evidence on the potential for bioaccumulation and biomagnification" and that further data and research is needed.

"Organophosphate ester pollution in the oceans", Z. Xie et al., Nat Rev Earth Environ (2022). https://doi.org/10.1038/s43017-022-00277-w

PUBLISHER INFORMATION

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