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Global occurrence, chemical properties, and ecological impacts of e-wastes (IUPAC Technical Report)

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Abstract: The waste stream of obsolete electronic equipment grows exponentially, creating a worldwide pollution and resource problem. Electrical and electronic waste (e-waste) comprises a heterogeneous mix of glass, plastics (including flame retardants and other additives), metals (including rare Earth elements), and metalloids. The e-waste issue is complex and multi-faceted. In examining the different aspects of e-waste, informal recycling in developing countries has been identified as a primary concern, due to widespread illegal shipments; weak environmental, as well as health and safety, regulations; lack of technology; and inadequate waste treatment structure. For example, Nigeria, Ghana, India, Pakistan, and China have all been identified as hotspots for the disposal of e-waste. This article presents a critical examination on the chemical nature of e-waste and the resulting environmental impacts on, for example, microbial biodiversity, flora, and fauna in e-waste recycling sites around the world. It highlights the different types of risk assessment approaches required when evaluating the ecological impact of e-waste. Additionally, it presents examples of chemistry playing a role in potential solutions. The information presented here will be informative to relevant stakeholders seeking to devise integrated management strategies to tackle this global environmental concern.

Keywords: chemical composition; ecological assessment; environmental impacts; e-waste; recycling.

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1 Introduction

Electrical and electronic waste (e-waste) is a broad term that describes electrical and electronic equipment (EEE) that has become unwanted, non-working, or obsolete, and has essentially reached the end of its useful life. In Europe, the revised Waste Electrical and Electronic Equipment Directive (WEEE 2012/19/EU) came into force in 2018, streamlining e-waste categories from 10 to 6 (Table 1) [1]. Over the last two decades, the lifespans of the related products have become shorter and the global market of e-waste has grown exponentially. In 2016, the total tonnage of e-waste worldwide reached 44.7×10^6 tonnes (t, often referred to as 'metric tons' in the US) and is expected to rise to 52.2 × 10⁶ t by 2021 [2]. By load (% tonnage), Asia is the biggest contributor (40.7 %), followed by Europe (27.5%). China produced the highest e-waste quantity in Asia and overtook the United States of America (USA) to be the highest generator of e-waste in the world $(7.2 \times 10^6 \text{ t})$ in 2017. A global map of e-waste generated (per capita) is presented in Fig. 1a. Norway produces the highest amount of e-waste per capita (~28.5 kg); North American countries, such as USA and Canada, produced approximately 20 kg per capita, whereas countries in Latin America (LATAM) contribute up to 10 % of the e-waste generated worldwide [3] and ~7 kg per capita [2]. Only a few LATAM countries have specific legislation on e-waste management, as the majority are regulated under general hazardous waste legislation, with e-waste management in the region generally linked to metal scrap processing by informal and private companies [3]. The Middle East and North Africa (MENA) is a relative newcomer to readily disposable electrical products, such as cellular phones and computers. Over the last decade, the consumption of electronic goods has increased markedly, especially in the Gulf nations (Saudi Arabia, Qatar, and the United Arab Emirates), Egypt, and Israel. The quantity of e-waste generated in the MENA region has been estimated to be 2.9×10^6 t, with Saudi Arabia the highest contributor (0.5×10^6) t) [2]. Whilst the take-up of computers, cellular phones, and household gadgets among these countries has been high, there have been little or no initiatives to handle the resulting e-waste, recover resources, and promote circularity. The African nations have the least number of direct manufacturers of EEE, but they produce around 5 % of the global e-waste $(2.2 \times 10^6 \text{ t})$. Up to 50 % of the e-waste generation in Africa results from transboundary imports from developed countries [4]. The actual amount of e-waste in Africa is believed to be much higher, as high levels of e-waste, enters the countries through illegal routes and is therefore not captured by official audits.

In terms of recycling of e-waste, Europe and Africa have the highest (35%) and lowest recycling rates (0.2%), respectively [2]. The percentage increase of e-waste production worldwide, based on data obtained in 2014 [5] and 2017 [2], is presented Fig. 1b. A number of key e-waste-producing countries appeared to produce similar (e. g., Norway) or even reduced quantities of e-waste (e.g., USA) over the 3-year period, probably as a result of tighter regulations and the introduction of measures to reduce e-waste. Several countries not usually associated with high volumes of e-waste production showed a rapid rate of increase, most markedly in Zimbabwe, Mongolia, and Iceland (2.0-, 1.6-, and 1.5-fold increases respectively). These countries currently do not have national regulations to control e-waste [2].

Several notable international initiatives, as well as legislation are in place to limit the adverse impact of ewaste (Tables 2 and 3), but substantial quantities of historical e-waste remain a challenge in waste management. Legislative loopholes have resulted in near end-of-life e-waste being exported from developed to developing countries [6], despite the Basel Convention, which prohibits transboundary movement of e-waste. For example, e-waste is being exported under the guise of second-hand or used electrical and electronic

Table 1: Waste categorisation according to the revised EU WEEE Directives 2012/19/EU [1].

Category	Post-14 August 2018
1	Temperature exchange equipment
2	Screens and monitors (surface area > 100 cm ²)
3	Lamps
4	Large equipment (any external dimension > 50 cm)
5	Small equipment (external dimension \leq 50 cm)
6	Small IT and telecommunication equipment (external dimension \leq 50 cm)

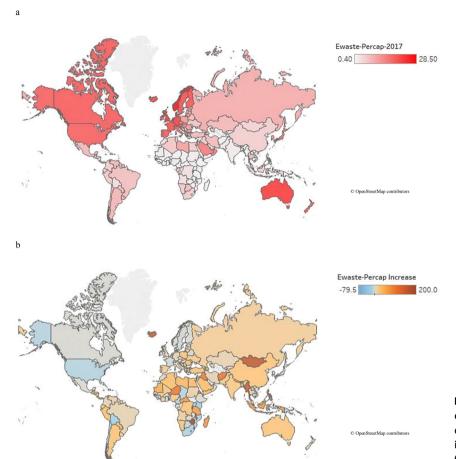


Fig. 1: (a) Global distribution of e-waste generated (kg per capita); (b) percentage increase of e-waste generated from worldwide 2014–2017.

equipment (UEEE) or recycling materials, which are not under the remit of the Basel Convention. Much of the UEEE destined for developed countries, such as the United States, Taiwan, Japan, South Korea, and Canada, is re-exported to international trade hubs, for example, Hong Kong, United Arab Emirates, Lebanon, and Macau [7–9], where the e-waste is transported to highly populated regions with very cheap labour [10, 11].

In developed countries, e-waste management has revolved around two major strategies, either: (i) recycling, recovery, and disposal within their own countries, or (ii) exportation to developing nations [9, 12]. For developing countries, the management of e-waste is further complicated by the illegal import of waste, as exemplified above, undermined by weak environmental regulations and constrained by inadequate organizational structures. Rudimentary methods, such as manual dismantling, chipping, melting, and burning, as well as uncontrolled chemical dissolution, such as leaching by strong oxidizing acids, primarily agua regia (1:3 HNO₃-HCl concentrated solutions), are often used by the informal sector in developing countries to salvage and recover the valuable materials present in e-waste, including copper, gold, and silver. These informal recycling practices contribute to the release of toxic leachate and fumes as well as persistent organic pollutants (POPs) into the local surroundings, thereby posing risks to humans and the environment, including its biota. A number of extensive reviews have been performed in an attempt to evaluate the impacts of e-waste on human health [6, 13–19]. The potential adverse health effects of exposure to informal e-waste disposal and recycling have been reported to include elevated levels of contaminants in blood, milk, and other bodily fluids, genotoxicity, endocrine disruption, immunotoxicity, nephrotoxicity, abnormal reproductive development, intellectual impairment, and damage to different organs. In contrast, information on ecological and environmental risk assessment is less well integrated. Here, we consolidate primary literature evidence to provide an extensive review on the global generation and distribution of e-waste, the complexity (chemical and physical) of e-waste, its potential environmental impact, and the diverse approaches used to appraise the associated environmental risks.

Table 2: Examples of notable multilateral international legislation on e-waste.

Legislation	Year of enactment	Notes
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (Basel Convention) (http://www.basel.int/ TheConvention/Overview/tabid/1271/Default.aspx)	1992	To protect human health and the environment against the adverse effects of hazardous wastes through reduction of shipment of hazardous waste between nations, particularly from developed to less developed countries.
EU Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS) Directive 2002/95/EC (https://ec.europa.eu/environment/waste/rohs_eee/legis_rohs1_en.htm)	2003	The directive bans the use of six hazardous substances (lead, cadmium, Mercury, hexavalent chromium, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) flame re-
RoHS revised Directive (RoHS 2) Directive 2011/65/EU (https://ec.europa.eu/environment/waste/rohs_eee/legis_en.htm)	2011	tardants) beyond agreed upon levels in the manufacture of EEE for products that are intended for sale in the European Union (EU) market.
RoHS 3 EU Directive 2015/863 (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32015L0863)	2019	The aim of the RoHS 2 was to reduce administrative burdens and ensure coherency with newer policies and legislation covering, for example, the use of hazardous substances in EEE equipment and the new legislative framework for the marketing of products in the EU. RoHS 3 contains an additional category (category 11 products) that includes all other electronic and electrical equipment not covered under the other categories, and four phthalates as new restrictive substances.
EU Waste Electrical and Electronic Equipment (WEEE) Directive 2002/96/EC (https://eur-lex.europa.eu/legal- content/EN/ALL/?uri= CELEX:32002L0096)	2003	This legislation requires manufacturers of EEE to provide for free collection and recycling of said equipment.
WEEE revised Directive 2012/19/EU (https://eur-lex. europa.eu/legal-content/EN/TXT/?uri=celex% 3A32012L0019)	2012	The revised Directive includes detailed lists of categories of electrical and electronics equipment and items within those categories. It sets minimum targets for their re-use and requires Member States to ensure that shipments of suspected E-waste are carried out in accordance with detailed shipping requirements.
The Stockholm Convention (http://www.pops.int/ TheConvention/Overview/tabid/3351/Default.aspx)	2004	This global treaty requires parties to eliminate or restrict the production and use of the intentionally produced persistent organic pollutants (POPs), prohibit and eliminate production and use or import of POPs, identify areas contaminated with POPs.
EU Registration, Evaluation, Authorisation and Restriction of Chemical Substances (REACH) Regulation EC 1907/2006 (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri = CELEX%3A02006R1907-20140410)	2007	Manufacturers and importers (e. g., of electronic components) are be required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database run by the European Chemicals Agency (ECHA).
EU Classification, Labelling, and Packaging (CLP) Regulation (https://ec.europa.eu/growth/sectors/chemicals/classification-labelling_en)	2009	This legislation complemented the REACH Regulation, which aligns the European Union system of classification, labelling and packaging chemical substances and mixtures to the Globally Harmonised System (GHS).

Rapid economic growth, coupled with urbanisation and the global demand of EEE, greatly accelerates the e-waste stream; the safe disposal and recycling of e-waste in both developed and developing countries are critical in tackling a waste phenomenon that could seriously impact human health, the ecosystem, and our

Table 3: Examples of notable multilateral initiatives on e-waste.

Initiatives	Year launched	Notes
The North American Commission for Environmental Cooperation (CEC) (http://www.cec.org/)	1994	A commission established by Canada, US and Mexico to implement environmentally sound management practices, estimate the amount of transnational movements of used computers and monitors and cooperate in enforcement against illegal trade in used electrical and electronic equipment.
The Mobile Phone Partnerships Initiative (MPPI) (http://www.basel.int/Implementation/TechnicalAssistance/ Partnerships/MPPI/Overview/tabid/3268/Default.aspx)	2002	An initiative established within the framework of the Basel Convention. The MPPI aims to address the issue of environmentally sound management of end-of-life mobile phones, including: collection and transboundary movement rules; material recovery and recycling; and design considerations.
European Association of Electrical and Electronic Waste Take Back Systems (WEEE Forum) (https://weee-forum.org/)	2002	The WEEE Forum provides a platform for producer responsibility organisations to take on the challenge of electrical and electronic waste in Europe by fostering ideas and sharing best practices whilst optimising environmental performance through a proper management of WEEE.
Responsible Business Alliance (formerly Electronic Industry Citizenship Coalition) (http://www.responsiblebusiness.org/)	2004	The RBA was founded to create an industry-wide standard on social, environmental and ethical issues in the global electronics industry supply chain.
Asia-Pacific E-waste partnership (http://www.basel.int/ Implementation/Ewaste/EwasteAsiaPacificregionproject/ tabid/4065/Default.aspx)	2005	The partnership aims at assisting parties of the Basel Convention to develop national inventories of e-waste; national e-waste management plans and formulate e-waste policies; regulatory frameworks and strategies for implementation; as well as develop pilot projects on collection and recycling of e-waste involving public-private partnerships.
Mercosur – Policy of Environmental Management of Special Universal Wastes and Post-Consumer Responsibility (https://www.who.int/ceh/publications/ewaste_latinamerica/en/)	2006	An agreement amongst the Latin American members to incorporate patterns of sustainable consumption and production in order to minimize the amount and hazardousness of waste generated.
Solving the E-waste Problem Initiative (StEP) (http://www.step-initiative.org/)	2007	A global consortium of companies, research institutes, governmental agencies, international organisations and NGOs, aims to provide a global platform for sharing information, knowledge and recommendations for management and development of environmentally, economically and ethically-sound E-waste resource recovery, re-use and prevention.
The Partnership for Action on Computing Equipment (PACE) (http://www.basel.int/Implementation/ TechnicalAssistance/Partnerships/PACE/Overview/tabid/ 3243/Default.aspx)	2008	The initiative is a multi-stakeholder public-private partnership that provides a forum for representatives of personal computer manufacturers, recyclers, international organizations, associations, academia, environmental groups and governments to tackle environmentally sound refurbishment, repair, material recovery, recycling and disposal of used and end-of-life computing equipment.

limited resources. The complex and multi-faceted issues of e-waste can only be managed by engaging all the stakeholders. The knowledge provided by this technical report will be valuable to academics, manufacturers, policy makers, waste professionals, and consumers in tackling this 21st century global challenge.

2 E-waste in 'hotspot' countries

Economic growth, advancement in technologies, and short hardware innovation cycles have led to a significantly higher turnover of devices compared to past decades [20-22]. It is estimated that 75 to 80 % of the estimated 50×10^6 t of e-waste generated worldwide is shipped to developing countries in Africa and Asia for 'recycling' and disposal [6, 10]. The major flow of e-waste exports globally is presented in Fig. 2. Nigeria, Ghana, India, Pakistan, and China have been identified as hotspot destinations of e-waste in a number of studies [18, 23-26]. Other popular destinations include Kenya, Chile, Malaysia, and the Philippines [10], with Dubai in UAE and Singapore serving as pre-distribution centres for e-waste coming from the EU and US to South Asian countries, mainly India and Pakistan [11, 27].

Determining the volume and global flow of individual e-waste categories and their generated constituents is challenging [28], particularly in developing countries, where there is a lack of official records and audit trails. This is further complicated by unreliable data keeping and uncontrolled importation, lack of historical sales data of WEEE, the dumping of e-waste in landfills without any assessment of quantity and quality, and the difficulties in tracking data related to informal recycling [29].

2.1 China

China accounts for approximately 20 % of the global volume of WEEE and is expected to produce 15.5 and 28.4×10^6 t per year by 2020 and 2030, respectively [30]. By 2025, the total mass of obsolete cellular phones alone is predicted to exceed 0.14×10^6 t in China [31]. In addition to being the world's leading producer of ewaste, hidden flows of e-waste also find their way into China despite the formal ban of e-waste importation by the government in 2002 [32]. In 2011, an estimated 70% of the global e-waste generated was sent to mainland China [33], primarily channelled through Hong Kong and Macau [11, 34, 35]. As a free port, e-waste is shipped to Hong Kong, and although entry regulations have tightened up in the past few years, it is still smuggled across the border to China. Hong Kong now has more than 100 sites for the storage and dismantling of e-waste; open-burning is rarely practiced. The amount of e-waste generated by Chinese enterprises is large, but the ratio of recycling through normal channels is relatively small, ~20 % of the e-waste generated were formally collected and recycled [2]. Most e-waste is primarily handled by small

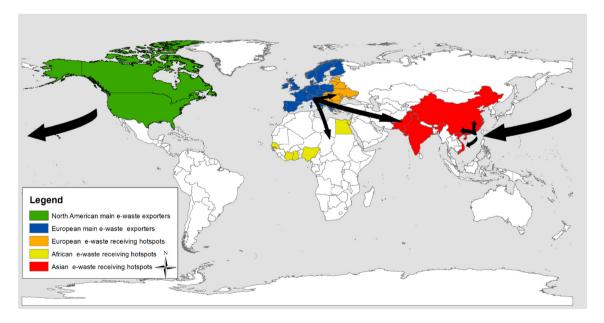


Fig. 2: The global flow of e-waste exports.

'backyard' e-waste trades, e. g., in places such as Guiyu, a cluster of towns in southeast China [36]. The crackdown on small recyclers is high on the Chinese environmental agenda, however, the cost of recycling ewaste by licensed recyclers remains high and leaves companies who are willing to treat the waste properly with much lower profit margins than illegal recyclers.

2.2 India and Pakistan

India is one of the largest consumers of EEE. Approximately 70 % of the e-waste processed or disposed of in India is believed to originate from abroad, with Delhi as its primary destination. The Associated Chambers of Commerce of India (ASSOCHAM) reported that an annual e-waste growth rate of 25% is likely to generate 15×10^6 t of e-waste in India by 2015 [37]. The report also ranked Mumbai as the city with the highest level of generated e-waste by mass, followed by Delhi and Bangalore.

Pakistan has also emerged as a hotspot destination for e-waste, as it receives large volumes from the EU, Australia, and the US. Most of the e-waste imported to Pakistan is currently not documented by its Customs department [38, 39]. Although there are provisions to prohibit e-waste imports to Pakistan, around 0.1×10^6 t of ewaste was still being imported to Pakistan as second-hand items annually as of 2017 [40]. The city of Karachi is the major e-waste recycling site in Pakistan, whilst Lahore, Faisalabad, Peshawar, Gujranwala, and Islamabad are also involved in the recycling and dismantling of the e-waste, but on a much smaller scale [39, 41].

2.3 Nigeria and Ghana

Nigerian cities, such as Lagos, Ibadan, and Aba, are densely populated and import a wide range of electronic products. Ibadan (in Oyo State) and Lagos are located in South-Western Nigeria and Aba (in Abia State) is located in the South-Eastern geopolitical zone of the country. The highest volume of imported electronic equipment (both legal and illegal) in Nigeria is concentrated in the Computer Village, Alaba International Market, and Westminster Market. The Basel Action Network (BAN) estimates that in the Computer Village alone, there are 3500 registered businesses engaged in all manner of sales and repair of electronic equipment [4]. The Alaba International Market features over 2500 shops responsible for the repair, renovation, and sale of UEEE products. In contrast, the Westminster Market, which is the smallest of the three, has about 300 shops dealing with the sale of used EEE appliances [25, 42]. In 2012, it was estimated that Nigeria received imports of e-waste from the United Kingdom (60%), Germany (16%), China (9%), US (3%), and other countries (12%), mainly through seaports (e. g., Tin Can Island Port, Lagos) and through the land border (Seme border) with the Republic of Benin [42].

Ghana, highlighted by UNEP [4], is a frequent destination of e-waste. One of the largest and most publicized e-waste sites in the world is located in Ghana's capital city of Accra, known as Agbogbloshie. Agbogbloshie is notable for scrap metal recycling, but over the past decade, it has grown to serve as an important recycling spot for e-waste as well. In 2009, about 0.15×10^6 t of e-waste from consumers, repair shops, and communal collection reached the informal recycling sector of Agbogbloshie. A considerable portion of this was scavenged for useable components, such as hard drives, power supplies, and waste printed circuit boards (WPCB) [43].

The absence of a structured management system and laxity in environmental laws and regulations in Nigeria and Ghana has led to an increased influx of e-waste into these countries. Consequently, it has created an avenue for the use of uncontrolled and crude methods to recover valuable materials from e-waste. The health and environmental effects of such informal crude recycling activities are not necessarily taken into consideration by the workers [44–46].



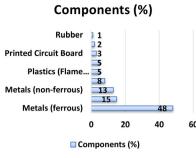


Fig. 3: (a) Example of e-waste ready for recycling (source: K. Isimekhai); (b) material constituents of some equipment that end up as e-waste (adapted from Ma et al. [50]).

3 Chemical composition of e-waste

The e-waste stream comprises a heterogeneous mix of metals (among them valuable elements, such as gold, silver, copper, and aluminium), metalloids, rare earth elements (REEs), glass, and plastics [including flame retardants (FRs) and other additives (Fig. 3a,b). Due to ongoing technological developments, the exact composition changes constantly, which makes e-waste distinct from other waste streams [48, 49].

The hazardous chemicals present in e-waste may be released into the environment, especially if the waste is disposed of or recycled improperly. Cayumil et al. [51] have classified these hazardous chemicals into primary and secondary contaminants. Primary contaminants are important constituents that are initially present in the manufacture of EEE due to their special intrinsic characteristics and includes metals such as copper, cadmium, lead, nickel, and zinc; metalloids, such as antimony (Sb); organic compounds like polychlorinated biphenyls (PCBs); liquid crystals; and FRs. In contrast, secondary contaminants are the by-products generated after the improper recycling of e-waste or during the recovery of valuable materials. For example, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo[1,4]dioxins and dibenzofurans (PCDD/Fs) are of particular concern in regions where there is a lack of environmental regulations.

3.1 Metal constituents in e-waste

An 'ecological rucksack' provides an estimate of the hidden material flow of an EEE. It is defined as the total quantity (in kg) of materials removed from nature to create a product or service, excluding the actual mass of the product. It represents the total amount of resources used during all the phases of a product's life cycle. High-tech devices have relatively elevated ecological rucksack values, as they have a high demand for resources, such as REEs and the less abundant minerals that are enriched in these elements [9]. For example, the production of a standard cellular phone that has 0.08 kg net mass has an ecological rucksack of 75.3 kg (35.3 kg raw material extraction, 31.7 kg utilisation of the phone from direct and indirect energy consumption, 8.2 kg production, and 0.1 kg disposal) [52].

A list of key elements found in EEE and their Relative Supply Risk (RSR)—an integrated supply risk index from 1 (very low risk) to 10 (very high risk)—is shown in Table 4. The RSR is calculated by combining the scores for abundance in the Earth's crust, reserve distribution, production concentration, substitutability, recycling rate, and political stability scores [53]. The majority of ferrous metals (those that mostly contain iron and small amounts of other metals or elements to give the required properties) and many non-ferrous metals (those that do not contain iron, are not magnetic, and are usually more resistant to corrosion than ferrous metals, e. g., aluminium) are widely recovered and recycled. As a number of precious metals are used in the manufacturing of EEE components (e.g., silver, gold, palladium, and platinum), they provide additional incentives to recover

¹ Metalloids (semimetals) have properties of metals and non-metals and include B, Si, Ge, As, Sb, and Te. Although there is no formal IUPAC definition of the term 'metalloid', it is widely used in the literature and is implemented in IUPAC technical report [47].

Table 4: Key elements found in e-waste and their use in EEE (compiled based on [10, 55–59]). Relative supply risk: 1 for very low risk to 10 for very high risk.

Element	Relative supply risk	Use in EEE
Li	6.7	As Li-ion battery, they are the most common battery type used in portable electronic devices.
Ве	8.1	Used in EEE as Be-Al alloy, typically containing 2 % Be. It is used in springs, relays, connections and historically computer mother board.
Al	4.8	Because of its lightweight, structural strength and thermal characteristics, Al is typically used as casing and frames of several electronics equipment. Often used as an alloy with Cu, Mn, Mg, and Si. Al is also good electrical conductors and can be found as metallisation in printed circuit boards, computer motherboards, hard drives, rotors and connectors. It is often recovered due to its economic values.
Si	No data	One of the most common semiconductors in Information and Communication Technology (ICT)-related equipment e. g., cathode ray tube (CRT), printed circuit board. Very often, Si is selectively doped with tiny amounts of B, Ga, P, or As to control its electrical properties.
Ar	No data	Present in incandescent light bulbs, fluorescent tubes and low-energy light bulbs.
Sc⁵	9.5	A rare Earth element (REE); due to its photophysical properties, it is often used as lasers in dentistry and high-intensity discharge lamps.
Ti	4.8	Commonly used as an alloy with Al, Mo and Fe as casing and is also increasingly used in electronic circuits and optical micro-devices (e. g., laser diodes) in multilayer metallisations, often paired with Pt.
V	6.7	Used in rechargeable flow battery. VO ₂ is used as semiconductors and in transistors.
Cr*	6.2	Cr ⁶⁺ is widely used as a corrosion inhibitor in corrosion protection in metal housing. Cr is a crucial component of stainless steel (where it is present at least at 10.5%) which is widely employed for EEE production. It can be also used in form of NiCr alloy, in multilayer metallisations in printed circuit boards, smart card chips and microdevices for ensuring adherence between metallic layers and between Au finishing and the device surface.
Mn	5.7	As an alloy with steel, Al or Cu, it has important metallurgical applications. As manganese oxides, they are used as a depolarizer in batteries, sensors and super capacitors.
Fe	5.2	There are numerous uses e. g., as electrical steel used in magnetic cores for transformers, generators and motors. As Fe_2O_3 it is used in hard drive and printed circuit boards. Widely recycled.
Co	7.6	As a magnetic alloy with Fe, Ni, Al, Nd, Sm (e. g., AlNiCo, SmCo, etc. magnets). It is widely used in Li-ion batteries. Often found in CRT, printed circuit boards and hard drives. It is often recovered due to its economic value.
Ni	6.2	As an alloy with steel, Cr, Mn, or Fe for corrosion protection in housing. Ni is widely used in batteries and CRT. It is employed as a coating in preserving NdFeB magnets from oxidation. It is often recovered due to its economic value.
Cu	4.3	Commonly used in electrical wiring. Copper wire is found in most electrical equipment and electronic circuitry. It is used for printed circuit boards pathways and as bulky material in multilayer connections where Au is the external finishing (e. g., smart card chips, printer cartridge connections and pathways). It represents the most abundant non-ferrous metal in de-manufactured printed circuit boards and small electronic equipment. Also forms important alloy with Al and Ti. It is often recovered due to its economic value.
Zn	4.8	Used in die-castings in electrical industries. As alloys such as Ni, Ag and Al solder. ZnO is widely used in the manufacture of rubber, plastics, inks, batteries and electrical equipment. ZnS is used in making luminous paints, fluorescent lights and X-ray screens. It is often recovered due to its economic value.
Ga	7.6	High purity Ga is used in the manufacturing of semiconductors. GaAs and GaN are used in electronic components e.g., integrated circuit, high speed logic chips, diode lasers and light emitting diodes (LEDs).
Ge	8.1	Commonly used in fluorescent lamps, LEDs, and transistors (historically). Si-Ge alloy, it is used in the manufacturing of semiconductor for high-speed integrated circuits.
As	7.6	As alloys with Pb or Ga. GaAs is a semiconductor material used in printed circuits boards and laser diodes.
Se	7.1	Used in Li–Se battery and ZnSe has been used in the manufacturing of LEDs and laser diodes.
Sr	8.6	Primarily used in the manufacturing of glass for CRT.
Υ [§]	9.5	A REE that is a key ingredient of $Ba_2Cu_3YO_7$ superconductor. Europium-doped yttrium oxide and oxysulfide (Y_2O_2S :Eu) are widely used in CRT and fluorescent lamps.
Nb	7.6	Used in the manufacturing of capacitors. As alloy with Ge, Sn, or Ti, it is used as superconductor wires. LiNbO ₃ is ferroelectric and used in mobile phones and optical modulators. It is often recovered due to its economic value.

Table 4: (continued)

Element	Relative supply risk	Use in EEE
Мо	8.6	Commonly used multilayer ceramic circuits and thermal-management applications when paired with Cu. Also used in diodes and rectifiers as well as field-emitter components in flat-panel displays. It is
_		sometimes recovered due to its economic value.
Ru	7.6	Commonly alloyed with Pt and Pd to make electrical contacts and to coat electrodes. Pb ₂ Ru ₂ O _{6.5} is used
		in the manufacturing of electrochemical capacitor. ${\rm Bi}_2{\rm Ru}_2{\rm O}_7$ is used in chip resistors. It is often recovered due to its economic value.
Rh	7.6	Commonly alloyed with Pt and Pd to make electrical contacts in printed circuit boards and to coat
KII	7.0	electrodes. It is often recovered due to its economic value.
Pd	7.6	Often used as soldering materials and as electrodes in multilayer ceramic capacitors in lap tops and
	,	mobile phones. It is often recovered due to its economic value.
Ag	6.2	Widely used in membrane switches and pathways, it is often present in printed circuit boards, plasma
J		display panels and photovoltaic panels (PVPs). Powdered Ag and its alloys are used in paste preparations for conductor layers and electrodes, ceramic capacitors, and other ceramic components. It is
Cd**	6.7	often recovered due to its economic value. Commonly used in contacts, switches and rechargeable Ni–Cd batteries. CdS is used in CRT.
In	7.6	Extensively used in liquid crystal display (LCD) as transparent electrodes (indium tin oxide) and thin-
	7.0	film transistors in the production of flat screen monitors, TVs and solar panels. GalnN and GalnP are
		used in LEDs and laser diodes.
Sn	6.7	Used in alloys with Pb as solder for electric circuits in historic electric and electronic equipment. Nb₃Sn is used in coils of superconducting magnets. Also used as electrode in Li-ion batteries. Stannate
		aqueous solutions are used to produce electrically conductive and corrosion resistant coatings on glass by electroplating and Zn_2SnO_4 is a fire-retardant used in plastics housing.
Sb	9	Used in antifriction alloys in electrical cable sheathing, as lead-free solder as well as fining agent in
30	,	glass for TV screens. As semiconductor materials, it is used in infrared detectors and diodes.
Те	No data	Used in the manufacturing of solar panels. It is often doped with Ag, Au, Cu or Sn in semiconductor applications.
Ва	8.1	BaO is used as coating on the electrodes in fluorescent lamps and $BaCO_3$ are used in the manufacturing of CRT.
La [§]	9.5	It is widely used for anodic material of nickel-metal hydride batteries, alone or, mostly, as the main component (>50%) of mischmetal. Used in carbon lighting applications such as studio lighting and cinema projection.
Ce [§]	9.5	An important component of phosphors in CRT and fluorescent lamps. It is also used in flat-screen TVs, low-energy light bulbs and floodlights.
Pr⁵	9.5	It is commonly used to produce magnets in small equipment such as printers, headphones and
		loudspeakers. It is also applied as activators in phosphors for lighting.
Nd [§]	9.5	It is the most abundant lanthanoid element in ${\rm Fe_{14}Nd_2B}$ permanent magnets, widely used for electronics e. g., in hard drives, mobile phones, headphones and loudspeakers. Neodymium-doped crystals are used in hand-held laser pointers.
Sm [§]	9.5	Used in carbon arc lighting for studio and projection. It is used to produce SmCo permanent magnets used in electronic equipment.
Eu§	9.5	Eu_2O_3 is widely used as a red phosphor in TV and fluorescent lamps.
Gd [§]	9.5	It has been used to produce magnets for miniaturisation of in electronic equipment and as dopant in optical fibres.
Tb [§]	9.5	Terbium is used as Tb_4O_7 in green phosphors in fluorescent, low energy light bulbs, Mercury lamps, CRT and as dopant in optical fibres.
Dy [§]	9.5	Widely used in the manufacturing of data-storage devices e. g., hard drives (it is contained in a 1 % amount in NdFeB-magnets where its presence preserves the magnetic properties at high temperature). It is also used in high-intensity metal-halide lamps and white LED.
Ho [§]	9.5	Used in yttrium-iron-garnet (YIG) and yttrium-lanthanum-fluoride (YLF) solid-state lasers found in microwave equipment.
Er§	9.5	Widely used in optical fibre cables.
Lu§	9.5	$Al_5Lu_3O_{12}$ is used as a phosphor in LED. It is also used as a dopant in computer memory devices.
Hf	No data	Used as electrical insulator in integrated circuits.

Table 4: (continued)

Element	Relative supply risk	Use in EEE
Та	7.1	Used in the production of electronic components e. g., capacitors and resistors for mobile phones and lap tops. It has also found uses as electrodes for neon lights and AC/DC rectifiers.
W	9.5	Widely used in old-style incandescent light bulbs, CRT, fluorescent lighting, and heating element. It is also used as an interconnect material in integrated circuits.
Re	6.2	It is used as an electrical contact material. It is often recovered due to its economic value.
Os	7.6	It is used as an electrical contact material. It is often recovered due to its economic value.
Pt	7.6	It is a component of the Co-Cr-Pt alloy used for hard drive platters coating; also found in fibreglass, liquid-crystal and flat-panel displays, and CRT. It is often recovered due to its economic value.
Au	5.7	Widely used in the production of corrosion-free connectors in electronic devices, cables and integrated circuits. It is often recovered due to its economic value.
Hg*	8.6	Historically used in mercury-vapour lamps and cold-cathode fluorescent lamps. It has also been used in switches, relays of older mainframe computers, LCD and batteries.
Tl	No data	Used by the electronic industry in photoelectric cells.
Pb*	6.2	Historically used in electrical solder with Sn on printed circuit boards and PbO is used in CRTs.
Bi	9	Used as a replacement of Pb as low melting point solders in printed circuit board.

^{*}According to the EU Restriction of Hazardous Substances (RoHS) regulation and new equipment should not contain a level greater than 0.1 % by weight since 2006.

these materials. Furthermore, gold and other valuable elements that are in relatively short supply are usually found in WEEE as high purity and quality materials, which make these secondary sources highly attractive for recovery [54]. It was estimated that the resource perspective for secondary raw materials of e-waste is worth 55×10^{9} € [2] and the gold content present in e-waste was projected to represent 11% of the global gold production from mines in 2013 [5]. Valuable metals can be recovered from e-waste, such as WPCBs, via state-ofthe-art metal smelting processes, although a number of other metals like lithium, REEs, and significant levels of cobalt and nickel are lost into the process slag [55]. In developing countries, the recovery process often involves rudimentary open-fire burning and acid stripping techniques [12].

3.2 Plastic in e-waste

Plastic is an important component of e-waste and comprises mainly thermoplastics that can be recycled by reprocessing [60–63]. More than 15 different types of engineering plastics have been documented in the manufacturing of EEE, including acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polypropylene (PP), polystyrene (PS), styrene-acrylonitrile (SAN), polyesters, polyurethane (PU), polyamide (PA), blends of polycarbonate (PC)/ABS, and blends of HIPS/poly(1,4-phenylene oxide) (PPO) [64]. Of these, ABS, PP, PS, and HIPS are the major constituents found in e-waste [65–67]. ABS is the most common plastic found in computers, computer monitors, and printers, whilst PP is used as an alternative to polyvinyl chloride (PVC) in insulation for electrical cables and HIPS has been found to be the predominant plastic in television housings [68]. Other large constituents in EEE include polycarbonate (PC) and the commercial blend of PC/ABS [61]. PVC is commonly used as cable insulation in many EEE due to its flexibility, ease of handling in installation and inherent flame retardation. Along with the heterogeneity of plastic materials, other additives are also incorporated to alter its physicochemical properties. These additives may be pigments (e. g., TiO₂, ZnO, Cr₂O₃, and Fe₂O₃), FRs, various stabilizers (e.g., compounds of barium, cadmium, lead, tin and zinc, or PCBs), or plasticisers (e. g., phosphate derivatives) [69–71].

^{**}According to the EU RoHS regulation and new equipment should not contain a level greater than 0.01 % by weight since 2006. § A rare Earth element.

3.3 Halogenated compounds in e-waste

A number of halogenated compounds are present in e-waste, mainly in the form of FRs used in WPCB, plastic housing, keyboards, chargers, and cables [72], and liquid crystals in LCDs. Many of these compounds are POPs regulated by the Stockholm Convention, for example chlorinated compounds like PCDD/Fs, PCBs, and the brominated flame retardant (BFR) group [e. g., polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and tetrabromobisphenol-A (TBBP-A)], amongst others. Liquid crystals found in LCDs are mainly organic compounds comprising carbon, hydrogen, oxygen, and fluorine. Liquid crystals used as mixtures in display technology have been deemed non-toxic, but their uncontrolled burning/incineration could well give rise to hydrogen fluoride and organofluoro-compounds.

As one of the main manufactured halogenated flame retardants, BFRs have been used in products since the 1960s [73]. The use of BFRs has been of concern for the past two decades due to their persistency and their bioaccumulative and toxicity characteristics [74]. PBDEs have been sold as three main commercial mixtures: pentaBDE, octaBDE, and decaBDE, each of which consists of several BDE congeners. The use of penta- and octaBDE in products was restricted in the EU in early 2000 [75] and this was followed in 2008 by the EU Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation banning the use of decaBDE in electronics in EU [76]. Congeners of penta- and octaBDE mixtures were added to the list of POPs covered by the Stockholm Convention in 2009. Additionally, commercial mixtures of decaBDE were added to the list in 2017 [76]. A high fraction (61%) of the cathode ray tube (CRT) casings contained more than 10,000 mg kg⁻¹ bromine from BFRs; decaBDE was the major FR used in TV sets and TBBP-A for computer CRTs [77, 78].

The halt in production and use of PBDEs has resulted in the increased application of alternative FRs with less well-known physicochemical properties. Examples of novel brominated flame retardants (NBFR) include: 1,2-bis(perbromophenyl)ethane, systematic name: 1,2,3,4,5-pentabromo-6-[2-(2,3,4,5,6-pentabromophenyl) ethyl]benzene)(DBDPE); 1,2-bis(2,4,6-tribromophenoxy)ethane, systematic name: 1,3,5-tribromo-2-[2-(2,4,6-tribromophenoxy)ethane, systematic name: 1,3,5-tribromo-2-[2-(2,4,6-tribromophenoxy)ethane, systematic name: 1,3,5-tribromophenoxy)ethane, systematic name: 1,3,5-tribromophenoxy, systematic name: 1,3,5-tribromophe tribromophenoxy)ethoxy]benzene (BTBPE); bis(2-ethyhexyl) tetrabromophthalate, systematic name: bis(2ethylhexyl) 3,4,5,6-tetrabromobenzene-1,2-dicarboxylate (TBPH); 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB); hexabromobenzene, systematic name: 1,2,3,4,5,6-hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP); decabromobiphenyl, systematic name: 1,2,3,4,5-pentabromo-6-(2,3,4,5,6-pentabromophenyl)benzene) (BB209); triphenyl phosphate (TPP); tri-p-cresyl phosphate, systematic name: tris(4-methylphenyl) phosphate (TCP); tris(2-chloroethyl) phosphate, systematic name: tris(2-chloroethyl) phosphate (TCEP), and tris(1chloropropan-2-yl) phosphate (TCPP). The physicochemical properties of a list of PBDE alternatives in electronic products are presented in Table 5.

4 Environmental levels of contaminants caused by e-waste recycling

In comparison to informal e-waste recycling, formal recycling of e-waste has received much less attention. Formal e-waste recycling activities are principally engaged in the dismantling and mechanical processing of EEE to recover valuable materials. A systematic review by Cellabos and Dong [79] reported the occupational exposure in formal recyclers is mainly via dust inhalation: the extent of exposure is dependent on the sophistication of the facilities. High levels of metal(loid)s, BFR, and novel flame retardants (NFRs) have been reported in formal e-waste recycling plants in Sweden [80], Australia [81], and China [82].

Labour intensive manual dismantling and crude recycling methods are involved in the informal recycling sector, especially in e-waste 'hot spots' countries (section 2). In comparison to the highly automated processes, informal recycling of e-waste can be generally grouped into three categories: (i) manual dismantling; (ii) recovery of valuable materials *via* open burning and/or acid stripping, and (iii) disposal of the unsalvageable waste (Fig. 4). Table 6 presents a list of informal recycling activities from different countries around the world. As a result of these crude techniques and inappropriate facilities, the informal recycling of e-waste has the

Table 5: Molar mass, M, and decadic logarithm of n-Octanol/Water Partition Coefficient, lg K_{ow} , of main FRs used as PBDE alternatives in electronic products.

Abbreviation/IUPAC name	CAS number	Structure and molecular formula	M/g mol⁻¹	lg Kow	Application in electronic products
BB209 Decabromobiphenyl IUPAC name: 1,2,3,4,5-pentabromo-6-(2,3,4,5,6- pentabromophenyl)benzene	13654-09-6	Br B	943.172	8.58	High impact polystyrene (HIPS)
DBDPE 1,2-bis(perbromophenyl)ethane IUPAC name: 1,2,3,4,5-pentabromo-6-[2- (2,3,4,5,6-pentabromophenyl)ethyl]benzene)	84852-53-9	Branch Br	971.226	11.1	Polystyrene (PS)
BTBPE 1,2-bis(2,4,6-tribromophenoxy)ethane IUPAC name: 1,3,5-tribromo-2-[2-(2,4,6-tri- bromophenoxy)ethoxy]benzene	37853-59-1	Br Br Br	687.640	8.31	HIPS, acrylonitrile–butadiene–styrene (ABS)
TBPH bis(2-ethyhexyl) tetrabromophthalate IUPAC name: bis(2-ethylhexyl) 3,4,5,6-tetra- bromobenzene-1,2-dicarboxylate	26040-51-7		706.148	9.34	Polyurethane (PU) foam
TBB 2-ethylhexyl 2,3,4,5-tetrabromobenzoate IUPAC name: 2 ethylhexyl 2,3,4,5-tetra- bromobenzoate	183658-27-7	Branch Br	549.923	7.73	PU foam

Table 5: (continued)

- Abbreviation/IUPAC name	CAS number	Structure and molecular formula	M/g mol⁴	lg Kow	Application in electronic products
HBB Hexabromobenzene IUPAC name: 1,2,3,4,5,6-hexabromobenzene	87-82-1	B F B F B F B F B F B F B F B F B F B F	551.490	6.07	Capacitors
TBP 2,4,6-tribromophenol IUPAC name: 2,4,6-tribromophenol	118-79-6	Br OH	330.801	3.89	As an intermediate of flame retardants (tribromophenyl allyl ether, 1,2-bis(2,4,6-tribromophenoxy)-ethane and as brominated epoxy resins
TPP triphenyl phosphate IUPAC name: triphenyl phosphate	115-86-6		326.288	4.59	Polymers
TCP tri-p-cresyl phosphate IIDAC namo: tric(//mathulphanu)) phosphate	1330-78-5		368.369	5.11	Plasticizer
TCEP tris(2-chloroethyl) phosphate IUPAC name: tris(2-chloroethyl) phosphate	115-96-8		285.482	1.47	Polymers such as polyurethanes, polyester resins and polyacrylates
TCPP tris(1-chloro-2-propyl) phosphate IUPAC name: tris(2-chloropropan-2-yl) phosphate	13674-84-5		327.563	2.59	PU





Fig. 4: Activties associated with informal e-waste recycling - (a) manual dismantling (source: D. Chatterjee); (b) open burning of e-waste to recover valuable materials (Source: O. E. Popoola).

potential to release a large quantity of contaminants into the recycling sites and the surrounding environment. Also, e-waste recycling sites are often located in or close to agricultural land [83] or close to water bodies [84]. Furthermore, many recycling activities have also been carried out in the backyard of family homes in India [85].

4.1 Metals/metalloids contamination in different environmental compartments

4.1.1 The terrestrial environment

A number of studies have been carried out on informal e-waste recycling sites that report on the elevated levels of contaminants in the related environment when compared to the guideline values or background levels (Table 7).

Due to the heterogeneous physico-chemical and biological properties of soils that affect the availability and mobility of metals, drawing direct comparisons between research findings from around the world needs to be more circumspect. Nevertheless, a general trend can be observed that significant levels of metals, in particular copper, lead, and zinc are detected around informal recycling sites [86, 87]. For instance, in China, the levels of metals in soils taken from an emerging e-waste recycling city, Taizhou, were found to exceed the values of the Level II quality standard (GB 15618-1995) stipulated by the Ministry of Ecology and Environment (formerly the State Environmental Protection Administration) for the protection of human health and agricultural production in China [87]. Similarly, in Guangdong province, Luo et al. [83] reported metal levels (cadmium, copper, lead, and zinc) that exceed the actionable values of the Dutch standard at a former e-waste incineration site. Soil samples collected from the acid leaching area in an informal recycling site in Guiyu were also found to contain high levels of antimony, cadmium, copper, lead, nickel, tin, and zinc [88]. The detection of the less common contaminants (antimony and tin) at levels higher than the principal contaminants suggests the need to take into account other chemical constituents of EEE. Elevated levels of cadmium, lead, Mercury, and zinc are still being detected in soil in Ziya, northern China, where informal e-waste recycling ceased in 2011 [89], highlighting the legacy of non-biodegradable and persistent pollutants and the need for the clean-up of historical e-waste recycling sites.

In India, [90] reported elevated levels of metals at e-waste dumping and recycling sites in Mandoli industrial area reached maximum levels of 6734 mg kg⁻¹ copper, 2645 mg kg⁻¹ lead, and 776 mg kg⁻¹ zinc. In Manila, Philippines, an analysis of 11 metal(loid)s (arsenic, cadmium, cobalt, copper, indium, iron, lead, manganese, nickel, silver, and zinc) in surface soil samples from both formal and informal e-waste recycling sites indicated that the contaminant levels at the informal recycling sites were higher than at the formal facility and similar to the levels measured in nearby Asian countries [89]. High levels of copper, lead, and zinc were also detected in soil samples collected from inside an informal recycling site and up to 12 m away, although the maximum levels of copper, lead, and zinc inside the recycling site were at least 10 times higher than those outside [91, 92].

Similarly, Isimekhai et al. [93] reported high levels of metals at the e-waste recycling site in Nigeria; the levels of copper (329 to 7106 mg kg⁻¹), lead (115 to 9623 mg kg⁻¹), and zinc (508 to 8178 mg kg⁻¹) were consistently

 Table 6:
 Examples of informal recycling activities in different countries.

Activities	Country										
	China [24, 104- 107]	Egypt [108]	Ghana [11, 84, 109- 112]	India Indoi [90, 107, [113] 112]	Indonesia [113]	Nigeria [46, 93, 98]	Pakistan [27, 39]	Philippines [91, 113]	South Africa [114]	Uruguay [115]	Vietnam [113]
Physical dismantling using bare hands and simple hand tools such as hammers, chisels screw drivers to separate different material	,	,	`	,	,	,	,	,	,	,	,
Removing components from printed circuit boards by burning	`>	>	`	`		`>	`>				
Printed circuit boards sold to informal ex-		>	`		>		`>	`		>	`
Stripping of metals in acid baths	> '		,	>	,		,	,	>	,	,
Crushing and/or melting plastics Burning cables to recover precious metals	> >	>	> >	>	> >	>	> >	> >	>	>	> >
Manual stripping of wires					`			`			`>
Burning unwanted materials in open air	>		`			`					
Disposing unsalvageable materials in fields/landfill/riverbanks	`>		`	`>		`>		`		`>	
Refilling of toner cartridges	`>					`>					

Table 7: Metal(loid)s as contaminants detected in e-waste sites.

Country and location	Environmental	Pollutants detected	Levels	References
•	matrix			
China: Taizhou	Soil	Cu, Cr, Cd, Pb, Zn, Hg, and As	0.37 to 1.2 mg kg ⁻¹	[87]
China: Longtang	Soil	Cd, Cu, Pb, and Zn	GM of 17.1, 11,140, 4500, 3690 mg kg ⁻¹ respectively	[83]
China: Longtang	Soil	Cd	Higher than 0.39 mg kg ⁻¹	[100]
	Ponds and	Cu	Higher than 31.17 mol L ⁻¹	
	Well water	Cd, Cr, Cu, Mn, Ni.	All significantly above the national guideline level	
China: Guiyu	Soil	Ni, Cu, Zn, Cd, Sn, Sb and Pb	GM of 278.4, 684.1, 572.8, 1.36, 3472, 1706, and 222.8 $\mathrm{mgkg^{-1}}$	[88]
			respectively	
China, Guiyu	Sediment	Cu, Zn, Cd, Sn, Sb and Pb in the sediments	Mean of 4820, 1260, 10.7, 2660, 5690 and 2570 mg kg ⁻¹ , respectively	[102]
China, Guiyu	Road dust	Cd, Cr, Mn, Pb	Mean of 1.94, 69.71 and 693.74 and 589.74 mg kg ⁻¹ , respectively. Cd and	[116]
			Pb was 4.10 and 3.18 times higher than the reference area	
China: Guiyu	Surface dust	Pb, Cu, Zn and Ni in workshop	GM of 110000, 8360, 4420 and 1500 mg kg ⁻¹ , respectively	[117]
		Pb, Cu, Zn and Ni in adjacent road	22,600, 6170, 2370 and 304 mg kg ⁻¹ , respectively	
China: Guiyu	Ambient air	Pb and Cd	GM of 160 and 5.7 mg m ⁻³	[118]
		PM2.5	49.9 µg m ⁻³	
China: southern rural	Groundwater	Cd, Pb, Zn, Cu, and Ni	Between 1.3 and 140 times higher than the national guideline values	[66]
region				
China: Guangdong	Soil	Cu, Zn, Pb, Ni, Cr, and Cd	GM of 590, 298, 320, 7,1, 19.7, and 0.22 mg kg ⁻¹ , respectively	[101]
India: New Delhi	Surface dust*	Cd (battery workshop), Cr, Cu, and	Up to 200,000, 103, 6850, 362,000, 460, and 4920 mg ${ m kg}^{\!\scriptscriptstyle -1}$, respectively	[85, 90,
		Hg (separation workshop), Pb (circuit board pro-		103]
		cessing workshop) and Zn (battery workshop)		
Philippines: Manila	Surface soil	Cd, Co, Cu, Mn, Ni, Pb and Zn	GM of 2.5, 30, 680, 950, 47, 800, and 900 mg kg ⁻¹ , respectively	[91, 92]
	Surface dust	Cd, Co, Cu, Mn, Ni, Pb and Zn	GM of 3.9, 33, 6300, 1800, 380, 800, and 2900 mg kg ⁻¹ , respectively	
Vietnam: Bui Dau	Soil	Cu and Pb	The highest values recorded were 3000 and 2200 mg kg $^{ extsf{-1}}$, respectively	[98]
village				
Ghana: Agbog-	Surface soil, Soil	Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn	GM of 0.24, 1.01, 2.35, 54.4, 124, 35.4, and 19.2 mg kg ⁻¹ , respectively	[95, 97]
bloshie		Cu, Zn, As, Cd, Sn, Sb, and Pb	GM 602, 1274, 6.69, 1.51, 33.3 36.6, and 442 mg kg ⁻¹ , respectively	
Ghana: Agbog- bloshie	Ambient air	Al, Cu, Fe and Pb	The highest values recorded were 6.5, 1.2, 8.9, 0.98 mg m-3, respectively	[119]
Ghana: Korle Lagoon	Sediment	Cu, Pb, and Zn	Up to 2260, 1685, and 2425 mg kg¹, respectively	[64]
Nigeria: Lagos	Soil	Cu, Pb, and Zn	329 to 7106 mg kg $^{\text{-1}}$, 115 to 9623 mg kg $^{\text{-1}}$, and 508 to 8178 mg kg $^{\text{-1}}$, respectively	[63]
Nigeria: Lagos, Aba, Ibadan	Surface dust	Significant high levels of As, Cd, Cr, Cu, Hg, Pb, and Sb.	Mean metal concentration at the e-waste recycling sites exceeded the Nigerian standard guideline values by 100 to 1000 s times	[86]
		ò		

*From a number of workshops; GM: geometric mean.

higher than the threshold values of national soil guideline values (e. g., for the Netherlands). In Ghana, antimony, arsenic, cadmium, copper, lead, tin, and zinc were detected in high levels in soil samples collected from informal e-waste recycling sites in Agbogbloshie (as much as 20 times higher than background values) by a number of studies [94, 95]. The elements aluminium, antimony, barium, cadmium, cobalt, copper, indium, lead, and zinc were detected in the mixtures of residual ash at the Agbogbloshie market as a direct consequence of e-waste burning [96]. Overall, burning appeared to be the most polluting activity. The highest levels of metals were detected in soils from the Agbogloshie e-waste processing site, as well as neighbouring residential, recreational, farming, and commercial areas [97], with the highest level found in the area where waste burning occurs. Isimekhai et al. [93] and Ohajinwa et al. [98] also found an increase in metals levels at ewaste recycling sites in Nigeria, which was dependent on the type/intensity of the recycling activity. Metal levels increased from the repair sites to dismantling sites and the highest levels were detected in the burning sites.

4.1.2 The aquatic environment

Groundwater collected from an e-waste recycling area located in the rural region of South China was reported to pose a significant risk for families that use it for drinking and cooking, as the concentration of metals (cadmium, copper, lead, nickel, and zinc) in the water was between 1.3 and 140 times higher than the national guideline values for groundwater in China [99]. In an abandoned e-waste recycling site in Longtang, China, the pond water was heavily acidified and contaminated with transition metals (especially cadmium and copper) as a result of the metals being transported from the surface soil to ponds [100]. Speciation and leaching experiments using metal contaminated soil from e-waste recycling sites also found copper and zinc in pore water and topsoil, from which the authors concluded that the pollutants might be mobilised by rainwater irrigation and plant growth [101]. E-waste recycling activities, such as acid stripping with strong oxidizing acids, e. g. an aqua regia mixture, have also been reported to cause soil acidification and the production of leachate effluents that pollute water and sediment in both China [102] and India [90, 103]. Metals such as copper, lead, and zinc were detected in the sediments of the Korle Lagoon, Ghana (Agbogbloshie is situated on its embankment). The levels of copper, lead, and zinc exceeded background levels (20, 15, and 6 times higher, respectively) compared to the sediment in control sites [84, 94].

4.1.3 The atmospheric environment

Release of atmospheric contaminants from processing sites can occur even in developed countries using more regulated and formal recycling methods [79–82]. The situation with informal recycling is considerably more critical. Many processes used within the informal e-waste recycling sector, including physically breaking apart the components and open pit or barrel burning, release large amounts of dust, fumes, and smoke into the atmosphere. These contains metals, NO_x, and other aqua regia gaseous by-products, such as NOCl, Cl₂, and organic pollutants. Surface dust samples collected from e-waste recycling workshops and adjacent roads in China have shown elevated levels of metals, such as copper, lead, nickel, and zinc [116, 117] (Table 7). The levels of lead, cadmium, and PM_{2.5} mass in an informal e-waste recycling site in Guiyu were significantly higher than the reference site in other Asian cities and constitutes a major public health concern [118].

Dust samples collected from different informal recycling workshops in New Delhi, India, were found to contain high levels of cadmium, chromium, copper, Mercury, lead, and zinc, with the distribution of the metals in the dust found to vary according to the nature of the e-waste (Table 7; [90]). Similarly, in Manila, Philippines, an analysis of 11 metal(loid)s (arsenic, cadmium, cobalt, copper, indium, iron, lead, manganese, nickel, silver, and zinc) in surface dust from both formal and informal e-waste recycling sites indicated higher levels of the metals at informal recycling sites than at a formal one [89]. Elevated levels of aluminium, copper, iron, lead, and zinc were also observed in the ambient air at the Agbogbloshie e-waste recycling site [119].

4.2 Halogenated compounds

Halogenated compounds such as PBDEs and PCBs have been detected in air and dust samples in formal recycling plants, indicating potential occupational health risks [79–82, 120, 121]. For example, the sum of seven PBDE congeners (Σ_7 PBDE) in the indoor air and dust samples from a formal recycling facility in China treating household goods (such as TV sets, washing machines, refrigerators, and WPCB) was between 55.28 to 369.66 ng m⁻³ and 158.07 to 669.81 µg g⁻¹, respectively; with BDE-209 as the most abundant congener [82]. At informal recycling sites, open burning is often used to remove the plastic components in WEEE to enable the salvage of the valuable materials within. The levels of halogenated compounds in these areas are therefore of considerable interest and concern.

Polychlorinated dibenzo[1,4]dioxins and dibenzofurans (PCDD/Fs) can be generated by the open burning of e-waste. For instance, in 2006 the total mass concentrations of 17 2,3,7,8-substituted PCDD/Fs in the air of an ewaste recycling site in Longtang, China was found to range from 52 to 548 pg m⁻³, with an average of 237 pg m⁻³, which was much higher than the reported range for global urban/industrial areas [122]. In another study, the atmospheric PCDD/F level in an e-waste site in Longtang (159.41 pg m⁻³ as toxic equivalents, TEQ) was 2 to 4 times higher than baseline levels reported for world urban cities [123]. However, since the implementation of laws forbidding open burning and acid washing by the Chinese government in the 2010s, the atmospheric PCDD/F level has been significantly reduced [122]. For example, a 7-fold and a 31-fold reduction was observed in Guiyu and Qunguan, respectively [124]. The reduction resulted in an average of 1.21 pg m⁻³ TEQ and 0.271 to 0.644 pg m⁻³ TEQ in Guiyu and Qunguan, respectively. These observations suggest that the use and enforcement of stricter legislation can influence the environmental pollution associated with the open burning of e-waste.

High levels of PCBs (53 ng g⁻¹) are also detected in the dust recovered from the informal e-waste metal recovery workshops in Chennai, India, compared to the dismantling site (35 ng g⁻¹) and suburban industrial roadsides (16 ng g⁻¹), where tetra-, penta-, and hexa-PCB homologues constitute the majority of the 26 PCB congeners detected [125]. Similar trends were also observed in other Indian cities (New Delhi, Kolkata, and Mumbai), with the range of Σ 26PCBs of 0.4 to 488 ng g⁻¹ and Σ PCDD/Fs of 1.0 to 10.6 ng g⁻¹ [126].

A number of publications reported the release of BFRs in the environment via uncontrolled recycling processes [127–135]. Informal recycling of e-waste also appeared to affect the air quality of the neighbouring areas. In a study carried out by Hong et al. [136], PCBs and halogenated flame retardants (HFRs) were detected in soil, water, reed, air, and dust samples collected from the e-waste recycling region in Ziya Town, Northern China, as a result of dry deposition. A record level of BFR (penta-BDE, TPP, BTBPE, and TBBP-A) was detected in sediments in the River Lian near to and downstream from the e-waste recycling zone in Guiyu, China, highlighting the risk of pollutant migration [137]. The levels of PCBs and PBDEs in indoor air samples of residential houses around two informal e-waste recycling sites in northern Vietnam were also observed to be significantly higher than in the control area, with the PCBs ranging between 1000 and 1800 pg m⁻³ TEQ and PBDE 620 to 720 pg m⁻³ TEQ [138]. Similarly, the levels of PBDEs in dust and top soil at several e-waste recycling sites in Nigeria exceeded the levels at the control sites by 100- to 1000-fold. In general, PBDE levels were the highest at burning sites, followed by dismantling sites, and repair sites [139]. The presence of contaminants as a result of the informal e-waste recycling in Ghana has been reported by a number of studies [43, 94, 128], where elevated levels (as much as 20 times higher than background values) in zinc, lead, copper, phthalates, and PBDEs were observed at the Agbogbloshie e-waste recycling site. Furthermore, the median TEQ of dioxinrelated compounds in soils subjected to open burning techniques has been found to be seven times higher (about 7000 pg g⁻¹ TEQ) than the US action levels [138].

As NFRs are used to replace BFR, Dechlorane Plus isomers (DPs) and organophosphate flame retardants (PFRs) have begun to emerge in environmental samples [79-81, 118, 119, 139-142]. Indoor dust samples from five villages located in three e-waste-recycling regions in Guangdong Province, China, showed medians of novel brominated flame retardants (NBFRs), and PFRs ranging from 1460 to 50,010 and 2180 to 29,000 ng g⁻¹, respectively [143]. Similarly, a study on the dust and soil around an informal recycling site in Karachi City, Pakistan showed NBFRs in high levels in soils (BDE-209, 726 ng g⁻¹; DBDPE, 551 ng g⁻¹; BTBPE, 362 ng g⁻¹, and TPP, 296 ng g⁻¹), while OPFRs dominated atmospheric samples (5903-2,4986 ng m⁻³) [38]. In an informal recycling site in the northern part of Vietnam, NBFRs were released into the environment. Soil and sediment around manual dismantling workshops and open burning areas were found to contain higher levels of DBDPE (up to 4200 ng g⁻¹), BTBPE (up to 350 ng g⁻¹), and DPs (up to 65 ng g⁻¹) [144, 145].

Since metals and organic pollutants often co-occur [e.g., 145-147], the use of certain metals as tracers for the contamination of a sample with BFR or other hazardous e-waste compounds may be considered. Such a concept may be beneficial in less developed countries, where facilities for organic analysis may be not available. The analysis of most of the relevant metals, on the other hand, is cheap and relatively easy to perform. At the least, a pre-selection of samples may be possible by this means, so that only a few suspicious samples (high content of tracer(s) indicating possible e-waste impact) must be analysed for organic pollutants to assess the potential risk. All samples should be analysed in comparison to appropriate reference samples from non-polluted sites of the same region to gain meaningful results. A case study on using metals as tracers for organic contaminants in potentially e-waste-polluted environment media is presented in Section 7.

5 Ecological impact of e-waste on biota

A major concern of soil contamination from e-waste recycling is its impact on the biota. Analysis of soil-air exchange of pollutants has shown that soil acts as a secondary source to the atmosphere only for a few low molecular mass compounds, while the direction of the flux of most detected chemicals was from air to soil [148]. Contaminants released by e-waste activities are directly transferred to soils, then to plants and other soil organisms. For example, the mean TBBP-A level measured in biota near e-waste recycling and disposal sites in China ranges from 3.62 to 42.26 ng g⁻¹ wet mass in plant materials, 28.2 to 103.4 ng g⁻¹ dry mass in birds, 0.98 ng g⁻¹ wet mass to 1.52 ng g⁻¹ dry mass [149], indicating the potential for bioaccumulation.

The soil microbial community at e-waste sites appeared to be significantly affected by the pollutants present (e.g., PAHs, PBDEs and metals), but did not appear to correlate to the distance away from the pollution source [150]. Metal(loid)s present in an e-waste recycling site in Ziya, northern China impacted negatively on soil microbial viability, even though the levels of the chemicals were not harmful to humans [89]. Bacterial diversity was not decreased at e-waste open-burning sites, compared with a control site, possibly due to adaptation of the bacterial consortium to the environmental pollutants [151]. Other major drivers affecting the microbial composition in e-waste soil include available phosphorus, soil moisture [152], pH, texture, cation exchange capacity, total phosphorus content, and organic carbon [152-154]. Examples of the impact of metals in the environment are presented in Table 8. Key microbial processes are influenced by elevated levels of metals in e-waste recycling sites and shifts in soil microbial diversity, population, and functional activity of the microbial communities have all been observed [152, 154-157]. A study that examined the combined effect of lead and BDE 209 at several e-waste recycling sites showed that the microbial richness and diversity was adversely affected [158]. Additionally, the soil biomass was significantly inhibited by these pollutants and an inverse relationship was observed for the soil respiration and metabolic quotient [159]. Metals released into the environment also affect the ecological balance in the aquatic environment or can settle into the sediment, from where they can be taken up by aquatic plants and organisms [160, 161].

Foliar uptake of atmospheric metals has been proven to be a significant pathway for metals entering into leaf and grain tissues [83]. Soil pH, redox potential, and soil composition, such as the organic matter content, play a role in the mobility and bioavailability of contaminants and, in the case of metals, chemical speciation also influences their toxicity in the plant system [162]. The root to shoot transportation of metal(loid)s is also a significant pathway. Vegetables, rice, and wild plants collected from areas surrounding residential gardens, paddy fields, and deserted land near a former e-waste incineration site in Guangdong province, China, showed levels of metals in the edible part of leafy vegetables that were significantly higher than in the edible portion of root vegetables [83, 163]. In the same studies, the levels of cadmium and lead in most vegetables exceeded the food safety limit in China. Bakare et al. [164] collected leachate from an open e-waste dumpsite in Alaba International Market in Lagos State, Nigeria, and water samples from wells between 100 and 150 m away from

Table 8: Impact of pollutants from e-waste on microbial communities.

Pollutant Group	Environmental matrix	Notes	References
PAHs, PBDEs and metals (Cu, Zn, and Pb)	Soil in e-waste recycling sites in Pakistan and China	The microbial community composition and diversity, at both whole and core community levels, were affected. The predominant phyla are: <i>Proteobacteria</i> , <i>Acidobacteria</i> and <i>Gemmatimonadetes</i> .	[150]
Metal (total-Cu, HCl- extractable Pb and Zn)	Soil in an e-waste site in Nigeria	The relative abundance of bacterial taxa changed with metal mass concentration and other soil properties (pH, texture, cation exchange capacity and organic carbon).	[153]
Hg	Soil in an e-waste site in China	Major factors affecting the microbial diversity include Hg and P levels, soil moisture and land use. The dominant microbial genera are <i>Candidatus</i> , <i>Nitrososphaera</i> and <i>Nitrospina</i> .	[152]
PAHs, PBDEs, and metals	Sediment from e-waste contaminated rivers in China	PAHs, PCBs and PBDEs are more toxic to soil ommunity structure and function than metals. In particular, benzo[a] pyrene, bioavailable Pb and electrical conductivity were the key drivers.	[155]
PBDEs and Pb	Soil in e-waste recycling site in China	Affected biomass adversely but appeared to stimulate soil metabolic quotient and respiration. Protebacteria, Acidobacteria and Actinobacteria are the dominant phyla.	[159]
POPs and metals	Soil in an e-waste recycling site in China	Higher ratios of fungal-to-bacterial and lower relative abundance of Gram-positive bacteria in rhizospheric soils as determined by phospholipid fatty acids analysis (PLFA).	[154]
POPs	Soil in an e-waste recycling site in China	The diversity of in situ bacterial communities in the rhizo- sphere decreased at the near open-burning site (by sup- pressing POPs-sensitive species) and increased at the open-burning site (by substantially favouring POPs- consuming species).	[151]
PCBs	Soil in an e-waste recycling site in China	A gradual change in soil bacteria diversity along the PCBs pollution gradient was observed, favouring <i>Proteobacteria</i> and <i>Bacteroidetes</i> closely related to the catabolism of PCBs.	[157]

the dumpsite. The leachate appeared to induce chromosome aberration, decreasing mitotic index, and root growth anomalies in onions (*Allium cepa*).

The accumulation of contaminants up the food chain is an important pathway for the transportation of contaminants within the ecological network. Persistent toxic substances (such as PBDEs, PCDDs/PCDFs) and metals (such as lead) may end up in the ocean and may re-distribute into the environment, where bioaccumulation and biomagnification may occur [165]. Bioaccumulation of PCBs and PBDEs was observed in a number of studies. Earthworms in soil from an e-waste dismantling area in Taizhou, China, indicated that PCBs and PBDEs had higher bioaccumulation potential compared to PCDD/Fs [166]. DP was also detected in earthworms around e-waste recycling sites in China, although the biota-to-soil-accumulation factor was low (0.0007 to 1.85), with an average value of 0.23 [167].

Fu et al. [168] analysed contaminants in soil samples and apple snails in Fengjiang, southeast China, and reported a correlation between the dismantling activities and the release and transport of PCBs and PBDEs in the surrounding areas, where PCB and the PBDE (excluding BDE 209) were found to accumulate in apple snails. High levels of BDE 47 and other PBDEs were also detected in Chinese Mystery Snails (Cipangopaludina chinensis) collected in several e-waste recycling sites in China [169, 170]. DP and related compounds were detected in wild frogs (Rana limnocharis) and the freshwater food web near e-waste recycling sites in southern China [169, 171].

Fish obtained from a reservoir surrounded by several e-waste dismantling workshops in Qingyuan, South China, were found to contain high levels of BDE 47 [170]. The levels of PBDEs found in fish and shellfish in the Nayang and Lianjiang rivers (around an active e-waste site in Guiyu, China) were 15,000 times higher than levels reported from other regions and about 200 to 600 times higher than PBDE levels in bottom sediments collected from the same rivers [172]. The accumulation of the PBDE congener appeared to be species-specific, with carnivorous fish appearing to accumulate more organic pollutants [173, 174]. Nuclear abnormalities were observed in peripheral erythrocytes of African sharptooth catfish (Clarias gariepinus) in Alaba International Market in Lagos State, Nigeria [164]. The data suggested that the water and leachate samples contained clastogenic and/or aneugenic substances capable of increasing DNA damage and genome instability in the tested organisms.

Relatively high levels of ΣPBDEs (1000 to 5200 ng g⁻¹ wet mass), PBBs (110 to 340 ng g⁻¹ wet mass), and polybutylene terephthalate (PBT; 0.5 to 1.2 ng g⁻¹ wet mass) were found in birds sampled at e-waste recycling areas in China [175]. These water birds feed predominately on berries, soft fruits, and vegetables, or insects and small animals. Therefore, the detection of PBDE congeners in their tissues indicates that bioaccumulation can occur in wild bird populations [175]. Elevated DP levels and ethoxyresorufin-O-deethylase (EROD), an enzyme used as a biomonitor of persistent organic pollutants exposure, was observed in common kingfishers (Alcedo atthis) near an e-waste site [176]. Furthermore, a population abundance and species diversity study on birds in areas extended beyond the point source of e-waste pollution in South China showed a severe decline of migratory and resident bird functional assemblages [177].

Six food groups from Taizhou, China were also found to contain high levels of PCDD/Fs (at least 30 times higher than a control site). The highest level of the total WHO-TEQ was in crucian carp (10.87 pg g⁻¹ wet mass), followed by duck (3.77 pg g⁻¹ wet mass), hen eggs (2.80 pg g⁻¹ wet mass), chicken (2.43 pg g⁻¹ wet mass), rice (0.08 pg g⁻¹ wet mass), and vegetables (0.022 pg g⁻¹ wet mass) [178]. A study measuring HFRs over six years in free-range eggs in Longtang, China, showed that there was no decline in HFR levels from 2010 to 2016, despite the legislation and regulation of informal e-waste recycling activities. PBDEs are the dominant compounds in eggs, followed by DPs, PBBs, HBCDD, and DBDPE [179].

6 Contamination indices

Currently, a number of pollution indices are widely used in the literature to indicate the degree or extent of soil contaminations due to e-waste, including: Pollution Load Index (PLI), Potential Ecological Risk Index (RI), Geoaccumulation index (I_{geo}), Nenerow Pollution Index (PI_{Nemerow}), and Enrichment Factor (EF). The formulae to calculate these indices are presented in Tables 9 and 10. Examples of their usage in e-waste literature is presented in Table 11. The PLI is an integrated index to calculate contamination of a number of pollutants; it is widely used to compare pollution in different sites, but omits the availability of metals [180]. The RI is based on the elemental abundance and release capacity data, and was introduced to assess the degree of ecological risks posed by metals in topsoil [181]. The I_{geo} determines and defines metal contamination in sediments by comparing current levels with pre-industrial levels in order to measure the effects of human activities on the environment. The PI_{Nemerow} is widely applied to reflect the total pollution level and evaluate environmental quality. Due to its universal formula, the EF is a relatively simple and easy tool for assessing the enrichment degree and comparing the contamination of different environmental media. Toxicity Characteristic Leaching Procedure (TCLP) is widely used to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. The method [EPA Method 1311 [182]] was developed by the United States Environmental Protection Agency in order to simulate leaching through landfills. The ecotoxicity impacts can be evaluated using the USEtox® models [183], which simulate the release of chemicals from a source to the environment *via* mass flows from a succession of homogenous compartments. The use of different pollution indices, each assessing different sets of criteria, requires careful interpretation of the information. For example, the mass concentration of an element may be higher, but in order to access the potential risk, the bioavailability of the metals should also be taken into account.

Over the past few years, there has been growing acknowledgment of the need to include bioavailability in risk assessment frameworks, as protecting an organism from a toxic chemical means that the bioavailability of

Table 9: Calculations of individual pollution indices used for single assessment of soil pollution containing particular metals.

Pollution Index	Formula	Parameters	Pollution status
Contamination Factor <i>C_f</i>	$C_f = \frac{c_i}{c_n}$	c_i : the level of metal i c_n : the pre-industrial reference level of the pollutant	$C_f^i < 1$, low contamination factor $1 \le C_f^i < 3$, moderate contamination factor $3 \le C_f^i < 6$, considerable contamination factor
Ecological Risk Factor E _r	$E_r = T_r \cdot C_f$	T_r : toxic response factor for a given substance C_f : contamination factor	$C_f^i > 6$, very high contamination factor $E_r^i < 40$, low potential ecological risk $40 \le E_r^i < 80$, moderate potential ecological risk $80 \le E_r^i < 160$, considerable potential ecological risk $160 \le E_r^i < 320$, high potential ecological risk $E_r^i \ge 320$, very high potential ecological risk
Enrichment factor <i>EF</i>	$EF = \frac{c_s}{c_{rs}}$	c_s : the ratio of element i to immobile element in the environmental sample c_{rs} : the ratio of element i to immobile element in	EF < 2, depletion of mineral enrichment 2 $\leq EF < 5$, moderate enrichment 5 $\leq EF < 20$, significant enrichment
		the selected reference sample	$20 \le EF < 40$, very high enrichment $EF \ge 40$, extremely high enrichment
Geoaccumulation Index I_{geo}	$I_{geo} = \left[\frac{c_{s}}{1.5c_{ri}}\right]$	 c_i: level of metal i c_{ii}: geochemical background of metal i 1.5: constant, allowing for an analysis of the 	$I_{\rm geo} \leq 0$, Class 0: unpolluted $0 < I_{\rm geo} \leq 1$, Class 1: between unpolluted and moderately polluted
		variability of element <i>i</i> as a result of natural processes	$1 < I_{geo} \le 2$, Class 2: moderately polluted $2 < I_{geo} \le 3$, Class 3: between moderately polluted and strongly polluted $3 < I_{geo} \le 4$, Class 4: strongly polluted $4 < I_{geo} \le 5$, Class 5: between strongly polluted and extremely polluted

the chemical for that organism should be known. In this research, it was observed that, of the extensive body of published literature on e-waste's impact on the health and the environment, relatively few publications measured the bioavailability and/or bioaccessibility of the pollutants (~1%). A comprehensive approach taking bioavailability and bioaccessibility of an e-waste pollutant into consideration is needed to help improve the evaluation and to understand its impact on health and the environment.

7 The role of chemistry in tackling the e-waste challenge

The e-waste issue is multi-faceted; in order to tackle this grand challenge successfully, a multidisciplinary approach and a shift in paradigm involving multiple stakeholders is needed. A white paper published by the American Chemical Society (ACS) examined the green chemistry developments in industrial applications and environmental impact reduction across a number of manufacturing and industry sectors [194]. It highlighted how chemistry could underpin a number of potential solutions, from the development of more sustainable and 'greener' raw materials (e. g., organic electronics) to the use of novel treatment processes to reduce harmful chemicals and/or recover valuable resources.

Prioritising potentially problematic chemicals substance in EEE manufacturing can be an effective strategy to facilitate the development and use of safer materials in the industry. An example of industry

Table 10: Calculations of complex pollution indices for more comprehensive evaluation of metal contamination in soil.

Pollution Index	Formula	Parameters	Pollution status		
Average Single Pollution Index Playg	$PI_{\text{avg}} = \frac{1}{n} \sum_{i=1}^{n} PI(i)$	n : number of studied metalsPI: calculated values for the SinglePollution Index	Pl _{avg} > 1, low soil quality and high contamination		
Pollution Load Index PLI	$PLI = \sqrt[n]{PI_1 \cdot PI_2 \cdot PI_3 \cdot PI_n}$	n: number of analysed metalsPI: calculated values for the SinglePollution Index	 PLI < 1, no pollution PLI = 1, baseline levels of pollution PLI > 1, deterioration of soil quality 		
Degree of Contamination C_{deg}	$C_{deg} = \sum_{i=1}^n C_{f}(i)$	C _f : Contamination factor (see Table 9)	$C_{\rm deg}$ < 8, low degree of contamination		
		n: number of analysed metals	$8 < C_{\rm deg} < 16$, moderate degree of contamination $16 < C_{\rm deg} < 32$, considerable degree of contamination $C_{\rm deg} > 32$, very high degree of		
	$(\frac{1}{2} \sum_{i=1}^{n} PI(i))^2 \perp PI^2$		contamination		
Newerow Pollution In- dex <i>PI</i> _{Newerow}	$PI_{\text{Newerow}} = \sqrt{\frac{(\frac{1}{n}\sum\limits_{i=1}^{n}PI(i))^{2} + PI_{\text{max}}^{2}}{n}}$	<i>PI</i> : calculated Single Pollution Index of metal <i>i</i>	PI _{Newerow} ≤ 0.7, clean		
		PI _{max} : maximum value for the Single Pollution Index of all metals n: number of metals	$0.7 \le PI_{Newerow} \le 1$, warning limit $1 \le PI_{Newerow} \le 2$, slight pollution $2 \le PI_{Newerow} \le 3$, moderate pollution		
Potential Ecological Risk Index RI	$RI = \sum_{i=1}^{n} E_{\mathrm{r}}(i)$	E_r : single index of Ecological Risk Factor (see Table 9)	PI _{Newerow} > 3, heavy pollution RI < 90, low potential ecological risk 90 < RI < 180, moderate potential ecological risk		
		n: number of metals	180 < RI < 360, strong potential ecological risk 360 < RI < 720, very strong potential ecological risk RI ≥ 720, highly-strong potential ecological risk		

initiative and good practice can be found in a strategy document published in 2018 on 'A Protocol for Prioritizing Chemicals of Concern in the Electronic Industry' by Apple Inc. [195]. The document presented the design and application of a protocol to systematically evaluate chemicals of interest to make products and materials safer for workers, customers, recyclers, and the environment.

On the other end of the spectrum, there is a need to support knowledge transfer to developing countries; they are often the most affected by health and environmental issues related to e-waste. In addition to capability building for safer recycling and environmental clean-up, an efficient monitoring and screening of environmental pollutants will also be of benefit. This project presents a case study to examine the concept of the use of certain metals as tracers for the contamination of BFR or other hazardous e-waste compounds that may be beneficial in developing countries, where facilities for organic analysis may be less available.

Table 11: Examples of assessment tools and indices used to evaluate environmental and health impact associated with e-waste recycling.

Assessment Type	Matrix	Observations	References	
TCLP, USEtox	Mobile phones	Contained excessive Pb content. Copper posed the most significant ecotoxicity risk, and Cr showed the most significant risk for both cancerous and non-cancerous diseases.	[184]	
USEtox	Discard mobile phones	Ashes contained dioxins from incinerated batteries that produced the largest ecotoxicological impact (1.07×10^{-4} to 3.64×10^{-4} PAF m3 kg ⁻¹).	[185]	
TCLP, WET, TTLC, USE-tox	WPCB	Pb poses the most significant risk for cancers; Zn for non-cancer diseases; Cu had the largest potential impact on ecosystem quality. Acenaphthylene had the largest risk for cancers; naphthalene for non-cancer diseases; pyrene has the highest potential for ecotoxicological impacts.	[186]	
TCLP	13 different types of electronic devices	Very device type leached contained above 5 mg L ⁻¹ Pb.	[187]	
TCLP, LCIA	Rechargeable Li-ion and Li-polymer batteries	The environmental impact associated with resource depletion, human toxicity is mainly associated with Co, Cu, Ni, Ta, and Ag.	[188]	
TCLP, EP, D-3987 and SPLP	WPCB	The most labile to least labile metal using acid digestion, from WPCBs was: Pb > Cu > Zn > Al > Ni > Cd > Se > As > Ba.	[189]	
Igeo, PI, EF, RI and HQ	Soil in the farmland e- waste recycling region in China	Cd, Cu, and Hg in soils were significantly enriched in the whole region.	[190]	
I _{geo} , PI, PI _{Newerow} , HQ	Soil in the biggest e-waste recycling park in northern China	Cd, Co, Cu, Sb, and Zn are significantly enriched but there is no health risk.	[89]	
PI, PI _{Newerow} , RI	Soil in paddy field near a e-waste dismantling area in China	The potential hazardous metals (Cd, Cu, Ni, Pb, and Zn) were enriched in paddy soil.	[163]	
RI, EFs and PI _{Newerow}	Soil in e-waste recycling area in Guiyu, China	RI exceed 300. Hg and Cd are the main contributors to the potential ecological risk.	[191]	
Chinese Hamster Overy cell line, earthworm mortality assay	Soil samples in e-waste recycling site, China	The ecology risk assessment showed that both PCBs and metal residue pose high risk to the ecosystem.	[192]	
PMF, TEQ	Soil in e-waste recycling site, India	The dominance of PCDF congeners and maximum toxicity equivalents (TEQ) for both PCDDs (17 pg g ⁻¹ TEQ) and PCDFs (82 pg g ⁻¹ TEQ) at Mandoli in India has been related to intensive precious metal recovery process using acid bath.	[126]	
RI	Soil in electronic recycling site in Nigeria	Cu contributes the most to the potential ecological risk and Cd gave rise to the greatest concern due to its high toxic-response factor within the study site.	[93]	
C _f and PLI	Soil, floor and roadside dusts from e-waste recy- cling sites in Nigeria	Soil as the most polluted, followed by floor dust, then roadside dust.	[98]	
$C_{\rm f}$ and $C_{ m deg}$	Soil from Agbogbloshie e- waste, Ghana	Pb > Cd > Hg > Cu > Zn > Cr > Co > Ba > Ni contributed significantly to the overall $C_{\rm deg}$.	[193]	

ADD: Average Daily Dose; D3987: American Society for Testing and Materials (ASTM), Method D-3987; C_{deg} : degree of contamination; Cf: contamination factor; EDI: Estimated Daily Intake; EP: Extraction Procedure test; HQ: Hazard Quotient; LCIA: Lifecycle impact assessment; MOE: Margin of Exposure; PAF: Potentially Affected Fraction; PI: Pollution Index; PLI: Pollution Load Index; PMF: Positive Matrix Factorisation model; RD: Reference dose absorbed both oral and dermal; RI: Potential Ecological Risk Index; SPLP: Synthetic Precipitation Leaching Procedure; TCLP: Toxicity Characteristic Leaching Procedure; TEQ: Toxicity Equivalents; TTLC: Total Threshold Limit Concentration; WET: Waste Extraction Test.

8 Case study: can metals be used as tracers for organic contaminants in potentially e-waste-polluted environmental media?

The scientific literature reports on the contamination of the ambient environment of e-waste dismantling and recycling facilities (section 4). Typical compounds emitted during e-waste recycling-related activities are toxic BFR (e. g., PBDEs) and metals (including toxic metals, such as cadmium or lead). PBDEs and metals can be detected, e. g., in the dust emitted from e-waste facilities and in soil near such sites.

E-waste recycling facilities are often operated in less developed countries, where the capabilities for environmental monitoring are limited. Environmental monitoring in order to protect the health of people living proximal to such sites is often not implemented.

Since organic (trace) analysis is expensive and sophisticated analytical equipment may not be commonly available in smaller laboratories, the use of tracers for e-waste contaminations as a screening tool would be beneficial. Here it is evaluated if one or several metal(s) could serve as tracer(s) for organic contaminants of ewaste. Analysis of most of the relevant metals is cheap and relatively easy to perform. At the least, a preselection of samples may be possible by this means, so that only a few suspicious samples (high content of tracer(s) indicating possible e-waste impact and presence of e-waste-related pollutants) have to be analysed for organic pollutants to assess the potential risk.

For the evaluation several questions are considered and discussed.

8.1 What typical contaminants are found in e-waste? Are there correlations between levels of organic compounds and certain metals in e-waste fractions?

E-waste fractions contain metals, such as cadmium or copper from wires, solders, batteries, or housings. In plastic parts or printed circuit board, organic compounds like flame retardants, including PBDEs or TBBP-A, are also applied. Both metals and organic FR are potentially emitted during treatment and recycling activities. However, due to the multitude of possible e-waste compositions (and the changes over time due to, e. g., product innovations and the banning of hazardous additives), it does not seem possible to specify certain compositions or fixed relations between compound levels (e. g., between metals and BFR).

8.2 Which contaminants were detected in environmental media (e.g., soil) in the vicinity of e-waste treatment and recycling facilities?

The scientific literature was searched for publications where both organic contaminants and metals were analysed in environmental samples taken in the vicinity of e-waste treatment and recycling facilities. Table 12 summarizes relevant studies and lists the organic compounds and metals investigated in soils in the retrieved reports.

8.3 Is there a co-occurrence of organic compounds and certain metals in environmental media near e-waste facilities and are there any correlations between levels of both groups of contaminants?

As expected, a general correlation between levels of PBDEs (or PCBs) and metals in soils from e-waste recycling sites could not be found in the evaluated data set. Probably, e-waste treatment methods and e-waste

Table 12: Investigations in which both, organic contaminants and metals in soils were analysed.

Metals/elements	PBDEs	ТВВРА	DRC	PAH	PCBs	References
Cu, Pb, Co, Zn, Br			✓		✓	Fujimori <i>et al</i> . [128]
Ag, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Zn	✓				✓	Li <i>et al</i> . [196]
Cd, Cu, Hg, Zn, Pb, Ni, Cr, As, Co, V	✓				✓	Liu <i>et al</i> . [145]§
Cd, Cu, Cr, Pb, Zn	✓			✓	✓	Lopez <i>et al</i> . [146]
Cu, Cr, Cd, Pb, Zn, Hg, As				✓	✓	Tang et al. [197]
Cu, Zn, Pb, Cd, Ni, Hg, As	✓	✓				Wang et al. [146]
Cd, Cr, Cu, Ni, Pb, Zn, Mn, As	✓		✓	✓	✓	Wong et al. [104]
aPb, Cd, Cr, Zn, As, Hg, Cu					✓	Zhang et al. [192]

DRC: dioxin-related compounds; PAH: polycyclic aromatic hydrocarbons; PCBs: polychlorinated biphenyls; § also other metals measured.

compositions are too variable to generalize. The database was not sufficient for a meta-analysis of data from all studies.

However, in some studies, correlations were already reported. Examples:

- Liu et al. investigated surface soil samples collected from e-waste recycling workshops (dismantling, e. g., by open burning). Significant correlations between copper (strong correlation), cadmium, zinc, lead, and PCBs or PBDEs (for most congeners p < 0.01) were detected [145].
- Tang et al. investigated soils influenced by different e-waste recycling plants (incl. large-scale recycling plants and household workshops) in China. A correlation between PCBs and Hg (p < 0.01) could be identified [197].
- Wang et al. investigated the relationships between total mass fractions of metals and BFRs in environmental samples (soils, plants, and sediments) influenced by illegal e-waste dismantling workshops in China. Strong positive correlations between metals (e.g., copper, lead, zinc, nickel, and cadmium) and TBBP-A and PBDEs were found in sediment and plant samples [147].
- Xu et al. found strong correlations between PBDEs mass fractions and lead and antimony in dust sampled at family-run e-waste recycling workshops [198].

8.4 Is there evidence from the gathered literature that metals can be used as tracers for other e-waste contaminants?

Literature data support the assumption that metals are found at higher levels than PBDEs in soil at e-waste sites (Table 13). Metals in such soils are mostly reported as mg kg⁻¹ dry mass, while PBDEs usually are reported as µg kg⁻¹ dry mass.

From this evaluation, the metals copper, zinc, and lead seem most appropriate as tracers for PBDEs and other organic e-waste-related pollutants. The following criteria for suspecting an organic e-waste burden in soils (e. g., PBDE) is suggested:

- Samples taken at a site near an e-waste facility;
- Soil dry mass fractions of (at least two) metals are higher than: 100 mg kg⁻¹ copper, 100 mg kg⁻¹ zinc, $100 \text{ mg kg}^{-1} \text{ lead.}$

If these criteria are applied to the sites investigated in the studies shown in Table 12, most of the covered sites would be characterized correctly as potential e-waste sites, since all three tracer metals were above 100 mg kg⁻¹ dry mass (sites where both metals and PBDE were reported). At the other four sites, at least two metals were above 100 mg kg⁻¹ dry mass.

Metal Soil mass fraction range of metal Ratio of metal mass fractions in contaminated/ Ratio of mass fractions: [mg kg⁻¹ dry mass] uncontaminated soil metal/sum PBDE Cu 16-1300 149-2159 2.3 - 5528-1300 Zn 140-1717 1.6 - 14Pb 106-3254 1.3 - 25100-950 Cd0.69 - 11.41.7-70 0.4 - 6.2

Table 13: Data for soils from seven e-waste facility sites (dismantling workshops, open burning sites (sources: [145-147]).

8.5 Are the levels of potential tracer metals high enough for easy detection with standard extraction/digestion and analytical approaches?

Metal mass fractions (colloquially concentrations) in e-waste-polluted soils were mostly in the mg kg⁻¹ range and thus seem sufficiently high to be quantified by routine instrumental analysis (e. g., AAS or ICP-OES after digestion with acids). Digestions of soils in e-waste related studies are typically performed with mixtures of nitric acid and perchloric acid in pressurized microwave heating systems.

For sampling, it should be considered that the pollutants are probably not homogenously distributed in the soil. Taking and mixing several representative subsamples from different positions at the site, as well as sampling from different soil depths may be appropriate.

All samples should be analysed in comparison to appropriate reference samples from non-polluted sites of the same region. Appropriate quality assurance measures should be implemented (test of positive and negative controls, sufficiently low limit of quantification).

9 Conclusions

Rapid advancements in consumer technology are leading to a continual increase in a challenging, heterogenic, and chemically complex e-waste stream that is difficult to manage. East Asia and West Africa are key destinations for ewaste globally and the informal recycling of e-waste provides significant income-generating activities in these countries. Our societies' current depletion of critical elements in the Periodic Table for use in high tech EEE is unsustainable, which is inadvertently driving backyard, uncontrolled recycling. To recover the valuable resources, ewaste is often dismantled manually, acid stripped, and burnt in an open fire. Metal(loid)s, POPs, and BFRs are frequently detected in many environmental compartments associated with e-waste recycling sites and surrounding areas. Moreover, as new alternative flame retardant compounds replace the banned substances, NBFRs have emerged as contaminants in environmental samples. In general, pollutant levels increase with the following order: control sites < repair sites < dismantling sites < burning sites. Currently, multiple pollution indices or risk models are used to evaluate the ecological impact of e-waste, making comparison of different studies challenging. Nevertheless, it is evident that pollutants related to e-wastes recycling are having an impact in multiple trophic levels (from microbial communities to migratory and resident bird populations and even humans). Future studies should take the bioavailability and bioaccessibility of e-waste pollutants, e. g., in water, soil, or dust, into consideration. Currently, these aspects seem not sufficiently considered in e-waste site risk assessments.

It is noteworthy that countries such as China have introduced policies and legislation to regulate informal e-waste recycling, but many of the POPs (e. g., PCBs and the PBDEs) remain for long periods in the environment and the food chain. To tackle the e-waste challenge, multiple strategies are needed, bringing together environmental, economic, and societal stakeholders (Fig. 5). These measures include: increase investment in the environment remediation of contaminated sites; improve monitoring, evaluation, and reporting of e-waste; develop better technologies for resource recovery and greener and sustainable manufacturing practices; offer incentives to valorise e-waste and promote responsible circular economy; encourage users to 'reduce, reuse and recycle' e-waste and increase education and awareness programmes. One strategy can involve building

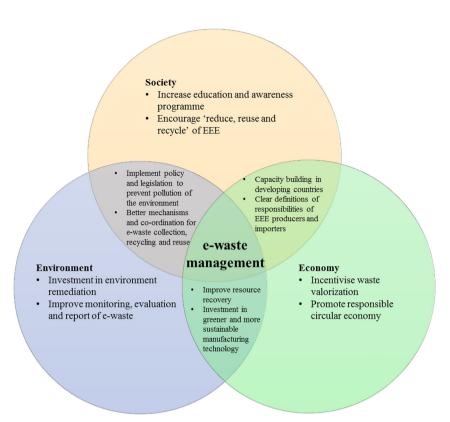


Fig. 5: Integrated strategies to manage e-waste.

the whole life cost into the original product by applying an appropriate tax, such that its proceeds are directed towards recycling operations. In addition, stronger governance is required to implement policies to prevent pollution of the environment, co-ordinate better e-waste collection, recycling, and reuse; to provide clearer definitions of the responsibility of producers of EEE and its importers; and to promote capacity building in developing countries to safeguard e-waste workers and the environment.

10 Membership of the sponsoring body

Membership of the IUPAC Chemistry and the Environment Division Committee for the 2020 was as follows:

President: Hemda Garelick (UK); Past President: Rai Kookana (Australia); Vice President: Roberto Terzano (Italy); Secretary: Annemieke Farenhorst (Canada); Titular Members: Doo Soo Chung (South Korea), Petr S. Fedotov (Russia), Bradley Miller (USA), Diane Purchase (UK), Fani L. Sakellariadou (Greece), Weiguo Song (China); Associate Members: Nadia Kandile (Egypt), Yong-Chien Ling (Taiwan), Irina Perminova (Russia), Bipul Behari Saha (India), John B. Unsworth (UK), Baoshan Xing (USA); National Representatives: Vladimir Beškoski (Serbia); Cristina Delerue-Matos (Portugal); Michal Galamboš (Slovakia), Joon Ching Juan (Malaysia), Bulent Mertoglu (Turkey), Oluseun Elizabeth Popoola (Nigeria), Yehuda Shevah (Israel), Tiina Sikanen (Findland), Monthip Sriratana (Thailand); Emeritus member: Laura L. McConnell (USA)

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List of acronyms

ABS arylonitrile-butadiene-styrene BAN **Basel Action Network**

BB209 decabromobiphenyl; systematic name: 1,2,3,4,5-pentabromo-6-(2,3,4,5,6-pentabromophenyl)benzene)

RFR Brominated flame retardant

BTBPE 1,2-bis(2,4,6-tribromophenoxy)ethane; systematic name: 1,3,5-tribromo-2-[2-(2,4,6-tribromophenoxy)ethoxy]

henzene

DBDPE 1,2-bis(perbromophenyl)ethane; systematic name: 1,2,3,4,5-pentabromo-6-[2-(2,3,4,5,6-pentabromophenyl)ethyl]

benzene)

Dechlorane Plus; systematic name: 1,6,7,8,9,14,15,16,17,17,18,18-dodecachloropentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}] DΡ

octadeca-7.15-diene

e-waste Electrical and electronic waste EEE Electrical and electronic equipment

FF **Enrichment factor** FR Flame retardant

HBB hexabromobenzene; systematic name: 1,2,3,4,5,6-hexabromobenzene

HBCDDs hexabromocyclododecanes HFR Halogenated flame retardant HIPS High-impact polystyrene Geoaccumulation index I_{geo}

NBFR Novel brominated flame retardant

PA polyamide; systematic name: 6-amino-N-[6-oxo-6-(6-oxohexylamino)hexyl]hexanamide

PAHs polycyclic aromatic hydrocarbons PBB polybrominated biphenyls **PBDEs** polybrominated diphenyl ethers

PC polycarbonate; systematic name: carbonic acid;4-[2-(4-hydroxyphenyl)propan-2-yl]phenol

PCBs polychlorinated biphenyls

PCDD/Fs polychlorinated dibenzo[1,4]dioxins and dibenzofurans

PFR Organophosphate flame retardant Newerow's Pollution Index **PI**_{Newerow} POP Persistent organic pollutant

PP polypropylene; systematic name: 12-[(25,3R)-3-octyloxiran-2-yl]dodecanoic acid

PPO poly(1,4-phenylene oxide)

polystyrene PS

PU polyurethane; systematic name: 1-ehylurea PVC polyvinyl chloride; systematic name: chloroethene

REEs Rare Earth Elements

RI Potential Ecological Risk Index

RSR Relative Supply risk SAN styrene-acrylonitrile

TBB 2-ethylhexyl 2,3,4,5-tetrabromobenzoate; systematic name: 2 ethylhexyl 2,3,4,5-tetrabromobenzoate

TBP 2,4,6-tribromophenol

TBPH bis(2-ethyhexyl) tetrabromophthalate; systematic name: bis(2-ethylhexyl) 3,4,5,6-tetrabromobenzene-1,2-

dicarboxylate

TCP tri-p-cresyl phosphate; systematic name: tris(4-methylphenyl) phosphate **TCEP** tris(2-chloroethyl) phosphate; systematic name: tris(2-chloroethyl) phosphate

TCPP tris(1-chloropropan-2-yl) phosphate; systematic name: tris(1-chloropropan-2-yl) phosphate

TBBP-A tetrabromobisphenol-A; systematic name: 2,6-dibromo-4-[2-(3,5-dibromo-4-hydroxyphenyl)propan-2-yl]phenol

TEQ Toxic Equivalent

triphenyl phosphate; systematic name: triphenyl phosphate TPP

UEEE Used electrical and electronic equipment UNEP United Nation Environmental Programme

WPCB Waste printed circuit board

WEEE Waste electrical and electronic equipment

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