Please cite this article in press as: Beil and Waldvogel, Upcycling of persistent pollutants: Toward an electrochemically driven circular halogen economy, Chem (2025), https://doi.org/10.1016/j.chempr.2025.102831

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Perspective

Upcycling of persistent pollutants: Toward an electrochemically driven circular halogen economy

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https://doi.org/10.1016/j.chempr.2025.102831

THE BIGGER PICTURE Halogenated chemicals find widespread applications in crop protection, flame retardants, or pharmaceuticals. Whereas iodides are more easily degraded because of their weaker bond with carbon, bromides and chlorides are particularly challenging to degrade. Aliphatic C–F bonds are even more difficult to break down (bond dissociation energy [BDE] = 115 kcal mol^{-1}). However, reusing halogenated organic pollutants as new halogen (re)sources could enable a circular economy of halogens instead of leaving them as otherwise persistent pollutants.

Currently, halogenated organic chemicals often undergo bioaccumulation or are deposited in landfills as a result of the formation of side products or restricted use. Additionally, assessing the scale of pollutant occurrence is essential for the development of viable recycling or upcycling business models.

Likewise, utilizing renewable energy and electricity would significantly decrease the carbon footprint of such chemical processes. Therefore, developing future-ready electrochemical transformations to reuse and recycle halogenated waste streams is highly desirable.

SUMMARY

Halogenated products find broad application in chemical products and feature high persistence in natural ecosystems. Whereas their slow natural degradation enables their use in applications such as crop protection, this property makes them persistent pollutants that do not reenter the value chain of chemical products. New electrochemical modifications could enable the circular use of halogenated chemicals. Huge deposits of pollutants could serve as feedstock for future applications and processes. We envision that an electrically driven circular economy powered by renewable energy and operating under CO$_2$-neutral conditions could liberate carbon skeletons as non-fossil feedstocks.

ORGANOHALIDES: THEIR OCCURRENCE AND POTENTIAL

Over the past century, chemistry has enabled a multitude of high-performance materials in various application areas. Understanding molecular properties and interactions with the environment has led to the use of halogenation reactions of organic molecules and their respective halogenated products in various applications (Figure 1). For example, fluorination leads to higher oleophilicity and lipophilicity in materials (e.g., polytetrafluoroethylene [PTFE], also known as Teflon) or drugs (e.g., trifluoromethyl group), chlorination increases the potency in agrochemicals (e.g., lindane), brominated products are effective flame retardants, and iodination enhances the contrast in X-ray imaging techniques (e.g., contrast agents). However, in the reverse order, the stability of the carbon-halide bond increases by almost 60 kcal mol^{-1} (~250 kJ mol^{-1} for C(sp^3)) or 70 kcal mol^{-1} (~290 kJ mol^{-1} for C(sp^2)), rendering incredibly stable chemical bonds that can be broken only under artificial conditions (Figure 1, bottom).[1] When applied in materials, halogenated compounds can nonetheless be released into the environment despite the high lipophilicity associated with extensive halogenation. Long-range and global accumulation into biological systems (i.e., bioaccumulation) is therefore a severe threat to humanity and the environment.[2] Hence, the United Nations created the Stockholm Convention in 2004[3] to tackle the problem of persistent organic pollutants (POPs) in the environment. Although the production of some of the most potent and persistent halogenated pollutants was abandoned, their bioaccumulation or deposition into landfill renders these chemicals

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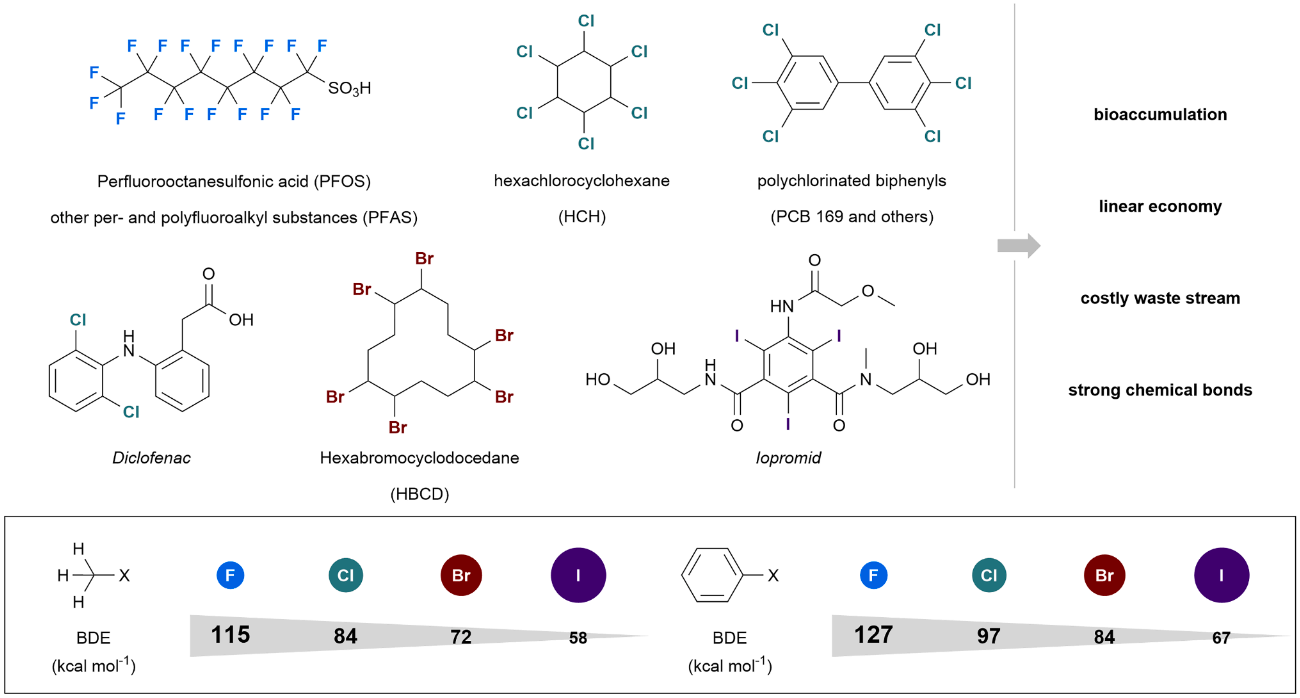

Figure 1. Halogenated chemicals show widespread application but feature severe environmental problems
Box: the chemical stability of C(sp^3) and C(sp^2) bonds greatly differs for halides. BDE values were obtained from Luo.[1]

a future problem that must be tackled by scientists, especially chemists.

In an ideal scenario, the prevalence of halogenated organic chemicals can be utilized as feedstock to fuel a circular halide economy. With the right chemistry in hand, it should be possible to selectively break C–X bonds on demand and reuse the obtained halides before they leak into the environment. We strongly believe that electrosynthesis is one of these technologies that, when powered by renewable energy, enables a circular and profitable halide economy. In the following sections, we discuss potential halide sources and deposits that are economically viable for chemical recycling and are thus privileged entry points into an electrochemically driven circular halogen economy.

Organofluoride compounds feature the most stable carbon-halide bonds, ranging from 115 kcal mol^{-1} for C(sp^3) to 127 kcal mol^{-1} for C(sp^2), and are therefore the most difficult to recycle. Most prominently, polyfluorinated alkyl sulfonic acids (PFAS), such as perfluorooctanesulfonic acid (PFOS), have gained attention because of their severely detrimental health effects.[4] However, as high-performance additives, these substances are a key component of PTFE production. In the context of PFAS recycling, initial success was achieved in the mineralization of perfluorocarboxylic acids under mild conditions.[5] Nevertheless, despite their toxicological profile, the margin of application is relatively low; consequently, waste streams contain very low PFAS concentrations, rendering them a less impactful resource for recycling on a global scale.

However, highly fluorinated neutral or ionic polymers—such as PTFE, sulfonated tetrafluoroethylene-based fluoropolymer-copolymer (Nafion), or polyvinylidene difluoride (PVDF)—are a significant resource because of their broad application and increasing production, which is estimated to reach 442,000 t by 2028.[6] Their recycling or depolymerization, however, is challenged by the high energy barrier of bond cleavage. Thermal decomposition above 450°C was established in the 1950s[7] and was recently supplemented with milder approaches, such as ball milling.[8] However, neither approach recovers molecular building blocks or halides for reuse. Hence, harnessing such polymeric materials as resources requires new technologies.

The incorporation of fluorine often significantly lowers the boiling points of organic compounds and has therefore been harnessed in applications such as anesthetic gases or refrigerants. However, the use of such compounds is often accompanied by uncontrolled release into the atmosphere, which prohibits their recycling or reuse. Freons, a class of halocarbon refrigerants, are well known for their global warming potential.[9] In particular, chlorofluorocarbons (CFCs) exhibit severe climatic impacts that have been recognized since the 1970s.[10] After the adoption of the Montreal Protocol, a promising decrease in atmospheric hydrochlorofluorocarbons (e.g., chlorodifluoromethane [HCFC-22]) was observed.[11] Likewise, halons, which include halomethanes (e.g., CH_3X, where X = F to I) and haloethanes (e.g., $C_2Br_2F_4$), and their ethers are used as volatile liquid anesthetics (e.g., isoflurane and sevoflurane).[12] Despite their effectiveness in critical-care sedation,[13] their uncontrolled release poses a major challenge because of their climate impact[14] and global warming potential.[15] Recently, efforts to reduce sevoflurane emissions from anesthetic maintenance areas have demonstrated promising progress.[16] Because of the high volatility and chemical inertness of Freons and halons, early strategies focused on their

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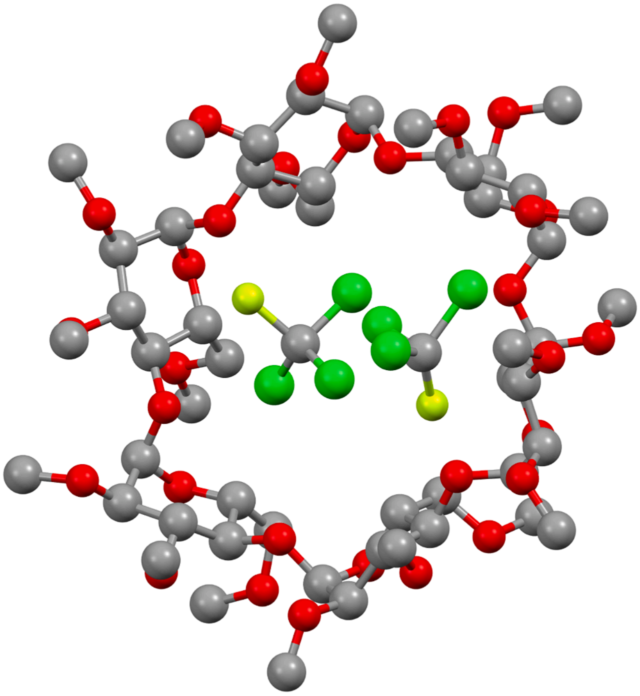

Figure 2. Methylated cyclodextrin enables binding of halogenated pollutants from the gas phase

The X-ray structure was recreated from CCDC: 1841752 of Ryvlin et al.[17]

selective binding and controlled release. One example is Freon-11 (trichlorofluoromethane). Our group succeeded in its binding and crystallographic characterization as a complex with a methylated cyclodextrin (Figure 2).[17] The capture and subsequent thermal release of CFCs provides a foundation for their recycling and reuse in the context of a circular economy. Hence, chemical recycling could enable access to pure or purified waste streams.

On a similar note, sulfur hexafluoride (SF_6) is a world-scale gaseous product with a global production and application as an insulating material, for example, by Solvay.[18] Because of its high dielectric strength and thermal stability, SF_6 is an important commodity chemical (see Ottinger et al.[19] for US consumption and supply). However, the environmental potential and formation of toxic byproducts make it a challenging product,[20] the recycling of which still lags behind its broad application. Hence, Solvay developed the SF_6 ReUse Program to keep this precious and chemically stable but environmentally harmful chemical in the loop of applications.[21]

Organochloride compounds are significantly easier to degrade and are applied at a high global volume. Many chlorinated organic molecules are, however, toxic or cancerogenic. Because of their toxicity, they have been broadly applied in crop protection as pesticides, and the most severe ones, including dichlorodiphenyltrichloroethane (DDT) and aldrin, have been banned by the Stockholm Convention.[3] Later on, hexachlorocyclohexane (HCH; lindane) joined the family of pesticides and was banned in 2010.[22] Despite being an effective chemical, its production posed an enormous concern because γ-HCH, the biologically active form, was obtained in only 8%–15% yield.[23] Hence, up to 85% waste isomers were generated, accounting for 4–7 Mt (mostly α-HCH in 55%–80% yield and β-HCH in 5%–14% yield) during the 60 years of lindane production, and mostly ended up in landfills in an uncontrolled fashion globally. This massive amount provides a suitable resource for recycling on a global scale.

Another source of chlorinated compounds is transformer oil, which is almost always contaminated with polychlorinated biphenyls (PCBs), and contamination usually reaches up to 50 ppm.[24] Although low concentrations are observed, the global amount of transformer oil is a viable resource for recovering PCBs and tackling their restitution into a circular halide economy. Regional differences in the production and depositions of PCBs apply, leading to accumulation in sediments.[25] In Germany, for example, old salt mines, such as the ''Mount Kali'' mine in Herfa-Neurode, are used as storage facilities for highly contagious chemical waste.[26,27] Nonetheless, highly pure chemicals are often deposited, thus rendering a potential resource for the (chemical) recycling of organic halides.

One of the biggest chlorinated feedstocks is polyvinylchloride (PVC), around 60 Mt of which was produced in 2022.[28] Although it has many applications in the construction industry, PVC is disposed of in landfills and is also highly chemically stable, so it cannot enter a circular economy. Hence, activating and recycling PVC are of paramount interest for generating large feedstocks of chlorine and chloride alongside the polymeric carbon backbone.

Lastly, chlorination facilitates pharmacologic activity in many drugs, such as diclofenac. However, as a result of resistance to degradation, bioaccumulation occurs rapidly up to a measurable extent. Unfortunately, the biotransformation is poorly understood.[29] Bio-methylation has been observed at lower formation rates, but enhanced concentrations lead to a more potent derivative. According to European environmental quality standards (EQSs), concentrations above 230 ng L^{-1} should not be exceeded,[30] resulting in a highly dilute resource that is much more difficult to recover than HCH or PVC, for instance.

Organo-bromine compounds are typically applied as additive flame retardants. Typical classes are polybrominated biphenyl (PBBs), polybrominated diphenyl ethers (PBDEs), and hexa-bromocyclodocedane (HBCD), which feature an extensive risk profile and were thus included in the Stockholm Convention.[31] These flame retardants, such as decabromodiphenyl ethers (Deca-BDE), are mostly applied to polystyrene (0.8–4 wt %) and high-impact polystyrene (11–15 wt %) packaging material. Depending on the polymer, up to 33 wt % is used as an additive, leading to highly contaminated waste streams.[32] In contrast to additive flame retardants, tetrabromobisphenol A (TBBPA) is a reactive flame retardant that is incorporated into the polymer backbone to inhibit combustion. Because of this huge market of polymer packaging and high amounts of flame-retarding additives, its recycling is of high interest for a circular halide economy.

Organo-iodide compounds find extensive applications as X-ray or computed tomography (CT) contrast agents, such as iopromide (Ultravist). Iodinated contrast media are usually ionic or non-ionic derivatives of triiodo benzoic acid derivatives.[33] In clinical applications, they are applied as infusions at high concentrations because of their fast clearance time from the human body. Hospital wastewater streams are often contaminated with

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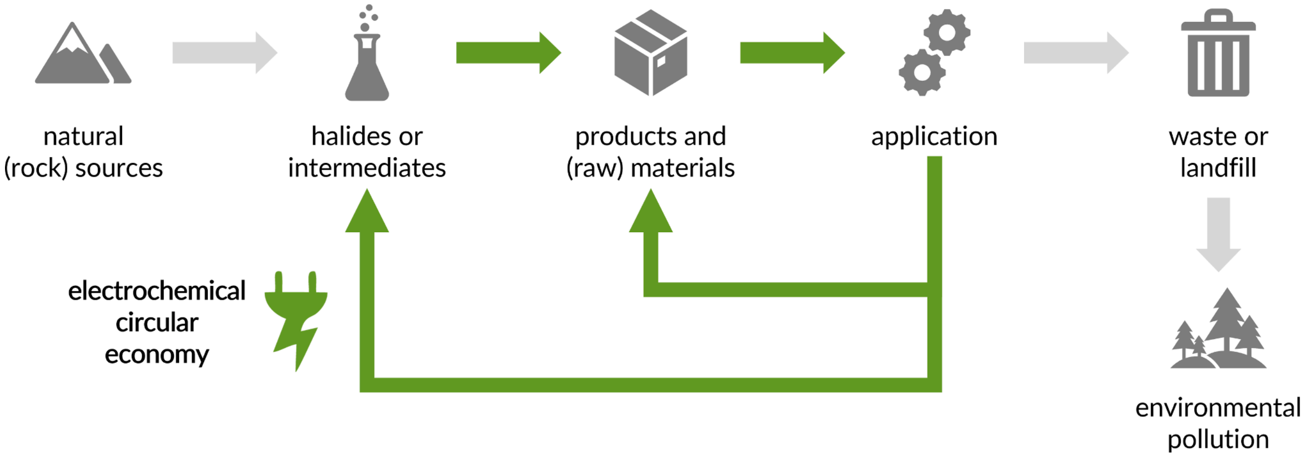

Figure 3. Anticipated circular economy utilizing renewable electricity as a green source for recycling halides from high-value products
The large scale (green arrows) ultimately avoids the influx of new resources and environmental pollution (gray arrows).

relatively high concentrations of water soluble triiodo arenes, which would be an interesting approach to iodide recovery at a defined local scale.

Hence, the high amounts of applied halogenated compounds, combined with their persistence and respective bioaccumulation, call for urgent strategies regarding recycling or upcycling. Highly effective chemical reactions might be able to feed halides from waste streams back to chemical production processes. However, because halides are used as base and fine chemicals, their recycling must be cost effective, and methods should be developed from a sustainability and economic perspective.[34]

It is evident that these persistent halogenated compounds could serve as interesting substrates wherein reagent-less activations by electrosynthesis (and photochemistry) appear most attractive for academic and technical applications.[35,36] Electrochemistry, and more importantly electro-organic synthesis, combines the use of renewable energy and selective chemical reactivity.[37–39] Electrosynthesis provides high spatial and temporal control over chemical reactions, is inherently safe (because reactions only occur with the electricity applied), and has been demonstrated at scale, all of which allow for industrial adaptation. The direct use of electricity to interconvert halogenated waste streams into pure (stabilized) halides or halogenated high-value products would enable a circular economy of halides (Figure 3). The electrochemical dehalogenation of organic pollutants has been reviewed before but only on a broad scale and without coverage of recent developments.[40] A key design feature could be the avoidance of the isolation of pure halides, which are often gaseous, corrosive, and difficult to handle on a large scale.[41,42] Hence, storage in inert carrier media is highly advantageous and could be realized through the formation of polyhalide anions as a way to store pure halides.[43]

HALOGENATION TRANSFER REACTIONS

To enable efficient (de-)halogenation reactions, the direct use of elemental halides should be avoided because of safety concerns related to toxicity and unfeasible storage capacities. An ideal solution would be the *in situ* transfer of functional groups (e.g., halides) from a stable chemical. Under (metal) catalytic control, this idea was coined "shuttle catalysis" by Bill Morandi.[44,45] However, palladium catalysis is particularly difficult to tame because of undesired side reactions, such as C–C coupling or β-hydride abstraction. Nonetheless organohalides are relatively easy to reduce with electrochemistry and form radical anions upon single-electron transfer (SET).

When coupled with first-row transition-metal catalysts, the electrochemical reduction of vicinal dichlorides and dibromides became a resource for halide shuttle catalysis. In a collaboration, the Waldvogel and Morandi groups identified conditions under which dibromo- or dichloroethane—the latter in combination with manganese catalysis—served as a halide source that was electrochemically transferred to olefins and thus yielded new vicinal dichlorides or dibromides and gaseous ethylene as byproducts (Figure 4).[46] More importantly, this chemistry is amenable to the use of γ-lindane (γ-HCH) as a threefold chlorine source, which liberates benzene as a valuable byproduct from a waste stream (Figure 4, top). *n*-Dodecene (3.5 equiv) could be dichlorinated in 91% isolated yield on a 16 g scale with lindane as a chlorinating agent while benzene was liberated (>95% GC yield). Even artificially contaminated (swiss) soil samples could be used as substrates, revealing the high robustness of electrochemical upcycling of lindane waste. This groundbreaking study opened up opportunities to repurpose halogenated organic pollutants for a circular economy of halogens. After this breakthrough, the same authors achieved a manganese-catalyzed electrochemical bromo-thiolation reaction of alkynes, expanding the scope of shuttle catalysis of vicinal di(pseudo)halides (Figure 4, bottom).[47]

Massive production volumes and end-of-life landfilling make PVC a major environmental threat, driving strong demand for its recycling. Recently, growing interest in the (electro-)chemical recycling and upcycling of PVC[48–50] has driven advances such as the electrification of recycling strategies,[51] the developments of greener solvents,[52] and dechlorinative electrochemical functionalization.[53] However, the primary focus is often

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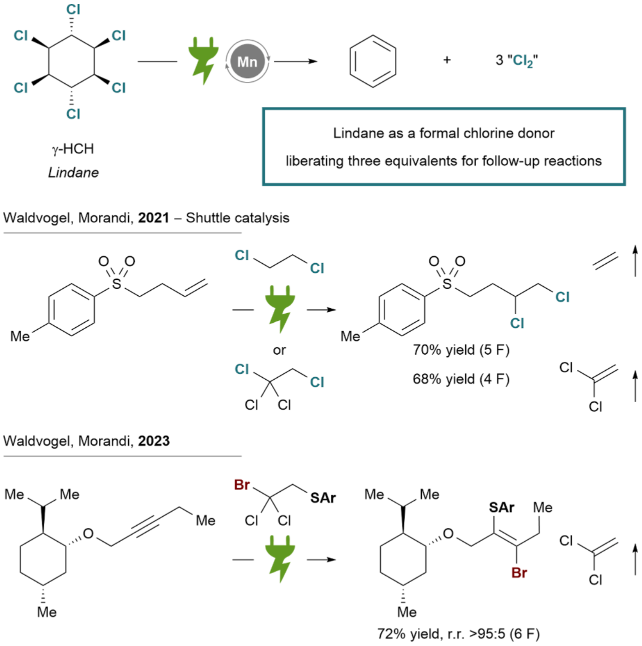

Figure 4. Manganese-catalyzed electrochemical shuttle catalysis enables vicinal *bis*-halogenation of alkenes and alkynes

Lindane waste, an organic pollutant, can be a non-fossil resource for a threefold chlorination reaction while liberating benzene as a base chemical. See Dong et al.[46,47]

dechlorinating PVC to recover the polymeric backbone, leading to additional halogenated waste streams. The Chen group utilized PVC and HBCD for the chlorination and bromination of α-carbonyl compounds in a DMSO-mediated thermal reaction.[54] In most cases, stoichiometric benzyl chloride was used as the chlorine source, but PVC was employed for selected examples (Figure 5). Iso-propyl bromide as the catalyst or mediator was required in DMSO at temperatures between 80°C and 110°C to facilitate the reaction. The high bromide content of HBCD was subsequently harnessed in the direct aromatic bromination of electron-rich arenes, such as phenols and indoles, in up to 71% yield. This proof-of-concept study is a promising starting

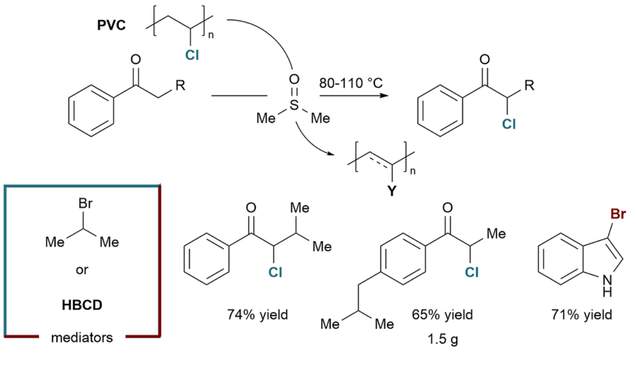

Figure 5. Thermal PVC recycling is coupled to α-carbonyl chlorination and arene bromination

See Liu et al.[54]

point for further optimization toward a more energy-efficient recycling procedure. Nonetheless, the formation of polyvinylalcohol (Y=OH) as a valuable byproduct and the recycling of halides are great examples of moving toward a circular economy.

Similarly, McNeil and co-workers successfully achieved an electrochemical conversion of PVC and were able to harness the liberated chloride in a direct electrochemical chlorination of arenes.[55] Under constant current conditions, they managed to use the plasticizer di(2-ethylhexyl) phthalate (DEHP) as a mediator to facilitate chloride abstraction from PVC in a divided cell setup. The generated chloride could subsequently be oxidized to facilitate the anodic chlorination of mostly electron-rich arene systems (Figure 6). This strategy is an elegant and energy-efficient example of waste recycling and halide circularity.

Precise control over PVC conversion products (PE-Y) must be targeted in the future to allow for easier separation and recycling of the polymeric (by)products from the pure halide.

Electrochemical debromination has been applied to flame retardants, such as polybrominated diphenyl ethers (PDBEs; in DE-83TM)[56] and HBCD.[57] For the latter, full selectivity was observed for cyclododecatriene (CDT) with the use of reticulated vitreous carbon (RVC) electrodes under potentiostatic conditions at −1.60 V (Figure 7, top). Fine control over the conversion products must be ensured, and the recovery and reuse of bromide are still lacking in real-world applications. In order to tackle the dehalogenation of potential wastewater streams, our group was interested in using polyoxometalate ionic liquids (POM-ILs) to efficiently remove anionic and cationic dyes.[58] In this study, removal of the anionic patent blue V sodium salt reached up to 95.5%, whereas removal of the cationic rhodamine B (RhB) chloride salt was as low as 58.6%. These results indicate that highly halogenated anionic dyes, such as bromophenol blue, can be efficiently removed from contaminated wastewater streams and thus recycled in the future.

The electrochemical deiodination of contrast agents (such as iomeprol[59] or iohexol[60]) and structurally similar thyroid hormones[61] has been reported. For example, iomeprol, was fully deiodinated at a nickel foam cathode under potentiostatic conditions at −1.0 V (Figure 7, bottom). The liberated iodine was quantitively recovered but with several byproducts, including partially deiodinated arenes and cleavage of the side chains. Bayer AG is pursuing the recovery and recycling of iodine from contrast agents to enable iodine reuse and provide a new feedstock for their world-scale production.[62]

Recently, simple iodine precursors and more sophisticated iodo-compounds could be degraded by electrochemically generated periodate with complete mineralization of the organic skeleton, providing a pure iodide reagent without cross-contamination.[63,64] This electrochemical upcycling could be scaled into a continuous reactor involving a "feed and bleed" concept[65] and is complementary to the described iodine recovery.

As mentioned above, SF_6 is a global product, but its recycling and utilization are hampered by its chemical inertness. A reduction potential as low as $E_{red} = -2.17$ V vs. FcH^+/FcH has been reported.[66] Hence, strong activation modes are necessary, and many researchers have used photochemical activation with strong UV light to access bond cleavage.[67] In 2016, McTeague and Jamison described a pioneering work for the

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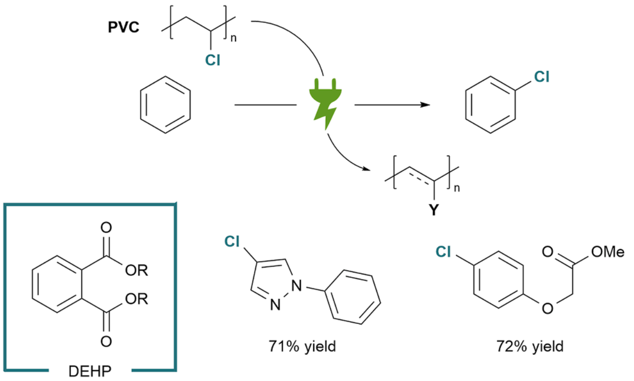

Figure 6. Electrochemical PVC recycling is coupled to arene chlorination
See Fagnani et al.[55]

desoxyfluorination of allylic alcohols by using visible-light photoredox catalysis.[68] However, this strategy liberates SF_5 fragments as a side product, which is not very atom economic. The chemical activation of SF_6 has been achieved with stoichiometric phosphines via nucleophilic attack[69] and with silanes that abstract fluoride in the presence of a rhodium catalyst,[70] among others. It is crucial to mention that despite their intriguing reactivity, such chemical conversions usually introduce additional often stoichiometric reagents that in turn generate (often halogenated) waste, which needs to be treated as new feedstock for halide recycling. Therefore, a more direct conversion should be prioritized. If a highly negative reduction is followed by an *in situ* excitation ($E_{exc} > 2$ eV, ~ 46 kcal mol^{-1}), the following reactivity can be obtained:[67]

$$\mathrm{SF_6} \xrightarrow{E_{red}} \mathrm{SF_6^{\cdot -}} \xrightarrow{E_{exc}} \mathrm{SF_5^{\cdot}} + \mathrm{F^-} \qquad \text{(Equation 1)}$$

Thus, the SF_5 fragment can be incorporated after radical reactivity and can find application as a highly lipophilic functional group in medicinal applications. In 2018, the Wagenknecht group developed the dual excitation by using UV and visible light for the pentafluorosulfanylation of olefins (Figure 8), which was later refined to an excitation using purely 368 nm light.[71,72]

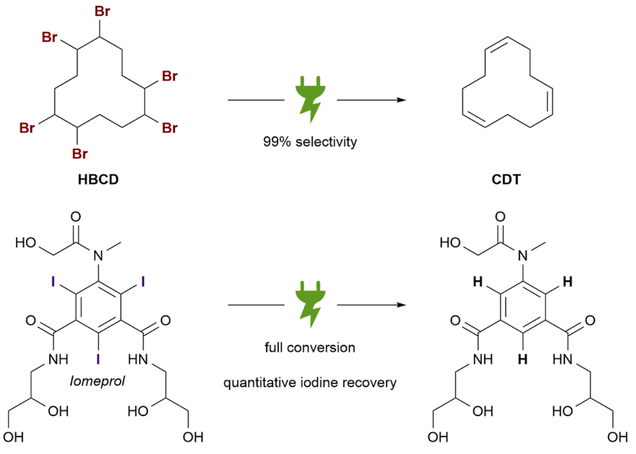

Figure 7. Electrochemical dehalogenation of flame retardant HBCD and contrast agent iomeprol
See Wagoner et al.[57] and Zwiener et al.[59]

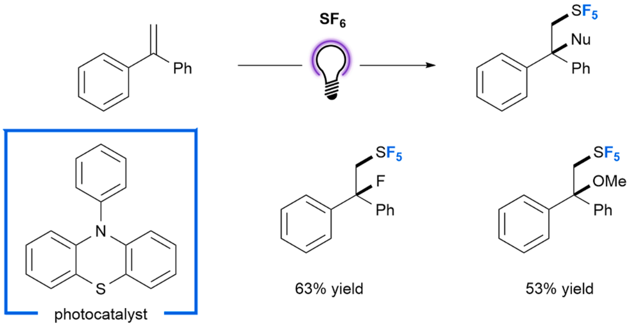

Figure 8. Photochemical pentafluorosulfanylation using SF_6 as a resource
See Rombach and Wagenknecht.[71]

Nonetheless, no electrosynthetic applications of SF_6 as a halide feedstock have been reported to date. The outlined challenges might be accessed by new strategies.

PERSPECTIVES AND FUTURE DIRECTIONS

The defossilization of chemistry—and of the chemical industry in particular—is inevitable and extends well beyond decarbonization alone. As humans and as researchers, we must conserve finite mineral resources and therefore reuse or upcycle (halogenated) waste streams. To date, this has been realized only for a few halogenated compounds, largely because of scale limitations and the lack of cost-efficient recycling strategies. Historically, hydrochloric acid waste was discharged into the oceans, whereas contemporary chemical plants instead employ electrolysis to recover chlorine from the same waste stream. This base chemical is broadly required, and its recovery substantially reduces the demand for mined rock salt, enabling circularity.[43] If the so-formed chlorine is not consumed on site, innovative and safe storage concepts are required. A particularly promising approach involves the formation of polychloride-based ionic liquids, which liberate the halide upon heating.[73–77] Thus, on-demand release of chlorine is achieved, and long-term storage of the corrosive gas is avoided. The electrochemical conversion of HCl further facilitates this process.

As outlined above, lindane waste can act as a viable and non-fossil chlorine source with about 75% chlorine content by mass while releasing benzene as a valuable byproduct. Because very large deposits of highly chlorinated (or halogenated) pollutants are generally globally available, these could be cost-efficiently upcycled and could provide non-fossil-based fine chemicals if the respective organic carbon backbone is utilized. Such a strategy will be also a good chance to generate revenue while supporting the environment.

At scale, the second most applied halogen is fluorine. In particular, for many advanced materials, it provides unique features that will be difficult to replace. Of utmost importance are polyfluorinated polymers such as PTFE, membranes (e.g., Nafion),

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and various PFAS used as surfactants or surface modifiers in the production of coatings, paints, or lubricants. The annual demand for fluorine-containing products in the form of hydrogen fluoride (HF) for fluorinated organic materials is projected to reach a market volume of 2.8 Mt by 2030.[78] Even though these highly fluorinated materials might be completely banned at any time, they are still inevitable for modern energy applications and will appear as waste stream for a long time.

Removing organic pollutants (such as halogenated dyes) originating from industrial processes and products from aqueous samples or wastewater is essential for improving water quality. Ideally, these compounds are recycled back into the value chain, achieving a dual benefit by preventing environmental pollution and enabling the recovery of valuable organic compounds.

Even if the scale of bromine and iodine chemicals available for innovative recycling and upcycling is much smaller, the ever-shrinking natural resources and rising costs make such an approach very attractive.[41] In particular, large quantities of brominated flame retardants, such as HBCD, which are generated during the recycling of home insulation, will be of paramount importance.

In all cases, activating these very stable compounds requires new strategies, among which photochemistry, mechanochemistry, and electrosynthesis are particularly attractive. Importantly, the halo-species should be obtained in a reactive form and for direct synthetic use. In terms of scalability and the transfer of halogenated species to other target molecules or storage systems, electrochemistry offers a promising route.[34,79] In electrochemical conversions, many misconceptions persist, but the technology has reached a level of maturity compatible with technical applications. The increasing interest in electrochemical and particularly electro-organic transformations within the chemical industry will further create momentum to drive a systematic change toward electrification. With more standardized reactor designs at hand and more trained chemists operating them, the implementation of circular feedstocks will be within reach.

However, many catastrophic chemical events (e.g., Seveso) have led to strict regulations that need to be modified accordingly. Addressing this challenge will require joint efforts by scientists, authorities, and policymakers. In this context, science communication plays a key mediating role between stakeholders, and chemists are well positioned to facilitate such discussions. We therefore encourage readers to consider creative chemical solutions toward a circular, electrochemically driven halogen economy and engage broadly in discussions of emerging opportunities.

ACKNOWLEDGMENTS

We acknowledge the project "Halocycles-Halogen cycles as important contributions to the stabilization of the power grid and the defossilization of the future industrial society," funded by the Carl Zeiss Foundation, as well as BMBF-Zukunftscluster "Elektrifizierung Technischer Organischer Synthesen (ETOS)" and its project Elektrochemische Valorisierung von hochchlorierten persistenten Abfällen (EVALINA; 03ZU125GD).

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Luo, Y.-R. (2007). Comprehensive Handbook of Chemical Bond Energies (CRC Press). https://doi.org/10.1201/9781420007282.
2. Jamieson, A.J., Malkocs, T., Piertney, S.B., Fujii, T., and Zhang, Z. (2017). Bioaccumulation of persistent organic pollutants in the deepest ocean fauna. Nat. Ecol. Evol. *1*, 51. https://doi.org/10.1038/s41559-016-0051.
3. Stockholm Convention. What are POPs? https://chm.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx.
4. Blake, B.E., and Fenton, S.E. (2020). Early life exposure to per- and polyfluoroalkyl substances (PFAS) and latent health outcomes: A review including the placenta as a target tissue and possible driver of peri- and postnatal effects. Toxicology *443*, 152565. https://doi.org/10.1016/j.tox.2020.152565.
5. Trang, B., Li, Y., Xue, X.-S., Ateia, M., Houk, K.N., and Dichtel, W.R. (2022). Low-temperature mineralization of perfluorocarboxylic acids. Science *377*, 839–845. https://doi.org/10.1126/science.abm8868.
6. BCC Research (2024). Fluoropolymer materials: Technologies and global markets. Report PLS080C. https://www.bccresearch.com/market-research/plastics/fluoropolymer-materials-technologies-global-markets-report.html.
7. Wall, L.A., and Michaelsen, J.D. (1956). Thermal decomposition of polytetrafluoroethylene in various gaseous atmospheres. J. Res. Natl. Bur. Stand. *56*, 27–34. https://doi.org/10.6028/jres.056.004.
8. Nag, A., Baksi, A., Ghosh, J., Kumar, V., Bag, S., Mondal, B., Ahuja, T., and Pradeep, T. (2019). Tribochemical degradation of polytetrafluoroethylene in water and generation of nanoplastics. ACS Sustainable Chem. Eng. *7*, 17554–17558. https://doi.org/10.1021/acssuschemeng.9b03573.
9. Roehl, C.M., Boglu, D., Brühl, C., and Moortgat, G.K. (1995). Infrared band intensities and global warming potentials of CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12}, and C_6F_{14}. Geophys. Res. Lett. *22*, 815–818. https://doi.org/10.1029/95GL00488.
10. Ramanathan, V. (1975). Greenhouse effect due to chlorofluorocarbons: Climatic implications. Science *190*, 50–52. https://doi.org/10.1126/science.190.4209.50.
11. Western, L.M., Daniel, J.S., Vollmer, M.K., Clingan, S., Crotwell, M., Fraser, P.J., Ganesan, A.L., Hall, B., Harth, C.M., Krummel, P.B., et al. (2024). A decrease in radiative forcing and equivalent effective chlorine from hydrochlorofluorocarbons. Nat. Clim. Chang. *14*, 805–807. https://doi.org/10.1038/s41558-024-02038-7.
12. Sakai, E.M., Connolly, L.A., and Klauck, J.A. (2005). Inhalation anesthesiology and volatile liquid anesthetics: Focus on isoflurane, desflurane, and sevoflurane. Pharmacotherapy *25*, 1773–1788. https://doi.org/10.1592/phco.2005.25.12.1773.
13. Jerath, A., Parotto, M., Wasowicz, M., and Ferguson, N.D. (2016). Volatile anesthetics. Is a new player emerging in critical care sedation? Am. J. Respir. Crit. Care Med. *193*, 1202–1212. https://doi.org/10.1164/rccm.201512-2435CP.
14. Sulbaek Andersen, M.P., Nielsen, O.J., and Sherman, J.D. (2023). Assessing the potential climate impact of anaesthetic gases. Lancet Planet. Health *7*, e622–e629. https://doi.org/10.1016/S2542-5196(23)00084-0.
15. Ryan, S.M., and Nielsen, C.J. (2010). Global warming potential of inhaled anesthetics: Application to clinical use. Anesth. Analg. *111*, 92–98. https://doi.org/10.1213/ANE.0b013e3181e058d7.
16. Mulier, H., Struys, M.M.R.F., Vereecke, H., Rex, S., Teunkens, A., and Kalmar, A.F. (2024). Efficiency of CONTRAfluran™ in reducing sevoflurane pollution from maintenance anaesthesia in minimal flow end-tidal control mode for laparoscopic surgery. Anaesthesia *79*, 849–855. https://doi.org/10.1111/anae.16289.
17. Ryvlin, D., Girschikofsky, M., Schollmeyer, D., Hellmann, R., and Waldvogel, S.R. (2018). Methyl-substituted α-cyclodextrin as affinity material for storage, separation, and detection of trichlorofluoromethane. Glob. Chall. *2*, 1800057. https://doi.org/10.1002/gch2.201800057.

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18. Solvay Special Chemicals. (2018). Sulphur hexafluoride. https://www.solvay.com/sites/g/files/srpend616/files/2018-08/SF6-Sulphur-Hexafluoride_0.pdf.

19. Ottinger, D., Averyt, M., and Harris, D. (2015). US consumption and supplies of sulphur hexafluoride reported under the greenhouse gas reporting program. J. Integr. Environ. Sci. *12*, 5–16. https://doi.org/10.1080/1943815X.2015.1092452.

20. Dervos, C.T., and Vassiliou, P. (2000). Sulfur hexafluoride (SF_6): Global environmental effects and toxic byproduct formation. J. Air Waste Manag. Assoc. *50*, 137–141. https://doi.org/10.1080/10473289.2000.10463996.

21. Solvay Special Chemicals. (2013). Advancing circularity at Solvay. https://www.solvay.com/en/sustainability/planet-progress/more-circularity.

22. Vijgen, J., de Borst, B., Weber, R., Stobiecki, T., and Forter, M. (2019). HCH and lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue. Environ. Pollut. *248*, 696–705. https://doi.org/10.1016/j.envpol.2019.02.029.

23. Vijgen, J., Abhilash, P.C., Li, Y.F., Lal, R., Forter, M., Torres, J., Singh, N., Yunus, M., Tian, C., Schäffer, A., et al. (2011). Hexachlorocyclohexane (HCH) as new Stockholm Convention POPs—A global perspective on the management of lindane and its waste isomers. Environ. Sci. Pollut. Res. Int. *18*, 152–162. https://doi.org/10.1007/s11356-010-0417-9.

24. Tiwari, R., Agrawal, P.S., Belkhode, P.N., Ruatpuia, J.V.L., and Rokhum, S.L. (2024). Hazardous effects of waste transformer oil and its prevention: A review. Next Sustain. *3*, 100026. https://doi.org/10.1016/j.nxsust.2024.100026.

25. National Research Council (2001). A Risk-Management Strategy for PCB-Contaminated Sediments (National Academies of Sciences, Engineering, and Medicine), pp. 23–51. https://www.nationalacademies.org/read/10041.

26. Fittkau, L. (2019). Die dunkle Seite des “Monte Kali”. Deutschlandfunk. April 14, 2019. https://www.deutschlandfunk.de/weltgroesste-untertage-giftmuell-deponie-die-dunkle-seite-100.html.

27. Nitschmann, J., and Hilt, O. (2018). Giftige Zeiten. Forum – Das Wochenmagazin. May 25, 2018. https://www.magazin-forum.de/de/node/9346.

28. Kudzin, M.H., Piwowarska, D., Festinger, N., and Chruściel, J.J. (2023). Risks associated with the presence of polyvinyl chloride in the environment and methods for its disposal and utilization. Materials *17*, 173. https://doi.org/10.3390/ma17010173.

29. Fu, Q., Fedrizzi, D., Kosfeld, V., Schlechtriem, C., Ganz, V., Derrer, S., Rentsch, D., and Hollender, J. (2020). Biotransformation changes bioaccumulation and toxicity of diclofenac in aquatic organisms. Environ. Sci. Technol. *54*, 4400–4408. https://doi.org/10.1021/acs.est.9b07127.

30. Peters, A., Crane, M., Merrington, G., and Ryan, J. (2022). Environmental quality standards for diclofenac derived under the European water framework directive: 2. Avian secondary poisoning. Environ. Sci. Eur. *34*, 28. https://doi.org/10.1186/s12302-022-00601-7.

31. Stockholm Convention on Persistent Organic Pollutants. (2010). Risk profile on hexabromocyclododecane. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.6-13-Add.2.English.pdf.

32. Alaee, M., Arias, P., Sjödin, A., and Bergman, A. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ. Int. *29*, 683–689. https://doi.org/10.1016/S0160-4120(03)00121-1.

33. Pasternak, J.J., and Williamson, E.E. (2012). Clinical pharmacology, uses, and adverse reactions of iodinated contrast agents: A primer for the non-radiologist. Mayo Clin. Proc. *87*, 390–402. https://doi.org/10.1016/j.mayocp.2012.01.012.

34. Seidler, J., Strugatchi, J., Gärtner, T., and Waldvogel, S.R. (2020). Does electrifying organic synthesis pay off? The energy efficiency of electro-organic conversions. MRS Energy Sustain. *7*, 42. https://doi.org/10.1557/mre.2020.42.

35. Möhle, S., Zirbes, M., Rodrigo, E., Gieshoff, T., Wiebe, A., and Waldvogel, S.R. (2018). Modern electrochemical aspects for the synthesis of value-added organic products. Angew. Chem. Int. Ed. *57*, 6018–6041. https://doi.org/10.1002/anie.201712732.

36. Wiebe, A., Gieshoff, T., Möhle, S., Rodrigo, E., Zirbes, M., and Waldvogel, S.R. (2018). Electrifying organic synthesis. Angew. Chem. Int. Ed. *57*, 5594–5619. https://doi.org/10.1002/anie.201711060.

37. Yan, M., Kawamata, Y., and Baran, P.S. (2017). Synthetic organic electrochemical methods since 2000: On the verge of a renaissance. Chem. Rev. *117*, 13230–13319. https://doi.org/10.1021/acs.chemrev.7b00397.

38. Pollok, D., and Waldvogel, S.R. (2020). Electro-organic synthesis – A 21st century technique. Chem. Sci. *11*, 12386–12400. https://doi.org/10.1039/D0SC01848A.

39. Zhu, C., Ang, N.W.J., Meyer, T.H., Qiu, Y., and Ackermann, L. (2021). Organic electrochemistry: Molecular syntheses with potential. ACS Cent. Sci. *7*, 415–431. https://doi.org/10.1021/acscentsci.0c01532.

40. Peters, D.G., McGuire, C.M., Pasciak, E.M., Peverly, A.A., Strawsine, L.M., Wagoner, E.R., and Barnes, J.T. (2017). Electrochemical dehalogenation of organic pollutants. J. Mex. Chem. Soc. *58*, 287–302. https://doi.org/10.29356/jmcs.v58i3.135.

41. Gombos, L.G., and Waldvogel, S.R. (2022). Electrochemical bromofunctionalization of alkenes and alkynes—To sustainability and beyond. Sustain. Chem. *3*, 430–454. https://doi.org/10.3390/suschem3040027.

42. Gombos, L.G., Nikl, J., and Waldvogel, S.R. (2024). Dual roles of supporting electrolytes in organic electrosynthesis. ChemElectroChem *11*, e202300730. https://doi.org/10.1002/celc.202300730.

43. Schwan, J., Kleoff, M., Dreyhsig, G.H., Voßnacker, P., Fiedler, T., Rosental, M., and Riedel, S. (2025). Rethinking chlorine: Essential chemical or replaceable risk? ChemSusChem *18*, e202402697. https://doi.org/10.1002/cssc.202402697.

44. Bhawal, B.N., and Morandi, B. (2016). Catalytic transfer functionalization through shuttle catalysis. ACS Catal. *6*, 7528–7535. https://doi.org/10.1021/acscatal.6b02333.

45. Bhawal, B.N., and Morandi, B. (2017). Shuttle catalysis—New strategies in organic synthesis. Chem. Eur. J. *23*, 12004–12013. https://doi.org/10.1002/chem.201605325.

46. Dong, X., Roeckl, J.L., Waldvogel, S.R., and Morandi, B. (2021). Merging shuttle reactions and paired electrolysis for reversible vicinal dihalogenations. Science *371*, 507–514. https://doi.org/10.1126/science.abf2974.

47. Dong, X., Klein, M., Waldvogel, S.R., and Morandi, B. (2023). Controlling selectivity in shuttle hetero-difunctionalization reactions: Electrochemical transfer halo-thiolation of alkynes. Angew. Chem. Int. Ed. *62*, e202213630. https://doi.org/10.1002/anie.202213630.

48. Hourtoule, M., Trienes, S., and Ackermann, L. (2025). Electrochemical commodity polymer up- and re-cycling: Toward sustainable and circular plastic treatment. Macromol. Rapid Commun. *46*, e2500143. https://doi.org/10.1002/marc.202500143.

49. Zhang, S., Han, H., Cao, M., Xie, Y., and Chen, J. (2025). Upvaluing chlorinated plastic wastes. Interdiscip. Mater. *4*, 5–23. https://doi.org/10.1002/idm2.12211.

50. Havaei, M., Akin, O., Locaspi, A., John Varghese, R., Minette, F., Romers, E., De Meester, S., and Van Geem, K.M. (2025). Beyond the landfill: A critical review of techniques for end-of-life polyvinyl chloride (PVC) valorization. Waste Manag. *193*, 105–134. https://doi.org/10.1016/j.wasman.2024.11.023.

51. Theofanidis, S.A., Delikonstantis, E., Yfanti, V.-L., Galvita, V.V., Lemonidou, A.A., and Van Geem, K. (2025). An electricity-powered future for mixed plastic waste chemical recycling. Waste Manag. *193*, 155–170. https://doi.org/10.1016/j.wasman.2024.12.003.

52. Razzaq, A.U., and Esfahani, M.R.G. (2025). Green(er) solvents for upcycling waste PVC into membranes. J. Membr. Sci. *717*, 123603. https://doi.org/10.1016/j.memsci.2024.123603.

53. Zackasee, J.L.S., Srivardhan, V., Truesdell, B.L., Vrana, E.J., and Sevov, C.S. (2025). Electrocatalytic grafting of polyvinyl chloride plastics. Chem *11*, 102298. https://doi.org/10.1016/j.chempr.2024.08.021.

Please cite this article in press as: Beil and Waldvogel, Upcycling of persistent pollutants: Toward an electrochemically driven circular halogen economy, Chem (2025), https://doi.org/10.1016/j.chempr.2025.102831

54. Liu, H., Ji, D.-W., Mei, Y.-K., Liu, Y., Liu, C.-H., Wang, X.-Y., and Chen, Q.-A. (2024). Repurposing of halogenated organic pollutants via alkyl bromide-catalysed transfer chlorination. Nat. Chem. *16*, 1505–1514. https://doi.org/10.1038/s41557-024-01551-8.

55. Fagnani, D.E., Kim, D., Camarero, S.I., Alfaro, J.F., and McNeil, A.J. (2023). Using waste poly(vinyl chloride) to synthesize chloroarenes by plasticizer-mediated electro(de)chlorination. Nat. Chem. *15*, 222–229. https://doi.org/10.1038/s41557-022-01078-w.

56. Konstantinov, A., Bejan, D., Bunce, N.J., Chittim, B., McCrindle, R., Potter, D., and Tashiro, C. (2008). Electrolytic debromination of PBDEs in DE-83^{TM} technical decabromodiphenyl ether. Chemosphere *72*, 1159–1162. https://doi.org/10.1016/j.chemosphere.2008.03.046.

57. Wagoner, E.R., Baumberger, C.P., Peverly, A.A., and Peters, D.G. (2014). Electrochemical reduction of 1,2,5,6,9,10-hexabromocyclododecane at carbon and silver cathodes in dimethylformamide. J. Electroanal. Chem. *713*, 136–142. https://doi.org/10.1016/j.jelechem.2013.11.033.

58. Oseghe, E.O., Guba, F., Misra, A., Gong, R., Liu, R., Waldvogel, S.R., Ziegenbalg, D., Streb, C., and Gao, D. (2023). A scalable flow device for the removal of organic and inorganic pollutants from water. Device *1*, 100020. https://doi.org/10.1016/j.device.2023.100020.

59. Zwiener, C., Glauner, T., Sturm, J., Wörner, M., and Frimmel, F.H. (2009). Electrochemical reduction of the iodinated contrast medium iomeprol: Iodine mass balance and identification of transformation products. Anal. Bioanal. Chem. *395*, 1885–1892. https://doi.org/10.1007/s00216-009-3098-9.

60. Zhang, W., Soutrel, I., Amrane, A., Fourcade, F., and Geneste, F. (2021). Electro-reductive deiodination of iohexol catalyzed by vitamin B12 and biodegradability investigation. J. Electroanal. Chem. *897*, 115559. https://doi.org/10.1016/j.jelechem.2021.115559.

61. Romańczyk, P.P., and Kurek, S.S. (2024). Noncatalytic reductive deiodination of thyroid hormones. Electrochemistry and quantum chemical calculations. ChemElectroChem *11*, e202300527. https://doi.org/10.1002/celc.202300527.

62. Bayer AG. (2025). Consolidated environmental statement 2025. https://www.bayer.com/sites/default/files/consolidated-environmetal-statement-2025-bayer-bergkamen.pdf.

63. Arndt, S., Weis, D., Donsbach, K., and Waldvogel, S.R. (2020). The "green" electrochemical synthesis of periodate. Angew. Chem. Int. Ed. *59*, 8036–8041. https://doi.org/10.1002/anie.202002717.

64. Kisukuri, C.M., Bednarz, R.J.-R., Kampf, C., Arndt, S., and Waldvogel, S.R. (2022). Robust and self-cleaning electrochemical production of periodate. ChemSusChem *15*, e202200874. https://doi.org/10.1002/cssc.202200874.

65. Arndt, S., Rücker, R., Stenglein, A., and Waldvogel, S.R. (2022). Reactor design for the direct electrosynthesis of periodate. Org. Process Res. Dev. *26*, 2447–2455. https://doi.org/10.1021/acs.oprd.2c00116.

66. Bouvet, S., Pégot, B., Sengmany, S., Le Gall, E., Léonel, E., Goncalves, A.-M., and Magnier, E. (2020). Controlled decomposition of SF_6 by electrochemical reduction. Beilstein J. Org. Chem. *16*, 2948–2953. https://doi.org/10.3762/bjoc.16.244.

67. Rombach, D., and Wagenknecht, H.-A. (2022). Photochemical activation of sulfur hexafluoride: A tool for fluorination and pentafluorosulfanylation reactions. Synthesis *54*, 4883–4894. https://doi.org/10.1055/a-1877-5231.

68. McTeague, T.A., and Jamison, T.F. (2016). Photoredox activation of SF_6 for fluorination. Angew. Chem. Int. Ed. *55*, 15072–15075. https://doi.org/10.1002/anie.201608792.

69. Buß, F., Mück-Lichtenfeld, C., Mehlmann, P., and Dielmann, F. (2018). Nucleophilic activation of sulfur hexafluoride: Metal-free, selective degradation by phosphines. Angew. Chem. Int. Ed. *57*, 4951–4955. https://doi.org/10.1002/anie.201713206.

70. Zámostná, L., Braun, T., and Braun, B.S. (2014). S–F and S–C activation of SF_6 and SF_5 derivatives at rhodium: Conversion of SF_6 into H_2S. Angew. Chem. Int. Ed. *53*, 2745–2749. https://doi.org/10.1002/anie.201308254.

71. Rombach, D., and Wagenknecht, H.-A. (2020). Photoredox catalytic α--alkoxypentafluorosulfanylation of α-methyl- and α-phenylstyrene using SF_6. Angew. Chem. Int. Ed. *59*, 300–303. https://doi.org/10.1002/anie.201910830.

72. Rombach, D., and Wagenknecht, H.-A. (2018). Photoredox catalytic activation of sulfur hexafluoride for pentafluorosulfanylation of α-methyl- and α-phenyl styrene. ChemCatChem *10*, 2955–2961. https://doi.org/10.1002/cctc.201800501.

73. Lorente, A., Sturm, J.S., Kleoff, M., Lorenz, F., Voßnacker, P., Wagner, O., Haag, R., and Riedel, S. (2025). Polyethyleneimine-based cryogels enabling the selective and reversible adsorption of chlorine. Adv. Sci. *12*, e2414274. https://doi.org/10.1002/advs.202414274.

74. Dreyhsig, G.H., Voßnacker, P., Kleoff, M., Baunis, H., Limberg, N., Lu, M., Schomäcker, R., and Riedel, S. (2024). Bichloride-based ionic liquids for the merged storage, processing, and electrolysis of hydrogen chloride. Sci. Adv. *10*, eadn5353. https://doi.org/10.1126/sciadv.adn5353.

75. Ernst, M.J., Kleoff, M., Voßnacker, P., Thiele, G., Müller, C., and Riedel, S. (2024). A polychloride-enabled synthesis of $[NEt_3Me][PCl_6]$ serving as a potential PCl_3-storage and PCl_5-reagent. Chem. Commun. *60*, 13372–13375. https://doi.org/10.1039/D4CC04319G.

76. Rathmann, S., Braune, F., Kleoff, M., Voßnacker, P., Pölloth, B., Müller, C., and Riedel, S. (2024). Polychlorides—A safe and convenient alternative for elemental chlorine in demonstration experiments. J. Chem. Educ. *101*, 1394–1401. https://doi.org/10.1021/acs.jchemed.3c01252.

77. Voßnacker, P., Schwarze, N., Keilhack, T., Kleoff, M., Steinhauer, S., Schiesser, Y., Paven, M., Yogendra, S., Weber, R., and Riedel, S. (2022). Alkyl ammonium chloride salts for efficient chlorine storage at ambient conditions. ACS Sustainable Chem. Eng. *10*, 9525–9531. https://doi.org/10.1021/acssuschemeng.2c02186.

78. Statista. (2022). Market volume of hydrofluoric acid worldwide from 2015 to 2022, with a forecast for 2023 to 2030. https://www.statista.com/statistics/1245196/hydrofluoric-acid-market-volume-worldwide/.

79. Beil, S.B., Pollok, D., and Waldvogel, S.R. (2021). Reproducibility in electroorganic synthesis—Myths and misunderstandings. Angew. Chem. Int. Ed. *60*, 14750–14759. https://doi.org/10.1002/anie.202014544.