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ENVIRONMENTAL CONTAMINANTS OF EMERGING CONCERN: OCCURRENCE AND REMEDIATION

Abstract: Certain contaminants are termed as emerging (Contaminants of Emerging Concern, CEC) since all aspects of these pollutants are not known and their regulation is not ununiform across the nations. The CECs include many classes of compounds that are used in various industries, plant protection chemicals, personal care products and medicines. They accumulate in waterbodies, soils, organisms including humans. They cause deleterious effects on plant animal and human health. Therefore, alternative greener synthesis of these chemicals, sustainable economic methods of waste disposal, scaling up and circular methods using sludge for removing the contaminants are innovative methods that are pursued. There are several improvements in chemical waste treatments using electro-oxidation coupled with solar energy, high performing recycled granular activated charcoal derived from biomass are few advances in the field. Similarly, use of enzymes from microbes for waste removals is a widely used technique for bioremediation. The organisms are genetically engineered to remove hazardous chemicals, dyes, and metals. Novel technologies for mining economically the precious and rare earth elements from e-waste can improve circular economy. However, there is additional need for participation of various nations in working towards greener Earth. There should be pollution awareness in local communities that can work along with Government legislations.

Keywords: contaminants of emerging concern, health hazards, chemical waste disposal, sludge and water treatments, bioremediation, engineered organisms

Introduction

The European Green Deal was set up to take account of pollution in the member states, suggest policies to the Governments to enact laws to achieve the goals of sustainable economic growth in the conditions of changing climatic conditions [1-5]. This initiative could improve circular economy in the implementing countries [6].The Net Zero emission concept includes that man should not impact climate and environment. However, to keep the rise in temperatures at check there should be zero emission by 2050 [7, 8]. Several nations including developed, developing, and underdeveloped countries are focussing their attention towards Zero emission strategies by 2050. Recently material footprints that are defined as the sum of the material footprint (MF) for biomass, fossil fuels, metal ores, and non-metal ores were studied in European countries. The study found MF increases carbon emission in general. However, carbon emissions increase is more pronounced in developing countries [9]. New Zealand goal of zero emissions by 2050 was modelled recently. The use

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of renewable energy and improved forest cover were suggested as possible factors that can make the Zero emission goal a reality [10, 11].

Environmental researchers are now interested in contaminants of emergent concern (CECs) because they contaminate air water and soil resources and are threat to human and animal health on the planet. They are defined as “A chemical for which there are increasing concerns regarding its potential risks to humans and ecological systems, including endocrine disruption and neurotoxicity”. However, the definition has undergone many changes recently. These CECs are not regulated in various countries increasing the concern. Several categories of chemicals including pharmaceuticals, personal care products, agrochemicals, industrial chemicals, microplastics, disinfection by-products, biotoxins, heavy metals including lead, cadmium, mercury arsenic, radioactive waste and waterborne pathogens, come under the class of contaminants of emerging concern [12, 13]. Personal care products, pathogens with emphasis on antibiotic resistance is reviewed by us before [14]. Some constituents of CECs such as microplastics can adsorb other class of CECs including toxic metals and are threat to aquatic life and humans necessitating the studies on removal of these pollutants [15, 16]. Further, the electronic waste generated could have hazardous chemicals including microplastics, chemicals heavy metals and Rare Earth Elements (REE). The CECs are found contaminating water bodies and pose great danger to human plant and animal health. Ex rivers in Brazil, South Africa and Spain are polluted with CECs [17, 18]. A group of 44 CECs were identified in Maumee river in Ohio. These pollutants were found to alter transcriptomic signatures and metabolite profile in the freshwater mussel [19]. The researchers concluded that the organism experienced altered metabolism in response to stress and could be the main reason for the reduction in mussel population in these waters. The threat to aquatic life is a huge matter of concern. Therefore, policies and regulations by governments and stringent surveillances are needed to reduce these pollutants. The present review focuses on some constituents of CECs, for Ex per- and poly-fluoroalkyl substances (PFAS), agrochemicals, e-waste microplastics and DBPs and latest remedial methods to lessen these constituents of CECs in the atmosphere.

Chemical methods of removing CECs

There is lot of research in progress utilising chemical treatments of CECs. The number of publications on CECs increased rapidly from 2000 to 2023 (Fig. 1). Several chemical methods are in use to treat CECs. Electro-oxidation (EO) process is one among them, that can be used to remove CECs. The pollutants can be oxidised directly or indirectly at the anode. Additionally, Fenton reaction is performed by the addition of Fe^{2+} ions and then irradiated using sunlight. This method is termed as Solar Electro-Fenton (SEF), and this process has more efficiency in removing CECs compared to EO process. UV light can be used too. However, Sunlight is more economically viable. Several CECs are removed using above method from contaminated water [20]. Granular activated charcoal (GAC) was used to adsorb CECs in a laboratory experiment. The CECs in water were measured using mass spectrometry. Then the process was scaled up to waste water treatment plant. It was observed that, this could be a viable option for removing multiple classes of CECs. A circular economy was envisaged when sludge based activated charcoal was using for CECs removal, especially PFAS. The contaminants are removed completely by the process of pyrolysis of carbon [21]. Another technology is to conserve the GAC used for repeated use so that contaminants can be removed economically. Hydrothermal alkali treatment was used to recycle GACs which could adsorb pollutants without losing its properties of adsorption [22]. The entire process is environmentally sustainable and no waste was generated. Titanium dioxide (TiO_2) mediated photocatalysis in another widely used the technology, for removing CECs [23]. The TiO_2 nanocomposites using other metals and polymers are employed to remove several classes of chemicals, microplastics and pesticides [24]. The methods employed for individual constituents of CECs such as PFAS, Agrochemicals, e-waste, DBP and microplastics are reviewed further.

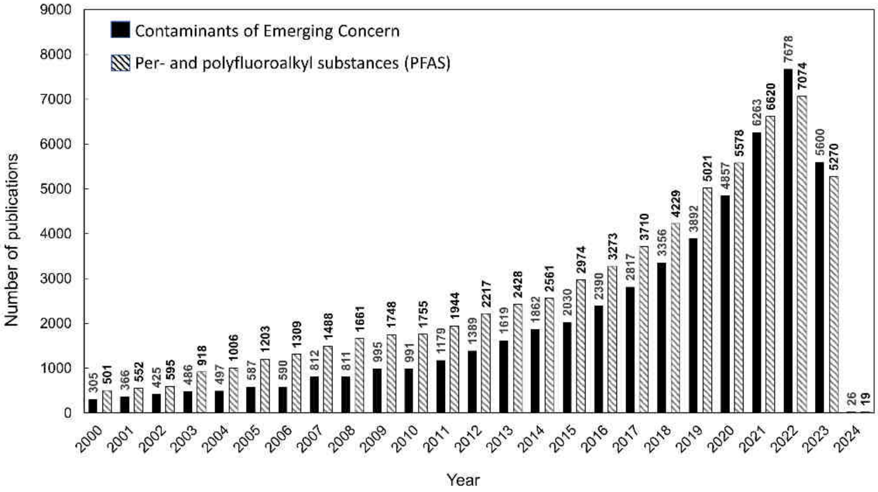

Fig. 1. Articles published in the past two and half decades beginning 2000 to 2023 on contaminants of emergent concern (CEC) based on www.scientificdirect. Keywords used CEC and used "PFAS"

Polyfluoroalkyl and perfluoroalkyl substances

The research on wide CECs especially, variety of man-made chemicals known as poly-/per-fluoroalkyl substances (PFAS) has increased in the recent years (Fig. 2). The revised definition of PFAS is “PFAS are fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)” by Organisation for Economic Cooperation and Development (2021). PFAS are used in non-stick cookware, paints, water-resistant clothes, personal protection equipment, ski waxes, and medical gadgets [25]. Per- and polyfluorinated alkyl compounds (PFAS) are a class of contaminants that are entirely man-made and do not occur in nature. PFAS include almost 4,700 different chemicals. PFAS are highly effective, persistent, and transportable. These partially fluorinated, so-called polyfluorinated substances - often referred to as "precursors" - can be converted into persistent, completely fluorinated (perfluorinated) molecules. These PFAS (for ever chemicals) were designated as emerging pollutants in 2014 [26]. Due to their distinct properties, such as resistance to heat, water, and oil, approximately greater than 8,000 different PFAS have been produced and utilised globally to date and the list is growing (US Environmental Protection Agency, “PFAS structures in DSSTox) [27]. Widely studied examples are: perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). PFAS can be used in both general-use products like food packaging and fabrics that are water- and stain-resistant as well as in more specialised uses like firefighting foams. Additionally, several uses are found in about 200 categories utilising 1400 PFAS [28]. PFAS remain in the environment and exhibit unpredictable behaviour after being released into the environment. PFAS content will change depending on the goods being produced or used at a certain source [29]. For instance, PFHpA (7 carbons) and other PFCAs with 5- to 8-carbon chains have been found to be present in wood fibre insulation. Digital cameras, cell phones, printers, and scanners have all been made using PFOS in the semiconductor sector. The PFAS contaminants were observed in waste streams grown lettuce [30] and in marine ecosystem in several marine animals [31]. To understand the PFAS terminology. The following criteria should be used for grouping PFAS by carbon chain length (ITRC, 2021c).

Perfluoroalkyl carboxylic acids (PFCAs) with 8 or more carbons (7 or more carbons are entirely fluorinated); perfluoroalkane sulfonates (PFSAs) with 6 or more carbons (6 or more carbons are completely fluorinated); and other compounds with long chains. Perfluoroalkyl carboxylic acids (PFCAs) with seven or fewer carbons (six or fewer of those carbons are totally fluorinated); and perfluoroalkane sulfonates (PFSAs) with five or fewer carbons are considered short chain (5 or fewer carbons are completely fluorinated). Short-chain PFAS are still produced, some of which may undergo chemical changes to produce long-chain PFAS, even though many of the long-chain PFAS have been phased out by their producers due to their possible effects on the environment and human health. The synthesis is a complex process utilising calcium fluoride (CaF_2) mineral and getting hydrogen fluoride (HF) which are reactants for producing starting material (perfluoroalkanoyl fluorides) by the process of fluorination. There are two methods used these are electrochemical fluorination and oligomerisation (process of polymer is formed by monomers). However, the former process is known to generate non targeted compounds of varying chain length compared to the later process. Further, many PFAS replacement products are observed as toxic pollutants at the industrial site soils suggesting air borne accumulation in soils [32]. The process of fluorination can generate many compounds that are used in personal care products and agrochemicals [33-35]. However, many manufacturing processes and intermediates, aerosols that can pollute is unknown to people due to commercial and confidentiality in the industry [36, 37].

PFAS are hazardous and bioaccumulative, and studies have linked them to negative effects on human health [38]. The PFAS are responsible for low birth weight of newborn babies. The source could be eggs, fish, dairy products and water and PFAS were found in mothers' milk [39]. Further, childhood obesity is attributed to PFAS [40]. The reduction in gestation, having more preterm babies correlated to altered metabolism suggesting effecting neuroendocrine function and redox homeostasis in newborn children. The researchers propose that the presence of PFAS may account for infant mortality in USA [41]. In adults PFAS identified in serum correlated to Type 2 Diabetes [42]. There are several studies that are underway to understand the effect of PFAS on human health. PFA exposure was associated with hepatocellular carcinoma progression [43]. The adverse effect on human health calls for regulations and remediation technologies.

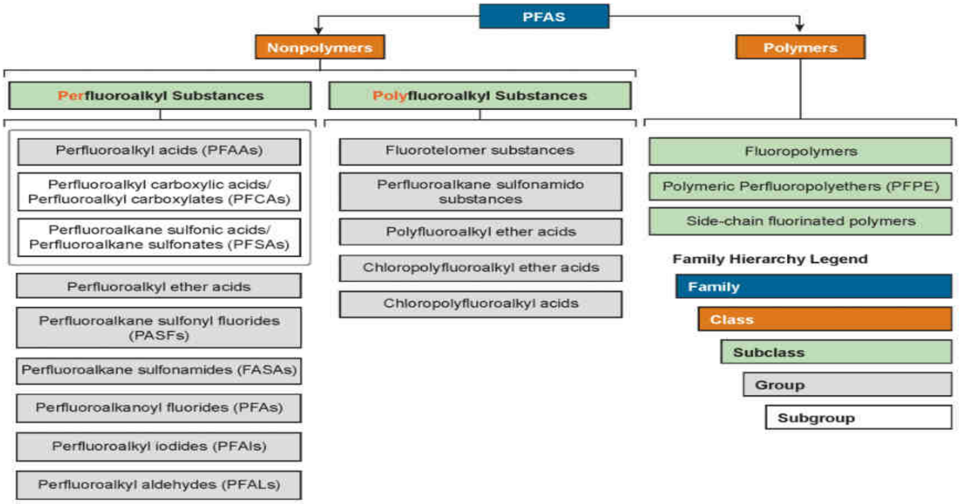

Fig. 2. The PFAS family [44]

Remediation methods must be created or modified to get rid of PFAS from the environment because it is such a widespread issue. The cleanup of PFAS has been researched using a range of approaches during the past five years, including chemical oxidation, photocatalytic degradation, and sorption by nanomaterials [26, 45]. The scientific literature on this subject has not yet made a mention of an observed complete microbial breakdown for the "for ever chemicals" i.e PFAS. PFAS contaminants, a subset of the CEC, are becoming more and more significant (Figs. 1 and 2) in the environment. Guidelines for PFAS management during remediation and evaluation of PFAS-contaminated locations need to be developed. Since each individual PFAS molecule has various chemical characteristics, different remedial measures are required for each one. Particularly in cases of widespread PFAS pollution, PFAS display high mobility and permanence, are of considerable public interest, and frequently involve a significant degree of uncertainty. No free-phase PFAS products are produced (non-aqueous phase liquids or NAPLs). They don’t have microbiological life, and they mostly build up in the unsaturated soil zone and at air/water interfaces. They are not microbially mineralisable and tend to accumulate in the unsaturated soil zone and at air/water interfaces. It is conceivable for PFAS to be enriched in thick or light NAPL or at the NAPL/water interface. Long-lasting pollutant plumes can be produced by PFAS that have gotten into the groundwater. Depending on the redox conditions in the source and at locations remote from the point of incursion, the biotransformation of precursors can result in the creation of new perfluoroalkane carboxylic and sulfonic acids. When choosing remediation techniques, their great resistance to microbiological, chemical, and thermal deterioration is very important. Several nanomaterials especially carbon-based nanomaterials including single walled carbon nanotubes, multiwalled carbon nanotubes are used for adsorbing PFAS. They usually work by the process of advanced oxidation and reduction reactions. Metal organic frame works, titanium oxide nanoparticles are extensively used for removing PFAS. However, scalability and cost are issues and hunt for ideal nanomaterials is ongoing [46].

Recently a metal organic framework compound termed PCN-222 that is made from zirconium tetroxide and the ligand tetrakis (4 carboxyphenyl) porphyrin (TCPP) showed high PFAS adsorption [46]. However, commercially scalable removal of PFAS was obtained by Surface-Active Foam Fractionation (SAFF) at the Telge Recycling plant in Sweden [47]. Piezoelectric materials can generate charge when mechanical stress is applied the charge density is proportional to external force applied. Several crystals, ceramic materials and biological materials are widely used applications. They are used in SONARs, sensors, laser beams etc. Now piezoelectric materials are used to generate charge (polarisation) and collisions on these materials can destroy PFAS. The nucleophilic substitution of hydroxyl radical to the carbon backbone results in PFAS degradation [47-49]. Research efforts for sustainable processes with keeping in mind circular economy for waste removal is need of the hour.

The term "bioremediation" refers to the use of biological interventions in biodiversity to lessen (and, whenever possible, completely eliminate) the negative impact that environmental toxins have on a particular location. In situ bioremediation is the term used when a process takes place directly in the area that was polluted. Ex situ treatment, on the other hand, refers to the purposeful transfer of the contaminated material (soil and water) to another area in order to enhance biocatalysis. Bioremediation requires biodiversity as a prerequisite. In these biological interventions, a wide range of plants - natural, transgenic, and/or those connected to rhizosphere microorganisms, are incredibly active at removing or immobilising pollutants. The most active agents are a variety of microorganisms, including fungi and their potent oxidative enzymes are crucial in recycling resistant materials [50]. Further, engineered microorganism were employed for cleaning PFAS. Bioremediation using *Delftia acidovorans* was identified in PPFA family pollutants contaminated soils [51] . The researchers identified dehalogenase enzymes in these microbes which can cleave the fluorinated carbon bonds. The genes encoding the dehalogenases were expressed in *E. coli*. The enzyme became functional performed the removal of fluorine bonds. A blue green alga *Syncosystis* spp could effectively sequester PFAS in continuous photobioreactor. The uptake of the PFAS family compounds was observed and mechanism behind the sequestration was not proposed yet. They found PFAS in the membrane fractions and the bioinformatic analysis found laccases and dehalogenases in the proteome of the blue green alga [52]. A bioinspired #D nanostructure consisting of cellulose and lignin fibres nanofibers was fabricated initially and then the fungus *Irpex lacteus* was cultured on the nanocomposite could effectively adsorb and remove PFAS. This composite with fungus was termed as Renewable Artificial Plant for In-situ Microbial Environmental Remediation (RAPIMER) [53]. *Juncus sarophorus* was used as phytoremidiation plant by accumulating PFOS, PFOA and PFHxS family of PFAS in a controlled glass house experiment. The long chain PFOA was difficult to accumulate, whereas shortchain PFAS could be accumulated inside the plants [54]. Another study examined the uptake of PFAS in constructed wetland model using 3 plants namely *Juncus krausii*, *Baumea articulata* and *Phragmites australis*. The accumulation was more pronounced in shoots compared to the roots. These studies indicate that bioremediation strategies could be utilised in removing PFAS from the polluted water and soils [55]. The fibre hemp plants for phytoremediation of per- and polyfluoroalkyl substances (PFAS). Nanozymes are recently explored for remediation [56].

Recently essential use approach has been advocated by scientists. In this approach some chemicals (Ex PFAS) that are harmful do not have absolutely essential-use. The second category consists of these chemicals that can be replaced by less harmful/toxic chemicals. The third category is essential use chemicals that are needed. After discussions with the expert committee essential-use chemicals can be used [57, 58]. European Union came up with its strategy to phase out PFAS and endocrine disruptors that are harmful [59]. The policy makers in various states of USA are trying to phase out PFAS [60] Environmental Business Journal remediation market survey 2019 showed that the demand for remediation of Polyfluoroalkyl and perfluoroalkyl substances, contaminants of emerging concern are the most amenable contaminants for bioremediation. A community-based approach involving local native people of Indian reservations (Micmac nation) and policy makers worked efficiently to remediate PFAS generated during US military operations at Lorimer airforce base in Maine USA. They used cultivation of fibre hemp plants for bioremediation of PFAS [61]. A similar initiative with local communities and government could help at other contaminated sites and water bodies. The empowering local communities at grass root level is another solution for the CECs removal from their neighbourhoods.

Agrochemicals (pesticides and fertilisers)

By the year 2050, the world's population is predicted to increase to 9.1 billion. According to projections, developing nations' demand for food production will increase by 70 % because of the increased population density. Additional agricultural resources are scarce, as is agricultural land. The decrease in current pest-related yield losses are a significant concern. Agrochemicals will be essential in this situation. Simple to complex ingredients are used in agrochemical formulations with the goal of maximising biological activity. The formulation of the active ingredient can enhance the handling, storage, application, and safety qualities in addition to maximising the biological activity on the target organism. Solvents, mineral clays, adhesives, wetting agents, dispersion agents, antifoam agents, bactericides, or other adjuvants are typical constituents used in agricultural formulations. About 2 million tonnes ([t] = 10^3 kg = 10^6 g) of pesticides are used globally each year, of which 45 % are used in just Europe, 25 % in the US, and 30 % in the rest of the globe. Using pesticides carelessly and randomly promotes disease and pest resistance, decreases soil biodiversity, eliminates beneficial soil bacteria, leads to a fall in pollinators and causes biomagnification of pesticides, and damages the natural habitat of farm animals like birds. Numerous scientific disciplines, including physics, chemistry, pharmaceutical science, material science, medicine, and agriculture, have used nanotechnology. The good outcomes in other fields greatly expanded the opportunities in the agricultural field as well. Precision agriculture is a farming management concept of the European Union's Directorate General for Internal Policies. Precision agriculture is now a reality thanks to the widespread usage of nanotechnology in modern agriculture. Therefore, the number of research publications increased substantially from 2000 to 2023 (Fig. 3).

Due to their small size, high surface-to-volume ratio, and distinctive optical features, nanopesticides have applications in plant feeding, protection, and management of agricultural activities. Metal oxides, ceramics, magnetic materials, semiconductors, quantum dots, lipids, polymers (natural or synthetic), dendrimers, and emulsions are just a few of the numerous materials that can be utilised to create nanoparticles. Chitosan nanoparticles are used in agriculture as biopesticides to assist plants fend off fungus infestations and to treat seeds [62, 63]. Different plants respond differently to nanoparticles' influence on growth and metabolic processes. Plant growth and germination processes are impacted by nanoparticle concentration. Emerging tactics include the use of nanoencapsulated fertilisers, delayed and sustained release of nutrients utilising zeolites, etc. [64]. Agriculture’s use of conventional methods, such as integrated pest control, is insufficient, and the use of chemical pesticides has negative effects on animals, beneficial soil bacteria, and soil fertility. The creation of more potent, non-persistent insecticides, such controlled release formulation, is required to address this issue. For successful routine pathogen monitoring, tools like quantum dots are being examined. The use of agrochemicals is currently being minimised or reduced, and nanotechnology and micro fabrication are being studied. Usually metals like Au, Ag and nonmetals like silica are used for making composite nanofertilisers. These can perform the function of agrochemicals more efficiently by sustained release. Additionally, they are more available to the plants. However, uniform regulatory laws are needed across various countries and their long-term toxicity to organisms should be investigated [65]. In addition to metallic nanoparticles Graphene derived nanomaterials have shown promising pesticides [66]. Graphene is 2D carbon structure with great tensile strength and high delivery molecule capacity. π-π interactions in graphene-based nanomaterials account for easy conjugation and delivery of plant protection chemicals [67]. The other polymers that were used are sodium alginates, β-Cyclodextrin, gelatin. The toxicities associated with nanoformulations have led to the use of biopolymers as composites for the delivery of agrochemicals [68-70].

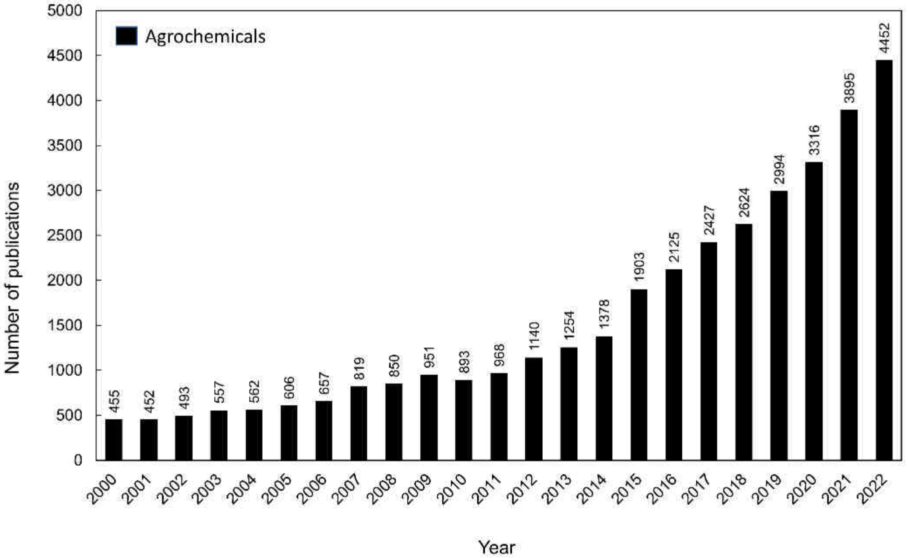

Fig. 3. Articles published in the past two and half decades beginning 2000 to 2023 on Agrochemicals from www.scientificdirect. Keywords used agrochemicals

The Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals & Pesticides is an International regulatory organisation with several member countries. Several countries adopted regulations to save environment animal and human health. It has listed 54 chemicals in its Annexure III. Further, 35 pesticides and

18 industrial chemicals and 1 in both categories are listed in the annexure. Recently, decabromodiphenyl ether and perfluorooctanoic acid are included in the list in 2022. Sustainable methods of farming system gained importance recently and call for regulations and international cooperations is advocated for achieving UN sustainability goals, human health and help the loss of biodiversity without the compromising economic growth of the people [71].

e-waste and waste electrical and electronic equipment (WEEE)

Over the past two decades, research on e-waste (also known as waste electric and electronic equipment, or WEEE) has expanded dramatically (Fig. 4). Researchers are being inspired to develop ground-breaking applications by the field's quick advancement. Due to many problems, managing hazardous substances is a topic of concern for all countries. Most of the countries have ratified or are party to the following international accords are notable in order to handle toxic/dangerous substances. This is reflected in the publications on this topic from 2000 to 2022. Further the focus of policy makers and people as been to recycle and extract precious metals from e-waste focus on circular economy rather than lowering the production of this waste [72]. The following are some international efforts to address problems associated with e-waste: The Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal, The Stockholm Convention on Persistent Organic Pollutants (POPs), Strategic Approach to International Chemicals Management (UN). The chemical management is intense topic of research to form policies, understand economics, trade in various countries. The electrical and electronic goods usage is higher in developed countries compared to underdeveloped countries. The WEEE generated by countries is increasing rapidly, which is about 54 Mt at present and may reach 74 Mt by 2030. However, recycling of the WEEE is higher in developed countries compared to developing countries [73]. A material flow analysis in WEEE was undertaken from material production to waste recycling. The researchers analysed the data from 115 publications on this topic. They observed that stringent methods and laws of recycling were absent in developing countries. The developed nations were dumping WEEE in underdeveloped nations that have less advanced recycling technologies [73]. The precious metals from WEEE are extracted using the techniques of pyrometallurgy, chemical leaching and latest techniques such as bio-metallurgy, super critical extraction technology. Research is ongoing on extraction of precious metals from WEEE in developed countries [74, 75]. The hazardous pollutants include heavy metals (Cd, Hg, As, Ni), PFAS, plastic polymers, polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and dioxins. These pollutants are causing higher health problems in the underdeveloped countries as they do not have latest methods of waste disposal and many developed countries are sending the hazardous materials to these nations for disposal. The later nations are accepting them for economic reasons. Therefore, African nations are now enacting laws to safeguard their countries from e-waste pollution. A committee was set up to regulate the e-waste handling for ex The East Africa Communication Organisation (EACO), in 2012. Developed countries are forming treaties with African countries to improve the methods of e-waste disposals [76]. However more stringent laws and regulations are needed since the WEEE causes health hazards including cancer.

REE elements have beneficial effects on plants at lower concentrations. In China they are used as fertilisers to improve photosynthesis, grain yield used as elicitors for secondary metabolite production, tolerance to stress including heavy metals. However, at higher concentration of REES, photosynthesis is affected, oxidative stress response increase and these metals accumulate into the enzymes. Ex lanthanum La ions can be taken up by calcium channels inside the plant systems. The research on the toxic aspects is still in its infancy and needs further investigations [77]. Rare earth metals are also constituents of WEEE as they are widely used in the electrical and electronic industries. The elements contain 15 lanthanide series of elements, scandium, and yttrium (according to International Union of Pure and Applied Chemistry). In nature they occur in same ore deposits and separation processes are expensive and time consuming. The rare earth metals are components of medical diagnostic, scanning equipments, cell phones, cables, rechargeable batteries, LED lamps etc. The waste generated has these elements and are known to be toxic to aquatic animals, soils, and humans. The current extraction of rare earth materials from WEEE include thermal, aqueous electrochemical processes. Separation techniques are difficult for the REE and there is ongoing scientific research for suitable methods to separate them [78]. Recently, using biphasic triamidoarene compounds (both acidic and basic) REE metals were precipitated as capsules from metallic nitrates. Ex tripodal amido- arene (soluble in nitic acid and toluene) reacted with lanthanide nitrate and precipitated lanthanide capsules. Two ligands of different properties one that is lipophilic and another that is hydrophilic are used to selectively series of lanthanide metals. The compounds used were water-soluble bis-lactam-1,10-phenanthroline and oil-soluble diglycolamide that could selectively bind different lanthanide metals and could be separated. However, these use chemicals for separation of metals and sustainable methodology is by using microbes. The methylotrophs are found attached to plant roots and some species are present in soil. These help plants with various functions such as nitrogen fixation and metal sequestration and protection from pathogens [79]. Recently protein derived from methanotrophs are explored to be used for separation in an efficient eco-friendly way. The proteins family belonging to lanthanide-binding proteins (LanM) from *M. extorquens* organism that can bind to lanthanide and actinide series of elements and are used for green extraction of metals [80]. The protein is engineered and aminoacids in the aspartate in the metal binding sites were replaced by methionine, alanine, histidine, aspargine, selenomethionine by site directed mutagenesis. The bioengineered proteins could separate actinide series of metals compared to REE for various applications. Recently, novel lanthanide protein is identified from *Hansschlegelia quercus* (*Hans*-LanM) that could bind to REE, and the protein has been engineered for higher efficiency [81]. The recycling of e-waste is considered as environmentally friendly process compared to mining from ores. Additionally, recycling costs are lower for extracting various metals from e-waste rather than conventional mining from ores. Recycling of rare earth metals is need of the hour for circular economy [82, 83]. The multinational companies can advocate using recycling of rare earth metals. Ex Apple computers is recycling and pledged to use these metals for manufacturing again. Robo dismantled and helped in getting Co, Cu, W, Sn, REE, Ag, Ta, Au and Pd from waste.

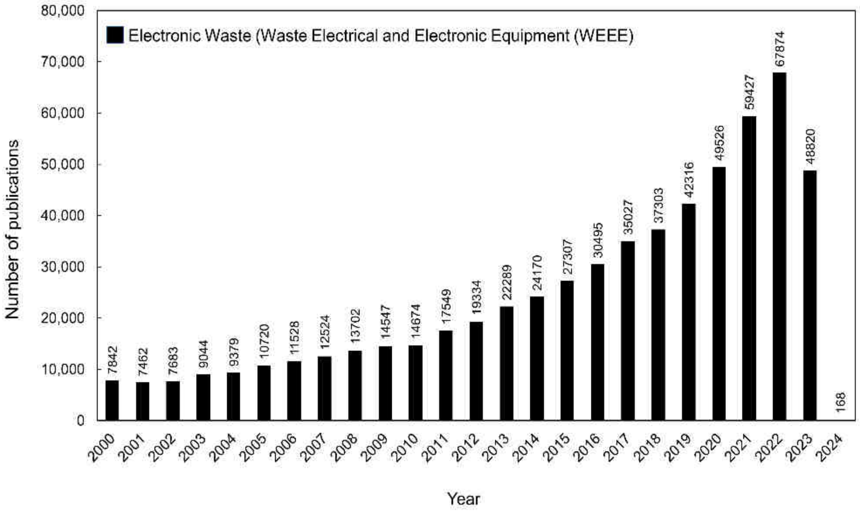

Fig. 4. Articles published in the past two and half decades beginning 2000 to 2023 on e-waste based on www.scientificdirect. Keyword used "e-waste"

Recycling of plastics found in WEEE is a challenge and polymers identification for efficient treatment options is a subject of intense research. Recently, acrylonitrile butadiene styrene (ABS) was the main polymer identified in WEEE and several other unidentified polymers are identified so the research is ongoing to manage these waste plastics [84]. Similarly, detection methods using mass spectrometry are developed to understand chemical pollutants associates with WEEE. A study found 56 additives including antioxidants, flame retardants, plasticisers, UV-stabilisers, and UV-filters could be identified using mass spectrometry. Surprisingly, similar additives were found in children’s toys made of recycled plastics raisin an alarm of children’s exposure to harmful plastic chemicals [85]. A handheld X-ray fluorescence devise is developed to estimate additives, flame retardants and Sb present in plastic components in WEEE at the landfills. The advancement in detection systems and constituent of e-waste is ongoing process. Robotics and artificial intelligence are devised to identify e-waste from dumping grounds to enhance the capacity to identify these waste substances from garbage for use in recycling in a developing country. The working process consists of: 1) collecting data, 2) next using machine learning to identify compounds, 3) then using internet of things approaches notify the collected data, 4) the requestor who gave the original data can know about the compositions. The neural network-based predictions were accurate by 94 % in identifying e-waste from house old waste. These are economically viable and can be used in circular economy [86]. Additionally, organisms that can degrade plastics in the WEEE in environmentally safe manner is need of the hour. Insect larvae of *Galleria mellonella* and *Tenebrio molitor* were capable of degrading plastics and the choice of plastics by the two species was different [87]. Similarly, many insect species are known that can degrade plastics. The insects preferred pristine plastics to plastics from WEEE because the later contains metals too. There are several insects that can degrade plastics. The insects are cable of degrading plastics due to the presence of bacteria and fungi in the insects. This is a symbiotic relationship, both host and gut microbiome work efficiently by secreting enzymes needed for the process. Initially polymers in the plastics gets converted into oligomers then into fatty acids which could be metabolised [88]. The plastics get converted into microplastics and nano plastics that pose additional threat to environment and biota. This aspect is discussed below.

Microplastics

Globally speaking, microplastics are emerging pollutants and toxins. These could be micrometers or nanometers in length, that could be produced as primary compounds for industrial consumption. They can be produced from secondary sources by the degradation of plastics by environmental factors [89]. The scientific community is becoming more and more interested in the topic of "Microplastics". These are present, in the soil, hydrosphere, and aerosphere. The majority of microplastics, however, are produced on land and eventually wind up in the marine environment. There are many different sources of microplastics in the environment, and they are widely dispersed everywhere in the world. In addition to domestic sources like personal care products and industrial uses like plastic pellets in manufacturing, transport, and recycling, synthetic textiles are also subject to abrasion from laundry, tire abrasion while driving, city dust, spills, road markings, weathering, and abrasion by vehicles. Road runoff, wastewater, wind, and ocean runoff are examples of global cycle pathways. As microplastics enter or accumulate in the food chain or participate in the food web, their fate in the ecosystem is very crucial. It is well known that microplastics have a great potential for adsorbing a range of contaminants. Hence these are heavily researched subjects (Fig. 5). Further, it is anticipated that all the findings will contribute to the establishment of necessary environmental laws and policies as well as close knowledge gaps in microplastics contamination. It is crucial to manage plastics and microplastics for the following reasons: 1) Annual leakage of primary and secondary microplastics into our oceans is estimated to be several million tonnes. 2) Disposable plastic goods account for half of marine trash. 3) The plastic waste we produce can encircle the planet four times in a single year. The waste rate for throwaway plastic packaging is over 95 %. 4) Plastics can last up to 500 years in the environment. 5) Plastic recycling uses 88 % less energy than producing new plastic. Recycling plastics allows us to significantly reduce our use of gasoline. Several biological methods are present in addition to conventional chemical methods degrading plastics including the use of bacteria, algae, fungi. These organisms are engineered using site directed mutagenesis, Crisper/Cas systems to efficiently degrade microplastics [90, 91]. Several microbes found in nature involved in microplastic degradations cannot be cultured in the lab. Therefore, sequencing the entire microbial genome and transcriptome enabled prediction of genes that could code for enzymes that can degrade microplastics [92]. The microplastics are polluting marine waters and these can be reduced only by international cooperations and legislations [93]. As these CECs are present in healthy oceans, seas, coastal, and inland waters, the European Commission published a document titled Mission Starfish 2030: Restore Our Ocean and Waters. By 2030, it hopes to have our oceans and seas back to normal. More specifically, the Mission, which was motivated by the starfish’s shape, highlighted the five overarching goals for 2030 by highlighting the four interdependent challenges of an unsustainable footprint, climate change, a lack of understanding, connection, and investment, and inadequate governance.

Disinfection by-products (DBP)

Producing safe drinking water is an age-old art. As far back as 4000 (Before Christian Era or Before the Common Era or Before the Current Era (BCE)), there are recorded methods for enhancing water quality. Even today, alum is frequently used to treat water. It was first employed for this purpose about 1500 BCE. Pathogen inactivation is a component of water disinfection that helps control acute waterborne disease while balancing the reduction of hazardous disinfection by-products (DBPs). Several DBPs are formed due to various processes (Table 1). Although interdisciplinary cooperation between chemists, biologists, epidemiologists, engineers, and regulators have grown during the past two decades, addressing the dangers of DBPs still adheres to an outdated paradigm. To identify the pollutants in source and drinking waters that increase health risks and to lay the groundwork for novel disinfection techniques, a new integrated strategy is needed. The major disinfectant that is most frequently used worldwide is chlorine. It has been used in a variety of ways to protect humans against waterborne illnesses such diarrhoea, cholera, legionellosis, and dysentery since it was first employed as a major disinfectant in 1908. Recently, there is focus and increase in research on DBPs (Fig. 5).

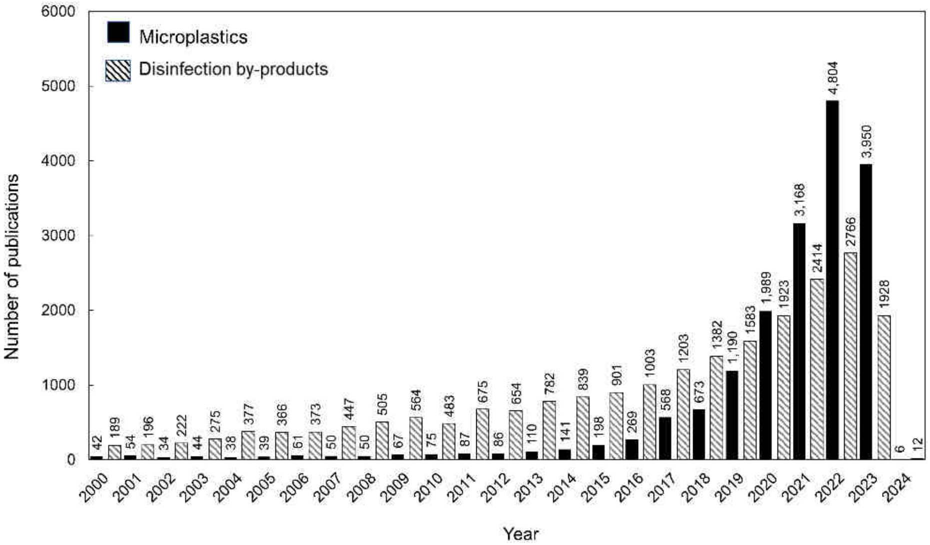

Fig. 5. Articles published in the past two and half decades beginning 2000 to 2023 on Disinfection by-products based on www.scientificdirect. Keywords used "DBPs" and "Microplastics". Number of papers in each year are labelled on the top of the respective bars

Unfortunately, some by-products of chlorine’s reaction with organics in water, known as DBPs, are carcinogenic in nature. DBP exposure is linked to unfavourable health outcomes, such as cancer development and problems during pregnancy and new-born children [94, 95]. Controlling DBP formation has emerged as one of the main concerns for drinking water since their discovery in drinking water in the 1970s and with growing knowledge of their prevalence and health impacts. To protect the public’s health, many nations throughout the world opted to regulate DBPs, which in turn made it necessary to conduct research and develop new treatment technologies. By 2025, the World Health Organisation of the United Nations projects that half of the world's population will be living in water-stressed areas. Therefore, water and wastewater recycling are global priorities. Recently DBPs from slaughterhouses could be recycled using UV treatment and micro algae [96].

Table 1

DBP (disinfection by-products) that have been oxidised because drinking water sources include bromide and iodide. The preferred by-products of disinfection and undesirable by-products are shown in this table

Chlorination	**Chloramination**	**Ozonation**	**References**
Preferred: $HOCl + Br^- \rightarrow HOBr + Cl^-$ $OCl^- + Br^- \rightarrow OBr^- + Cl^-$ $HOBr/OBr^- + NOM \rightarrow Br - DBPs$ Slow: $HOBr + HOBr \rightarrow BrO_2^- + Br^- + H^+$ $OBr^- + OBr^- \rightarrow BrO^- + Br_2^-$ $HOBr + BrO_2^- \rightarrow BrO_3^- + Br^- + H^+$	Preferred: $HOCl + I^- \rightarrow HOI + Cl^-$ $OCl^- + I^- \rightarrow OI^- + Cl^-$ $HOI + HOCl \rightarrow IO_2^- + Cl^- + H^+$ $HOCl + IO_2^- \rightarrow IO_3^- + Cl^- + H^+$ Slow: $HOI/OI^- + NOM \rightarrow I - DBPs$	Preferred: $Br^- + O_3 \rightarrow HOBr/OBr^-$ $OBr^- + O_3 \rightarrow BrO_2^-$ $BrO^- + O_3 \rightarrow BrO_3^-$ Slow: $HOBr/OBr^- + NOM \rightarrow Br - DBPs$	[97-101]
Preferred: $NH_2Cl + H_2O \rightarrow HOCl + NH_3$ $HOCl + Br^- \rightarrow HOBr + Cl^-$ $HOBr/OBr^- + NOM \rightarrow Br - DBPs$ Slow: $HOBr + HOBr \rightarrow BrO^- + Br_2^- + H^+$ $OBr^- + OBr^- \rightarrow BrO^- + Br_2^-$ $HOBr + BrO_2^- \rightarrow BrO_3^- + Br^- + H^+$	Preferred: $NH_2Cl + H_2O \rightarrow HOCl + NH_3$ $HOCl + I^- \rightarrow HOI + Cl^-$ $HOI/OI^- + NOM \rightarrow I - DBPs$ Slow: $HOI + NH_2Cl \rightarrow IO_2^- + Cl^- + H^+$ $HOCl + IO_2^- \rightarrow IO_3^- + Cl^- + H^+$	Preferred: $I^- + O_3 \rightarrow HOI/OI^-$ $OI^- + O_3 \rightarrow IO_2^-$ $IO^- + O_3 \rightarrow IO_2^-$ $HOI/OI^- \leftrightarrow I^- + IO_3^-$ Slow: $HOI/OI^- + NOM \rightarrow I - DBPs$	[99-102]

The recent trends of bioremediation of CECs for achieving the sustainable goals is shown in Figure 6. Additionally, synthetic biology approaches and genome editing by CRISPER-CAS system gained importance recently [103]. The uses of biological products and organisms for recycling should be researched further for achieving SDG. CECs are major concerns for health and recycling of these is needed for circular economy and achieving SDG. The management of water and environmental resources are needed for the health of all organisms including humans [104-109]. Web based servers can be set up for individual countries especially developing countries to understand the nature of pollutants in the water and their soils. A knowledge hub that is web based was generated for CECs in South Africa to aid in CECs research and could be useful for policy and remediation technologies too. The knowledge base has about 560 data entries for various regions in South Africa [110]. As the editorials in the journal Nature warns us all nations should come together to march towards goals of SDGs by addressing issues of pollution for the wellbeing of Planet Earth [111-113].

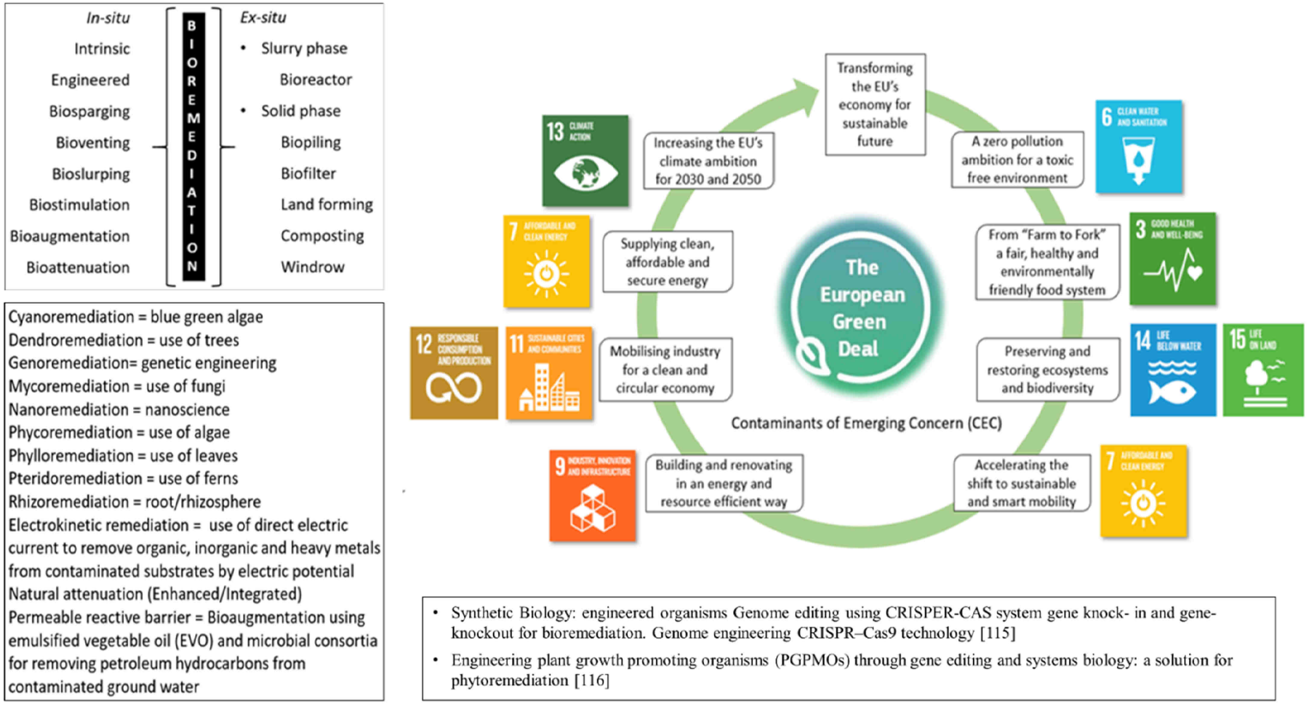

Fig. 6. Remediation of CECs for achieving sustainability goals. Biodiversity is the tool box for nature based solutions (Bioremediation) for a large number of CEC. In addition assisted and amendment enhanced (integrated) sustainable remediation technologies associating biodiversity are successful in different situation [114, 115]

Conclusion

CECs pose a serious threat to the health of planet Earth. Rigid international laws across all nations is necessary to address the detrimental impacts of these contaminants to safeguard “Man and Biosphere”. All nations can benefit from efficient pollution abatement as they contribute for achieving the UN Sustainable Development Goals and EU Green Deal ambitions. Combined efforts of not only scientists and regulatory agencies but also non-government organizations are required to practice several of the known remediation technologies for control and treatment of these contaminants.

Credit authorship contribution statement

MNVP delivered keynote on ”Emerging contaminants and micropollutants in the environment - selected remediation technologies” on 21st October 2022 at the 31st annual Central European Conference ECOpole’22, organised in Krakow by the Ecological Chemistry and Engineering Society, Poland. MNVP mentored SE and contributed equally to the manuscript.

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