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Application of tiered human health and environmental risk assessment to develop safe and sustainable by design perovskite-based devices

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ABSTRACT

Metal halide perovskite materials have gained significant attention in recent years due to their potential energy and lighting applications. They are potentially vital materials for the current energy transition which aims to minimize the dependence on fossil fuels and limited land resources by the increased use of cost-effective and efficient renewable energy sources. The European Green Deal policy, which sets out its ambitions in the Chemicals Strategy for Sustainability, can help its transition to a Safe and Sustainable by Design (SSbD) development. In this context, we applied the SSbD approach to selected perovskite-based devices which are still in their development state, by assessing potential human health and environmental risks along their life cycle. We applied the SSbD approach in a tiered manner so that it aligns with successive Technology Readiness Levels (TRL) to help the innovators ensuring safety and sustainability aspects throughout the various stages of their product development. Thus, the SSbD assessment began right from the start of the development (TRL 1–2), when there can be (huge) gaps and uncertainty in the product knowledge, up to the later stages of higher TRL when the product knowledge is more abundant and certain. In our assessment, we mainly focused on the human health risk of the perovskite-based devices and considered the implications of environmental emissions of hazardous substances on the human health. We further bring attention to the alternatives which could help mitigate concerns over their safety and sustainability for a responsible technology development and deployment. Results of this study are important to understand the detailed sustainability assessment in which we look at multiple sustainability aspects and its potential future impacts due to technology scale-up in the future.

Abbreviations

Characterization Factor	CF	Occupational Exposure Limit	OEL
Disability-Adjusted Life Years	DALY	Organic Light Emitting Diodes	OLED
Effect Factors	EF	Organic Photovoltaics	OPV
End of Life	EoL	Perovskite-based devices	PbD
Environmental Release Category	ERC	Perovskite-based light emitting diodes	PeLED
European Commission	EC	Perovskite-based photovoltaics	PePV
European Union System for the Evaluation of Substances	EUSES	Perovskite-based wearables	PeW
Fate Factors	FF	Photovoltaics	PV
Hotspot Scan	HSS	Polyethylene terephthalate	PET
Human Exposure Factors	XF	Registration, Evaluation, Authorisation and Restriction of Chemicals	REACH
Human Health Risk Assessment	HHRA	Safe and Sustainable by design	SSbD
Impact Score	IS	specific Environmental Release Categories	spERC
Intake Fraction	iF	Technology Readiness Level	TRL
Life Cycle Assessment	LCA	Waste Water	WW
Life Cycle Stage	LCS		

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1. Introduction

Perovskites are an emerging technology for organic and large area electronics-based devices that have the potential to revolutionize the photovoltaic and lighting sectors. They are a class of low-cost but high-quality materials which can exhibit performances similar to "conventional" semiconductors (e.g. silicon, III-V materials). Consequently, market launch of efficient perovskite-based flexible and lightweight electronic devices is foreseen in a near future (e.g. <5 years). The EU H2020-funded PeroCUBE project (https://perocube.eu/) aims to facilitate the emerging perovskites technology advancement and commercialization towards real-life photovoltaic and lighting applications. Nevertheless, recent research has shown that their poor operational stability, module scalability, and material toxicity pose major concerns for their practical commercialization and widespread application (Babayigit et al., 2016; Brunetti et al., 2016; Correa-Baena et al., 2017; Hailegnaw et al., 2015; Leijtens et al., 2015).

It is crucial to assess the safety and sustainability of perovskites in an early design phase to ensure their responsible development and deployment. One of the ideal ways to ensure this is through a Safe and Sustainable by design (SSbD) approach, i.e. a pre-market approach to chemicals and materials design that focuses on providing a function (or service), while avoiding volumes and chemical and material properties that may be harmful to human health or the environment, in particular groups of chemicals likely to be (eco)toxic, persistent, bio-accumulative or mobile (EC, 2020). Contrary to the past handful of investigative studies which followed a "fragmented" approach towards their safety and sustainability assessment (e.g. Hailegnaw et al., 2015; Horváth et al., 2021; Ju et al., 2018; Goetz et al., 2021; Mallick et al., 2023; Panthi et al., 2021; Su et al., 2020), or a quantitative approach (e.g. Goetz et al. 2021; Vidal et al., 2020), which is seldom employable at early innovation stages, SSbD approach offers a holistic and pre-emptive way to thoroughly evaluate these aspects right from the start, ensuring long-term viability of perovskite-based devices (PbD). Considering safety and sustainability in earlier development stage(s) or at low TRL(s) does not only ensure human health and environmental safety but also ensures a positive image of the developer (as a responsible organization), quality control and no loss in profits due to any resource-intensive product recall based on unforeseen environmental and/or human health problems in its supply chain.

In this paper, we quantify the human health and environmental risks posed by the perovskite-based energy harvesting and lighting devices along their life cycle. We follow a tiered approach in our assessment. Based on the findings, several issues are discussed in the paper which could impede the sustainable development of the PbD. Alternatives, based on the state-of-the-art of these devices, are suggested to help overcome such impediments. In our assessment, sustainability aspects (e.g. environmental risks) are considered only when they become relevant for or have implications on human health risk assessment (HHRA) (e.g. exposure of human population to perovskite material through contaminated tap water). An extensive sustainability assessment through a complete life cycle assessment will be published separately. This will also include the quantitative impact evaluation of the PbD supply chain during stages like raw material procurement, storage, distribution etc.

2. Material and methods

In this section, information is provided on the investigated PbD, their life cycle stages (LCS) and the implemented SSbD approach.

2.1. Perovskite-based devices

In our analysis the following three devices are considered:

Perovskite-based photovoltaics (PePV): PePV are a type of solar cell or a photovoltaic device that uses organo-metallic perovskite as the active material to produce electricity from sunlight through the photovoltaic effect for power applications. The assessed perovskites are lead halide compounds.

Perovskite-based light emitting diodes (PeLED): PeLED utilize lead halide perovskite for electroluminescence in the red, green and blue regions of the visible light range with potentially high-colour purity and low-cost light emission. They have a tuneable optical bandgap in the visible to infrared regions and, thus, useful in a range of optoelectronics applications, e.g. TV screens.

Perovskite-based wearables (PeW): PeW mainly serve as demonstrator for the perovskite-based technology application and the devices using it in different forms, e.g. watch, bracelet. It is generally produced using an in-mould integration technology where a flexible foil containing the light emitting PeLED areas, printed conductors and the solar energy harvesting PePV are integrated into one seamless part via an injection moulding process.

Our analysis spans over the entire life cycle of these devices (as illustrated in Fig. 1) including devices production, use and disposal. The following sections give detailed information of the different LCS of the PbD which has been collected over 3 years of devices development in the Perocube project.

2.1.1. Production phase

2.1.1.1. Precursor ink formulation. To produce any PbD, precursor ink is first formulated. For each device, Table 1 provides a list of compounds which were mixed in specific quantities (shown in parenthesis) to formulate 1 L of respective precursor inks. Since PeW is considered as an integrated PePV and PeLED system, the list of relevant compounds are the same as for PePV and PeLED combined.

As per the current sector-specific practice, 1–2 operators carry out the precursor ink formulation inside a laboratory within their breathing zone (i.e. distance head-product <1 m) but in the conformity of glove box which is situated in a typical 600 m^2 sized clean room. The operator (s) wears full face respirator masks and no one else is present around him within a distance of 1 m during the entire duration of the task, i.e. no by-standers.

2.1.1.2. Device fabrication. During device fabrication, a thin layer of lead halide perovskite is synthesized from the precursor ink while printing it on a substrate (i.e. in-situ synthesis of perovskite crystalline thin films), on substrates of flexible PET (by means of roll to roll deposition) or rigid glass (by means of sheet to sheet deposition). In general, the bulk density of the printed perovskite crystalline film is around 4.03 g/cm^3 for PePV. With a 500 nm-thickness, the perovskite crystalline film surface density is equal to 2.015 g/m^2. Since the molar content of lead metal represents 32.83% of the total molecular weight of the film, its surface density is equal to 0.67 g/m^2 in the film. For PeLED, the average film thickness is equal to 40 nm approx. which corresponds to a perovskite film with surface density of lead metal equal to 0.17 g/m^2. These estimations are also valid for PeW. In the typical sector-specific practice, the printing task is generally carried out in a 109 m^3 volume room equipped with local exhaust ventilation. Once the printing is over, the left over residual solvents are generally blow dried inside a ventilated oven and the generated vapours are entrapped inside an activated carbon filter which is disposed of by a special recycling company.

It should be noted that we exclude the materials from our assessment which are generally used for technology demonstration or application purposes (e.g. substrate, aluminium for PePV mounting, parts of the watch/bracelet for PeW).

2.1.2. Use phase

The lifetime or usage of PePV is mainly affected by its hygroscopicity and ion migration (Meng et al., 2018). The moisture absorption and consequent lead leaching during the PbD use, is related to

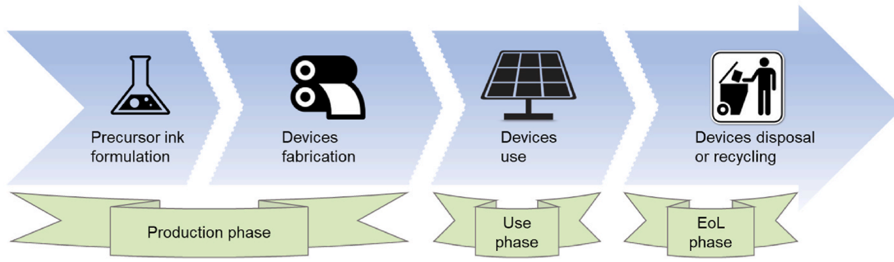

Fig. 1. Life cycle stages of a perovskite-based device.

Table 1
List of the compounds used for the respective precursor inks formulation for PePV (structure: $Cs_{0.17}FA_{0.83}Pb(I_{0.77}Br_{0.23})_3$), green PeLED (structure: $(BABr)_{0.5}(CsPbBr_3)_{0.5}$), blue PeLED (structure: $(BEACl)_{0.8}$ $CsPbBr_3$) and red PeLED (structure: $CsPbI_2Br$).

PePV	PeLED		
	Green	Blue	Red
Dimethylformamide (DMF) (755.2 g)	Dimethyl Sulfoxide (DMSO) (1100 g)	Dimethyl Sulfoxide (DMSO) (1100 g)	Dimethylformamide (DMF) (944 g)
Dimethyl Sulfoxide (DMSO) (220 g)	N-Butylammonium bromide (n-BABr) (22.47)	3-Butenylamine hydrochloride (BEACl) (16.66 g)	Formamidinium iodide (FAI) (51.6 g)
1,3-Di-tert-butylimidazolium tetrafluoroborate, 97% (Di-tBIM) (0.67 g)	18-crown-6 (4 g)	18-crown-6 (4 g)	2,2′-(Ethylenedioxy)bis (ethylamine) (EDEA) (6.6 g)
Formamidinium iodide (FAI) (206.97 g)	Lead bromide ($PbBr_2$) (52.7 g)	Lead bromide ($PbBr_2$) (60.6 g)	Lead iodide (PbI_2) (69.2 g)
Methylammonium chloride (MACl) (6.74 g)	Cesium bromide (CsBr) (30.72 g)	Cesium bromide (CsBr) (35.19 g)	Cesium bromide (CsBr) (63.6 g)
Lead iodide (PbI_2) (437.8 g)			
Lead bromide ($PbBr_2$) (183.6 g)			
Cesium iodide (CsI) (63.1 g)			

environmental factors (e.g. rain, water acidity) and the condition of the perovskite encapsulation within the device which can break due to mechanical damage, such as being hit by hailstones, and lead to material run-off (Meng et al., 2018; Panthi et al., 2021). The perovskite physical encapsulation, e.g. by using titania, alumina or PET, is generally done to protect them from any moisture absorption or water contact and avoid perovskite degradation. However, preliminary studies show that while the encapsulation results in lower leaching concentrations of the crystal components compared with non-encapsulated crystals, it does not fully prevent leaching, especially under weak acidic conditions in real life (Panthi et al., 2021). Upon run-off, the perovskite crystals start degrading and decomposing into lead halide which is a solid water insoluble compound and is known for its bio-persistence and acute toxicity to the humans and environment Ligthart (2006); Panthi et al., 2021; Su et al., 2020; Wu et al., 2020; Hailegnaw et al., 2015 observed that almost all of the entire lead content in the PePV perovskite crystals can get released (60–93%) when the perovskite film is exposed to simulated rain water with pH 4–6. With an encapsulation layer present, the losses of the perovskite crystals is lesser and can be approximated to be 5% in real life conditions. It is thus critical to consider the leaching scenario as one of the potential release mechanisms of perovskite crystals and the lead components in the environment during the use phase of PePV. To accommodate this, we consider four potential scenarios:

Scenario 1: Encapsulation layer remains completely intact and there is no leaching from the device; 100% of perovskite crystals reach the End-of-Life (EoL) phase.

Scenario 2: Slight wear of the encapsulation layer and 5% of the substances from the perovskite crystals in PePV leach to the ground water and soil; 95% of perovskite crystals reach the EoL.

Scenario 3: Significant wear of the encapsulation layer and 50% of the substances from the perovskite crystals in PePV leach to the ground water and soil; 50% of perovskite crystals reach the EoL.

Scenario 4: Complete breach of the encapsulation layer, and all substances from the perovskite crystals in PePV leach to the ground water and soil; no perovskite crystals reach the EoL.

For the current assessment, we assume that the PeLED and PeW are used indoors or under moderate environmental conditions, that will not lead to any mechanical damages to the encapsulation and thus no leaching during their use. Any accidental breakage of these devices during their use is beyond the scope of our study because we focus on the regular potential exposure scenarios.

2.1.3. *End of life phase*

Three different EoL routes are considered in the current assessment of the PbD: landfilling, incineration and recycling. For each route, different calculations have been carried out in accordance with the four scenarios described in the section 2.1.2.

2.2. *Safe and sustainable by design approach*

A tiered approach was used to implement the SSbD strategy in the development of the PbD (Fig. 2). Since the devices were still in their early development phase, it was critical that our assessment approach was able to cope with big gaps in data and knowledge in the beginning of the innovation value chain. With time progression and at higher tier levels, more data on their safety and sustainability could be collected to fill in the knowledge gaps and reduce uncertainty. Therefore, our analysis started with a qualitative tier 1 assessment when the TRL is low and the PbD development value is restricted to basic technology research. Limited information is needed but the outcome has a higher uncertainty. When the TRL increases and the PbD development value moves towards its successful demonstration, we move to a more quantitative assessment (i.e. relatively more data and information needs but lower output uncertainty). This gradual qualitative-quantitative switch in our approach allows flexibility in SSbD application within the technology value chain. The assessed safety, functionality, and sustainability aspects are in alignment with the step-wise approach of the SSbD framework of the European Commission (EC) Joint Research Centre (Caldeira et al., 2022). It allows to start evaluating the hazard assessment, human health and safety aspects, environmental and economic sustainability right from the early stages of the innovation value chain across all possible LCS of these devices, although not in the same

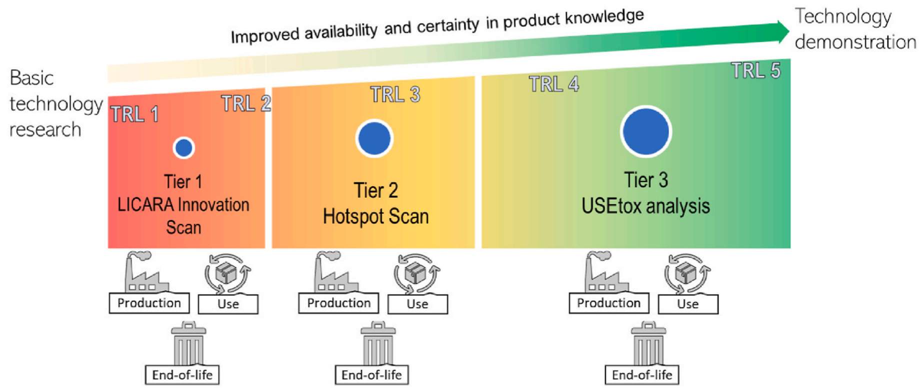

Fig. 2. SSbD implementation through tiered approach.

hierarchical order as considered in the EC's SSbD framework (*Note*: Environmental and socio-economic sustainability are to be executed only after the fulfilment of the chemical safety in the EC's SSbD). In the following sections, details are provided on the respective assessments done at different tier levels.

2.2.1. Tier 1

Tier 1 represents a qualitative assessment which is essentially a quick scan of risks and benefits of PbD and an early identification of relevant 'red flags' (related to the potential risks). For this purpose, we developed and used the online LICARA Innovation Scan (https://diamonds.tno.nl/projects/licara). It is broader in its scope than its predecessor, LICARA nanoSCAN (van Harmelen et al., 2016) which is limited to only nanomaterials or nano-enabled products. The new LICARA Innovation Scan guided the decision-making process about PbD at tier 1 by:

- scanning both the benefits and risks over a device's life cycle in comparison to a conventional product or technology with a similar functionality;
- estimating its economic, environmental and social benefits;
- identifying the specific risks for consumers, workers, the public and the environment;
- identifying knowledge uncertainties and gaps.

Each of the PbD were individually scanned for their risks and benefits. In each scan, the PbD was compared with its conventional counterpart or benchmark. Most of the available knowledge at this tier level is on the conventional thin-film counterpart to these devices like flexible/rigid organic photovoltaics (OPV), amorphous silicon-based PV, organic light emitting diodes (OLED) etc. Therefore, the tool asks questions on the PbD which could be answered in a qualitative manner with responses like "better/worse", "equal", "don't know" etc. in comparison to its conventional counterpart. This implies that there is no need for detailed materials and technology expertise on the PbD to run the scans. The tool is designed in a modular way and delivers the final result on the basis of the principles of LCA, risk assessment and multi-criteria decision analysis.

2.2.2. Tier 2

The tier 1 qualitative assessment findings were further refined by a tier 2 assessment by identifying substance release hotspots in a quick manner. The online Hotspot Scan (HSS) tool (https://diamonds.tno.nl/hotspotscan) determines such hotspots (i.e. critical or risk prone stages) during the entire life cycle of the devices where high emissions of a substance (compounds, elements, chemical groups etc.) to air, water or soil can occur (Boukris et al., 2014). The HSS puts the use phase central in the life cycle, i.e. a reference amount for the substance of interest at the use phase is selected, and the mass of the substance flows before and after the use phase (i.e. production and EoL phases) are all defined relative to this reference value. We selected a reference value of 1000 kg of perovskite in PbD for our assessment (equal to threshold quantity for REACH registration and correspond to 5×10^5 m^2 of PePV). Nevertheless, one can easily deduce the environmental emissions in case of other reference values too (e.g. 1 g, 1 kg or 100 kg) by decreasing them in the same proportion as the decrease in reference value. The HSS was done for all those substances in the PbD life cycle which pose a high or unknown risk during any LCS of the devices. The use of the HSS leads to the identification of the hotspots in the LCS where significant (hazardous) release/emissions (corresponds to $m_{x,i}$ in equation (1)) can occur to the different environmental compartments. Recommendations for the early improvements in the product development are thus made to lower any negative impacts on human health and/or the environment.

Contrary to the LCA, which often requires collection of large data amount for each LCS, the online HSS tool requires qualitative to semi-quantitative information on substance and process properties which the tool automatically gathers from different sources in its database like European Union System for the Evaluation of Substances (EUSES) (EC, 2004), Environmental Release Categories (ERC) (ECHA, 2010), specific Environmental Release Categories (spERCs) (ECHA Use maps), integrated Risk Management Measure library (ECEL), PubChem, (PubChem), ECHA Substances of Concern In articles as such or in complex objects and Products database (SCIP,), ecoinvent tool (DOKA LCA tool,), OECD's emission scenarios (OECD, 2014) and other pertinent literature, for example, Adrian et al., 2020; Buchert et al., 2012; Doka 2013; Hailegnaw et al., 2015; Hauck et al., 2017; Ligthart (2006); Panthi et al., 2021; Rotter et al., 2016; Su et al., 2020. This makes it possible to use the HSS tool even during early to mid-stages of the product development.

2.2.3. Tier 3

Based on the identified release hotspots in tier 2, we quantitatively assessed human health impact based on the environmental distribution and fate of the different substance releases in the compartments of air, water and soil, the consequent human exposure through these environmental compartments and toxicity-related effects associated with the human exposure at each LCS. This was done using the USEtox v2.13 tool (https://usetox.org/). It calculates an Impact Score (*IS*) which is, in the context of human health risk assessment, a measure of human health impact of the emissions in life cycle inventories of different compounds and metals. The *IS* is calculated for the general population using a weighted summation of the releases of substances of a product system with help of characterization factors (equation (1)).

$$IS = \sum_{i}\sum_{x} CF_{x,i} \times m_{x,i} \tag{1}$$

In the present context, *IS* is the human health impact score (measured in terms of disability-adjusted life years, DALY); $CF_{x,i}$ is the human toxicity characterization factor of substance x emitted to compartment i (DALY/$kg_{emitted}$) and $m_{x,i}$ is the released mass of substance x to compartment i

($kg_{emitted}$, as estimated in the tier 2 assessment). DALY is the sum of the years of life lost due to premature mortality and the years lived with a disability due to the toxicity of the substance to which a person is exposed. One DALY represents the loss of the equivalent of one year of full health. Substances that have a potential to increase human disease have a human health characterization factor that is derived from the product of three matrices including fate factors (*FF*), human exposure factors (XF), and human toxicological effect factors (*EF*), as shown in equation (2).

$$CF = EF.XF.FF \quad (2)$$

Human intake fraction (*iF*) is the product of the *FF* and *XF*. It represents the fraction of the mass emitted into a specific compartment that is taken in by the human population (equation (3)).

$$iF = XF.FF \quad (3)$$

In our assessment, intake through inhalation and ingestion routes are considered in *iF* calculations. Dermal route remains excluded. *FF* links the quantity released into the environment to the chemical masses (or concentrations) in a given compartment. The data for substance-specific physico-chemical parameters to determine *XF* and *FF* (e.g. molar mass, vapor pressure, solubility, constant degradation rate, bioaccumulation factor; more details in Supplementary information) were gathered from the tool inbuilt Estimation Programs Interface (EPI) Suite database, as well as from the external sources (OECD QSAR toolbox, Safety data sheets, C&L Inventory database, REACH factsheets, ChemSpider database,) and other studies (EPA, 2011; Footprint, 2015; Leistra, 2011; Mallick et al., 2023; Peng et al., 2021; Rosenbaum et al., 2015; Sinkkonen and Paasivirta, 2000).

Effect factors matrix (*EF*) reflects the change in life time disease probability due to change in life time intake of a substance (cases/kg). USEtox can determine *EF* for 1569 substances based on their physico-chemical properties in its EPI suite database. However, there were several substances (relevant to PbD), for which there is no information available in the EPI suite database (details of these substances are provided in Supplementary information). For such substances, several sources, e.g. ECHA database, IRIS database, PubMed etc. were consulted. If there was no animal study on genotoxicity or carcinogenicity, a QSAR was performed to give an indication of genotoxicity or mutagenicity using four VEGA models: Antares, ISSCAN-CGX, CAESAR and ISS. More details on this part are provided in Supplementary Information. In the present assessment, we consider an aggregated *CF* which combines both carcinogenic and non-carcinogenic impacts for substance emissions to the following environmental compartments: industrial/occupational indoor air, outside air (including urban and continental air), water (including fresh and sea water) and soil (including natural and agricultural soil).

As mentioned earlier, *IS* is estimated on a population level. To account for the risk at an individual occupational level during the production and EoL of the PbD, we compared m_x of a substance (in the indoor industrial air compartment) with its regulatory established Occupational Exposure Limit (OEL), if any. To make comparison with OEL, m_x was first converted into exposure amounts by multiplying them with the *XF*, followed by conversion to mass-based concentrations (mass per unit volume) by dividing the exposure amounts (in mass) with the archetypical volume of industrial settings (=350 m^3) for manufacturing facilities in OECD countries (Rosenbaum et al., 2015). The calculations were done considering the presence of one worker during the activity and daily time at work to be equal to 8 h.

3. Results

3.1. Tier 1 assessment

From the analysis, we found that all assessed PbD have consistently low risk (≤0.33 out of 1) and moderate benefit scores (≥0.33 and ≤ 0.66 out of 1) compared to conventional reference devices. For instance, the qualitative benefit score for the PeLED (flexible or rigid) varied from 0.33 to 0.4 and qualitative risk score was equal to 0.25 when compared to OLED (Fig. 3 (a)). The highest score was observed for its economic benefits (=1) but it suffers from negative environmental benefits (=−0.33 to −0.13) (Fig. 3 (b)). Similarly, all risk types (Fig. 3 (c)) fall under low risk category (<0.33), except for the risk due to the environmental effects of potential emissions from the flexible PeLED in which medium risk is observed (i.e. >0.33).

These low risk and moderate benefit scores put the PbD in a transit 'Undecided' yellow coloured zone of LICARA Innovation Scan (as shown in Fig. 3 (a)) which signifies that these devices are promising developments and have the potential to be sustainable over their entire life cycle. The perovskite crystals in these devices primarily consist of abundant elements, e.g. carbon, hydrogen, nitrogen. This ensures a more sustainable supply chain compared to other materials that rely on scarce resources. Furthermore, perovskite crystals can be synthesized using low-cost and readily available precursors, making them an attractive option for large-scale production. Nevertheless, given the state of the production, they needed additional benefits or reduced risks at the time for them to lie in the LICARA Innovation Scan's green zone which signifies a clear 'go-ahead' with their further development in the innovation value chain.

The identified aspects which could be significant for the green zone transition of these devices are shown in Fig. 4. More control over the in-situ synthesis of perovskite crystals during the printing process was observed to be the most significant aspect of the devices development which had the highest impact on sustainable devices development. This need arose from the fact that the perovskite printing was a hard to control process due to which consistency and replicability of the final crystalline perovskite film in the device could not be guaranteed at the time. In addition, increasing the devices' use life time and efficiency were among other process quality and performance aspects which were observed to be significant in improving the devices' potential benefits. These findings were clearly communicated to the devices developing team so that they were aware of them at the early stage. Along with them, there were three potential environmental and human health risks (use of lead, hazardous solvents during production phase and potential emissions knowledge along the life cycle (particularly at EoL)) which were selected for their assessment at tier 2. It should be noted that the findings from Fig. 4 should not be considered in an absolute manner, i.e. one aspect is absolutely more significant than the other. Instead, it should be interpreted as the order of aspects' significance for the decision making at the initial stage of the devices development.

With the identification of these specific aspects related to the devices development, the use of LICARA Innovation Scan tool, thus, proved to be a useful mean to derive the tier-1 risk-benefit analysis with even qualitative and limited information.

3.2. Tier 2 assessment

3.2.1. Lead and lead compounds emission

Lead metal (Pb) is a substance of very high concern. In Fig. 5, its release amounts for each LCS is shown for PePV as an example if 1000 kg of perovskite crystals were to be present during the use of PePV. This corresponds to 328.3 kg of Pb metal. From this reference value, the quantities of Pb necessary for the upstream production and downstream EoL processes are calculated, taking into account the loss of Pb at every step. The sources of the HSS estimates are colour coded and shown as legend in Fig. 5. Similar estimates were derived for other PbD too (shown in Supplementary information). The three environmental compartments considered are air, water and soil. The release or emission amounts in air includes emission to both indoor and outdoor air. The Pb emission to water, during production stage, consists of emission to waste (sewage) water reaching wastewater treatment plants (WWTP) during production phase. For use stage, the release in water implies release in

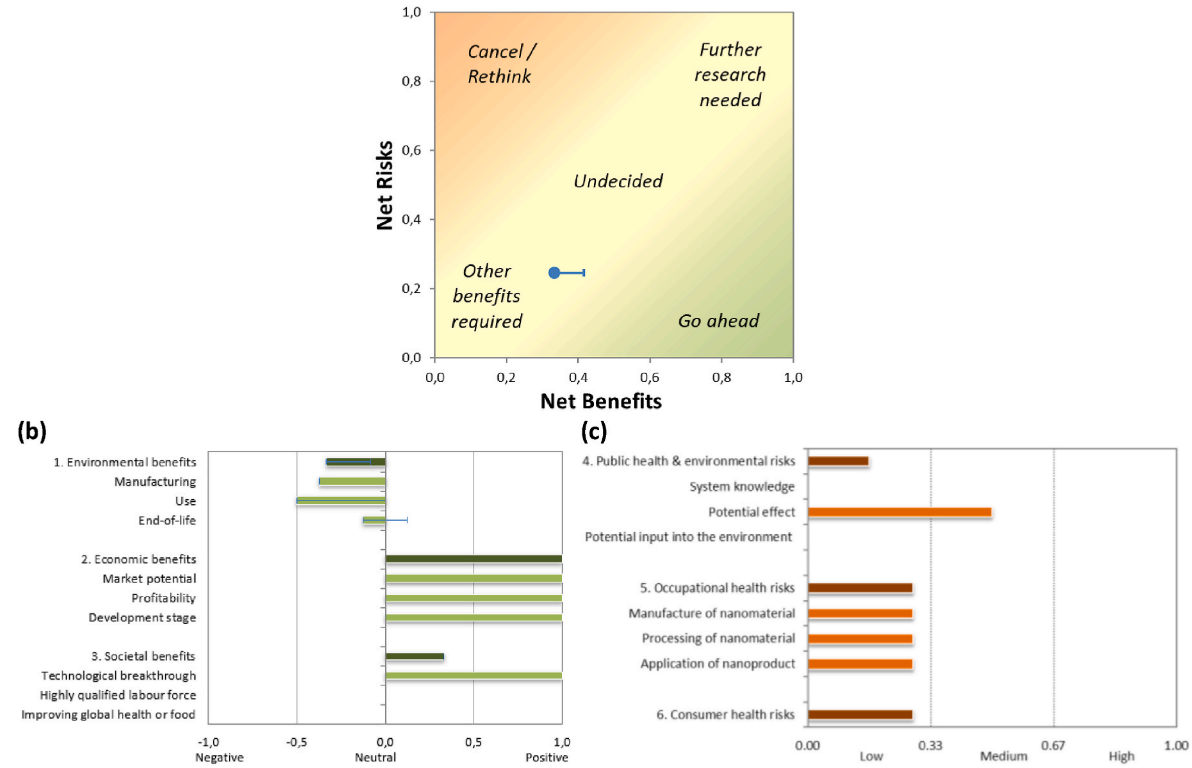

Fig. 3. **(a)** Risk-benefit assessment for the development of PeLED over flexible OLED with its individual comparative scans for potential **(b)** benefits and **(c)** risks.

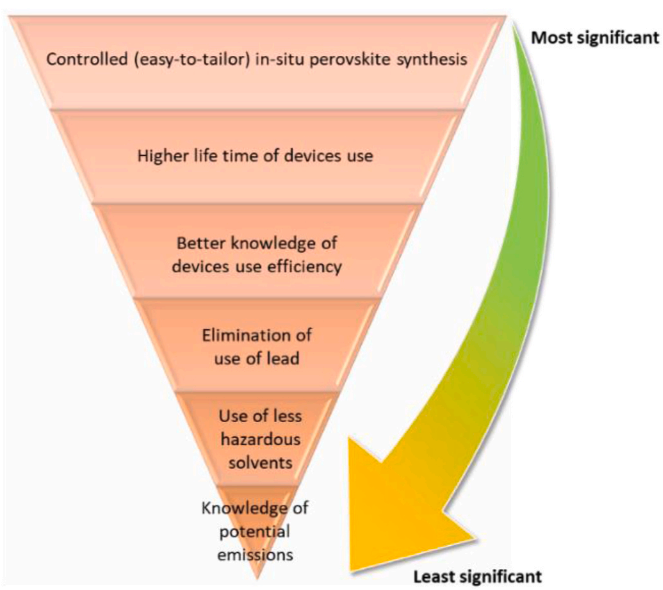

Fig. 4. Decreasing order of significance of the aspects in the decision making related to PbD development to help their transition towards green zone of the LICARA Innovation scan (i.e. low risks with high benefits).

both surface and ground waters as well as wastewater. For EoL stage, the release in water implies release in surface and ground waters. The emission to soil encompasses the emissions generated during any LCS which are disposed or leached to the ground.

3.2.1.1. Production. The production phase of the PePV starts with the raw material synthesis and their mixing together to formulate the precursor ink which is used to produce the perovskite crystalline film in the PePV during printing over a specific substrate. There are three processes in the production phase which lead to the release of Pb into the environment: Pb halide synthesis, precursor ink formulation and PePV fabrication.

Out of the three processes, the Pb halide synthesis emits the highest amount of lead metal to the environment (6.6 kg), almost all amount to the wastewater (WW, 6.57 kg). During the fabrication of PePV, the highest amount of lead is estimated to be released to air (0.16 kg). With the use of a fume hood as a worker exposure control measure, the Pb release amount to the indoor air is substantially reduced to 10% (0.02 kg) and the rest of the Pb released to the air is entrapped by the activated carbon filter present in the fume hood. The filter is mostly incinerated when it is out of use which can also be a source of Pb emission to the environment but it was kept excluded from the scope of the scan. The total Pb emissions into the environment during the entire production phase was estimated to be equal to 6.9 kg approx., i.e. 5% of the total Pb emission over whole life cycle. In Table 2, release amounts of PbI_2 and $PbBr_2$ are shown during their synthesis. To produce 1000 kg of perovskite crystals, 746.46 kg of PbI_2 and 594.25 kg of $PbBr_2$ are to be produced, out of which 14.92 kg and 11.88 kg are the respective fractions released to the water with 0.07 kg and 0.06 kg respectively in the soil.

3.2.1.2. Use. During the use phase, as shown in Fig. 5, out of the 328.3 kg of initial lead content, a total amount of 16.41 kg of lead can leach into the environment over its assumed entire service lifespan (i.e. 5% of the Pb initially present in the use phase). Out of the 16.41 kg, 7.6 kg and 7.75 kg are estimated to leach into the fresh water (surface and ground waters) and wastewater respectively. Each of these fractions represent approx. 5.7% of the total Pb emission over the whole life cycle. The rest, i.e. 1.07 kg, leaches into soil. The total lead emissions into the environment during the use phase amounts to approx. 12% of the total lead emission over whole life cycle.

3.2.1.3. End-of-life. Fig. 5 shows that an estimated total of 311.89 kg of Pb reaches the EoL stage out of which 140.35 kg is estimated to be disposed of via incineration (approx. 45%) and 14% is disposed of via

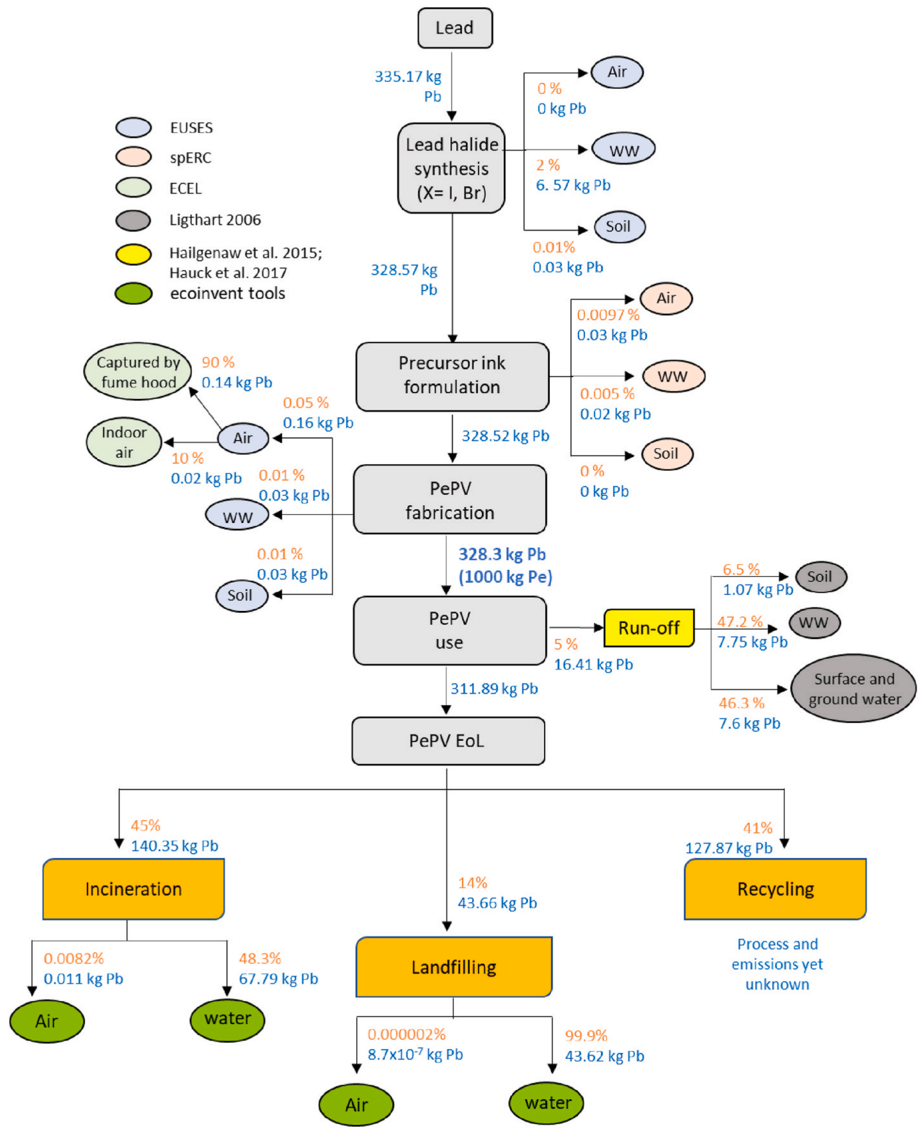

Fig. 5. HSS of the Pb metal release along the PePV life cycle; WW: Waste Water.

Table 2
HSS estimates of Pb halides release to each environmental compartment during their synthesis in case of PePV.

Compound	Produced amount (kg)	Released amount (kg)			
		Air[a]	Water[b]	Soil	Total
Lead iodide (PbI_2)	746.46	0	14.92	0.07	14.99
Lead bromide ($PbBr_2$)	594.25	0	11.88	0.06	11.94

[a] Includes release to both indoor and outdoor air.
[b] Includes release to wastewater.

landfilling (43.66 kg). During incineration, it is estimated that 0.011 kg of Pb is released to the air and 67.79 kg is released to the surface and ground waters. The latter represent approx. 50% of the total Pb emission over the whole PePV life cycle.

The rest is converted to ash (further landfilling of incineration residuals have not been accounted for in this study). In the case of landfilling, almost all of the Pb (i.e. 43.62 kg) is leached to water which is approx. 32% of the total Pb emission over the whole PePV life cycle. Therefore, the EoL accounts for approx. 82% of total Pb emission. It should be noted that these are long term emissions which are estimated to occur over a long period of 100 years (or more) after the landfilling. Nonetheless, it is essential to implement recycling strategies to recover the lead to completely avoid these emissions.

3.2.2. *Other hazardous substances emission*

The HSS estimates for respective release amounts of FAI, DMF and precursor ink are shown in Table 3. These substances are only used and released in the production stage of the PePV life cycle. The highest released amount is estimated for DMF solvent (157.5 kg) which is estimated to be produced in the quantity of 7464.58 kg for producing 1000 kg of perovskite crystals in the PePV. Approx. 95% of DMF release occurs in wastewater (149.29 kg). The second highest release is estimated for

Table 3
HSS estimates of release amounts of other substances during the production of 1000 kg of perovskite crystals used in PePV.

Compound	Produced amount (kg)	Released amount (kg)			
		Air[a]	Water[b]	Soil	Total
FAI	2239.38	0	44.79	0.22	45.01
DMF	7464.58	7.46	149.29	0.75	157.5
Precursor ink	2472.31	0.24	0.12	0	0.36

[a] Includes release to both indoor and outdoor air.
[b] Includes release to wastewater.

FAI (total release: 45.01 kg; dominant release in water: 44.79 kg).

3.3. Tier 3 assessment

In the following sections, results of the risk assessment, expressed in terms of *IS* values, are shown for all relevant compounds at each LCS of the PbD. Details on the derivation of *EF*, *XF* and *FF*, which were used to calculate *IS*, are provided in the Supplementary information. It should be noted that by the time tier 3 assessment was started, two strategic decisions were made by the devices development team in the project:

(i) to acquire the raw materials for the precursor ink (shown in Table 1) from their respective commercial suppliers, instead of synthesizing them in the laboratory, for cost-effectiveness reasons. As a result, the stage of lead halide synthesis which was considered during tier 2 assessment, was not considered in tier 3 assessment (it does not mean though that the lead halide synthesis will not lead to health effects; these risks will be included in the subsequent full LCA). Consequently, in the following sections, the production phase is divided in only two stages: precursor ink formulation and devices fabrication. The use and EoL phases remain same as considered in previous tiers.

(ii) to restrict the devices development to a TRL 5, equivalent to pilot scale manufacturing of small surface applications (10 cm^2). This corresponds to 2 mg and 0.18 mg of perovskite crystals in PePV and PeLED respectively (and their combined amount in PeW). Therefore, the *IS* values were estimated for 2 mg and 0.18 mg of perovskite crystals, depending on the PbD type, in the tier 3 assessment, instead of 1000 kg as was done for tier 2 assessment.

3.3.1. Risk assessment during production phase

3.3.1.1. Precursor ink formulation. In Table 4, calculated *IS* for the general population are shown for different compounds which were used during the precursor ink formulation for PePV. DMF and DMSO, being solvents, are the only compounds that are estimated to release mass into the industrial indoor air and thus have a direct impact on human health upon direct worker exposure through aerosols. The highest human health impact is estimated for CsI (total $IS = 7.32 \times 10^{-8}$ DALY) mainly based on the release to water (due to its higher persistence and insolubility) and secondly for PbI_2 (total $IS = 2.30 \times 10^{-8}$ DALY) mainly based on the release to soil (due to its low degradation rate in the soil). The total *IS* is estimated to be highest for the water compartment, which shows that it is the most likely route to impact the human health to show any carcinogenic/non-carcinogenic effect depending on the compound. When all environmental compartments are combined, the overall *IS* of the precursor ink formulation stage is estimated to be equal to 1.04×10^{-7} DALY. These results are compared with PeLED and PeW in Fig. 6. In Table 5, worker exposure concentration on an individual level is estimated to be equal to 9.98×10^{-7} mg/m^3 and 2.49×10^{-7} mg/m^3 for DMF and DMSO respectively. Both of these exposure concentrations are below their respective OELs. There is no release into the indoor air and thus no worker exposure to the rest of the compounds, i.e. MACl, PbI2, $PbBr_2$ and CsI. Similar results are also obtained for PeLED and PeW. It has been noted for MACl that it decomposes into Methylamine and HCl during thermal annealing process. Due to this, the worker is prone to the inhalation exposure of Methylamine particularly. However, we do not expect its released amount to be greater than its OEL (=12 mg/m^3).

3.3.1.2. Device fabrication. The *IS* for the exposure to perovskite crystals during PbD fabrication are shown in Fig. 6. Although highest *IS* is estimated for soil compartment (=3.08×10^{-10} DALY for PePV and 5.47×10^{-11} DALY for RGB PeLED), it is much lower than the *IS* values obtained for other LCS. Since the Pb^{2+} ions from the perovskite crystals tend to adsorb to the upper soil layers (Amadi and Osinubi, 2018; Lu et al., 2016), the Pb intake by the human body (through ingestion) becomes highly likely and thus has the highest impact. When all environmental compartments are combined, the overall *IS* is estimated to be equal to 6.45×10^{-10} DALY for PePV. The worker exposure concentration is estimated to be equal to 5.73×10^{-8} mg/m^3 for PePV (Table 5) which is below the OEL for Pb metal (=0.1 mg/m^3; EUSC, 2002). For PeLED and PeW, exposure concentrations are also estimated to be lower than OEL.

3.3.2. Risk assessment during use phase

In Fig. 6, calculated *IS* values are shown for the four potential scenarios during use phase of the PbD. Among the 4 potential scenarios, as expected, scenario 4 has the highest total *IS* (=2.45×10^{-7} DALY) in which there is assumed to be 100% breach of the encapsulation layer, while scenario 1 has the least total *IS* (=0) in which there is assumed to be no breach in the encapsulation layer. When the two compartments are compared, the human health impact through soil is consistently higher for all 4 scenarios despite greater release amounts to water. This observation is supported by Mallick et al., 2023 which demonstrated that, upon leaching, Pb^{2+} ions from the perovskite crystals are strongly retained into the soil and thus are more available for human intake than from water. This shows that soil is the compartment to most likely have the greater human health impact upon contamination than water during use phase. For PeLED and PeW, due to the absence of any perovskite

Table 4
Calculated Impact scores (in terms of DALY) for exposure to compounds relevant during precursor ink formulation for producing 10 cm^2 of perovskite material in PePV; $IS = CF \times m$.

Compound	Industrial indoor air			Outside air			Water			Soil			Total *IS* per compound (DALY)
	CF (DALY/$kg_{emitted}$)	*m* ($kg_{emitted}$)	*IS* (DALY)	*CF* (DALY/$kg_{emitted}$)	*m* ($kg_{emitted}$)	*IS* (DALY)	*CF* (DALY/$kg_{emitted}$)	*m* ($kg_{emitted}$)	*IS* (DALY)	*CF* (DALY/$kg_{emitted}$)	*m* ($kg_{emitted}$)	*IS* (DALY)	
DMF	5.24E-05	1.76E-06	9.22E-11	1.16E-05	0	0	8.92E-06	3.52E-05	3.14E-10	1.24E-05	1.76E-07	2.17E-12	4.08E-10
DMSO	1.22E-07	4.39E-07	5.37E-14	2.95E-08	0	0	2.69E-08	8.79E-06	2.37E-13	3.78E-08	4.39E-08	1.66E-15	2.92E-13
MACl	1.36E-07	0	0	6.38E-08	0	0	5.52E-08	9.02E-05	4.98E-12	7.87E-08	4.43E-07	3.49E-14	5.01E-12
PbI_2	4.61E-02	0	0	8.80E-02	0	0	1.65E-04	2.55E-05	4.22E-09	1.47E-01	1.28E-07	1.88E-08	2.30E-08
$PbBr_2$	4.61E-02	0	0	8.80E-02	0	0	1.65E-04	8.55E-06	1.41E-09	1.47E-01	4.27E-08	6.29E-09	7.70E-09
CsI	7.80E-03	0	0	1.58E-02	0	0	1.98E-02	3.68E-06	7.29E-08	1.57E-02	1.84E-08	2.90E-10	7.32E-08
		Total *IS*	9.22E-11		Total *IS*	0		Total *IS*	7.89E-08		Total *IS*	2.54E-08	

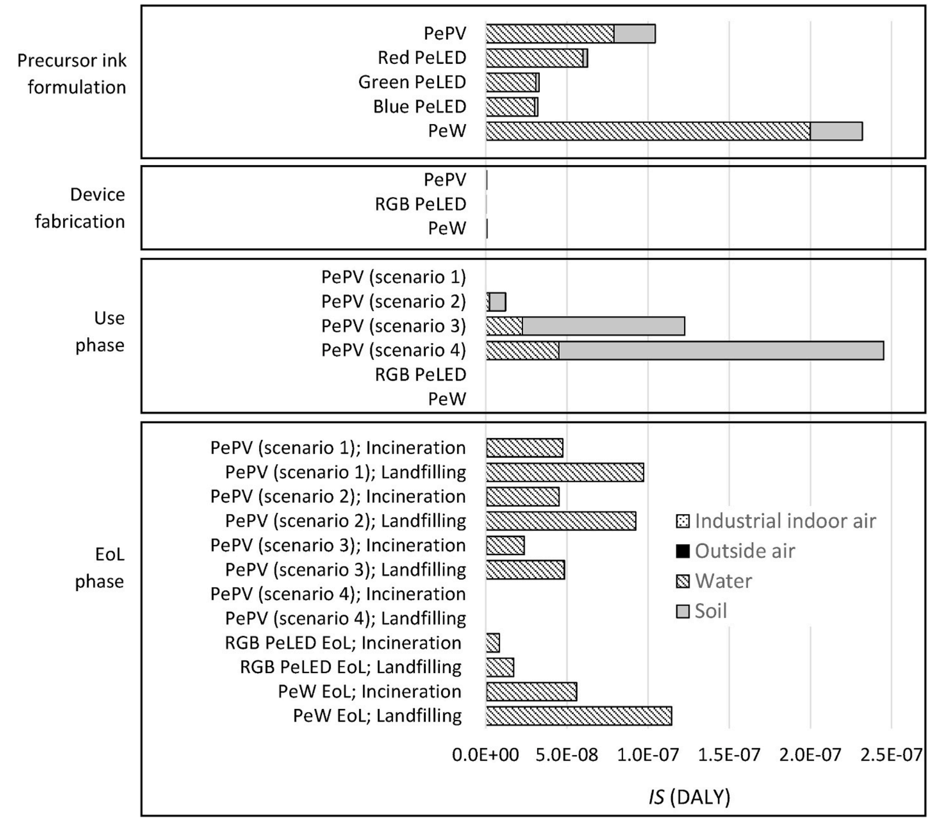

Fig. 6. Estimated Impact Score at each LCS for all assessed devices; RGB PeLED: System of red, green and blue PeLED.

Table 5
Calculated worker exposure concentration for 10 cm^2 of perovskite material in PePV at each applicable LCS.

LCS	Compound	Released mass, $mg_{emitted}$	*XF* (–)	Exposed mass, $mg_{exposed}$	Exposure concentration (mg/m^3)	OEL (mg/m^3)	<OEL?
Precursor ink formulation	DMF	1.76	1.98E-04	3.49E-04	9.98E-07	29.9	Yes
	DMSO	0.44	1.98E-04	8.71E-05	2.49E-07	160	Yes
Device fabrication	Perovskite crystals	0.1	2E-04	2.00E-05	5.71E-08	0.1	Yes
EoL scenario 1	Perovskite crystals	0.16	1.98E-04	3.27E-08	9.35E-08	0.1	Yes
EoL scenario 2	Perovskite crystals	0.16	1.98E-04	3.12E-08	8.90E-08	0.1	Yes
EoL scenario 3	Perovskite crystals	8.26E-02	1.98E-04	1.64E-08	4.68E-08	0.1	Yes
EoL scenario 4	Perovskite crystals	0	1.98E-04	0	0	0.1	Yes

release, any risk to the human health is highly unlikely and thus the *IS* is equal to 0 for both devices.

3.3.3. *Risk assessment during EoL phase*

The use phase of the PePV has direct consequences on the *IS* calculation during its EoL phase. The four potential scenarios have different perovskite crystals amounts reaching the device's EoL. Thus, the EoL phase, also has four potential scenarios, each scenario as a result of the use phase scenario (Fig. 6). Scenario 1 in which it is assumed that 100% of the perovskite crystals reach their EoL has the highest total *IS* equal to 1.45×10^{-7} DALY for PePV with all environmental compartments combined, followed by scenario 2 with total *IS* equal to 1.38×10^{-7} DALY. On the other hand, scenario 4 with no perovskite available (assuming 100% of it leached out during use phase), has the least *IS* (=0). For all 4 scenarios, there is no expected emission to soil and, compared to air, the higher impact is through water for which impact on the human health is consistently seen to be higher due to perovskite leaching during landfilling. For outside air, *IS* values are calculated to be in the order of 10^{-13} DALY during landfilling. The worker exposure concentration during PePV incineration is expected to be highest during scenario 1 ($=9.35 \times 10^{-8}$ mg/m^3) but it is lower than the OEL for Pb metal (Table 5). For the PeLED (RGB), since all perovskite content reaches EoL, there is only one scenario in which highest *IS* ($=1.73 \times 10^{-8}$ DALY) is calculated for water during landfilling. The worker exposure concentration during PeLED (RGB) incineration is estimated to be equal to 8.39×10^{-9} mg/m^3 which is lower than the OEL for lead. For the PeW too, all perovskite content reaches the end of life. Therefore, combined estimations from scenario 1 of the PePV and PeLED remain valid for the PeW.

4. Discussion

4.1. SSbD

EC's SSbD framework proposes (re)design of chemicals and materials based on a safety and sustainability assessment as early as possible in the innovation process to ensure that SSbD principles are being applied to a chemical's or material's design. The tiered approach presented in this paper supports the SSbD framework implementation and subsequent decision making for the PbD by allowing a holistic evaluation of the safety, functionality and sustainability right from the early stages of the innovation value chain across all possible LCS of PbD. Each tier follows the progression of the TRL (or the successive innovation stages, as considered in widely accepted innovation stage-gate model; Jiménez et al., 2022; Shandilya et al., 2020a) and increases the complexity of the employed assessment methods as well as the time, resources, data and level of expertise required for their application (Shandilya et al., 2020b). It is believed that such tiered approach renders SSbD to be "innovation enabler" rather than "innovation disabler" as often there is lack of time and/or expertise to engage in resource-intensive safety and sustainability evaluations by the companies.

4.2. Tier 1 assessment

The use of the LICARA Innovation Scan as a tier 1 tool proved to be useful at the early stage of devices development when the innovators had a very limited knowledge of all chemical compounds in the devices. Most of the available innovators' knowledge was observed to be available on the conventional counterparts/benchmarks which they have been developing in the past and are intended to be replaced by these PbD. Since LICARA Innovation Scan works on a qualitative and comparative assessment, it is an ideal tool to use in such conditions. We observed that the average time needed to fill in the LICARA Innovation Scan tool was <1 h which is reasonable, for instance, for an SME developing an innovative product. The information could be relatively easily filled in the tool by choosing the qualitatively categorised answers from a dropdown menu to the simply worded questions. Therefore, there was no specific expertise needed to work with the tool, except for its Stoffenmanager® component which may require some (basic) knowledge of certain technical terms in occupational hygiene and epidemiology (e.g. source domains, local controls, dustiness) but their descriptions are easily available online to understand. Furthermore, it paved the way to focus further development on six key aspects which could ensure the balance between safety, functionality and sustainability along the entire value chain. In addition, it also paved the way to focus our higher tier health and environmental risk assessments on three of these key aspects.

4.3. Tier 2 assessment

In the PePV design, if an on-device sequestration is present which is capable of lead-absorption upon any leakage, recent research has shown that, under the conditions of normal wear, the considered 5% lead release amount (i.e. scenario 2) can even get reduced to 0.15% (i.e. more than 96% reduction in the lead leakage). Li et al., 2021 showed that this is achievable by using a transparent lead-absorbing molecular film containing phosphonic acid groups that bind strongly to lead on one side. On the other side, a polymer film blended with lead-chelating agents is placed between the metal electrode and a standard photovoltaic packing film.

In case of PeLED and PeW, we assume that their indoor use would not induce any mechanical damage to the devices and thus no lead release. However, there can be some accidental exposure to perovskite and its lead content when the PeLED and PeW accidently break. Inhalation exposure to lead fumes/dust might occur but given its accidental nature (i.e. not a regular exposure scenario) and low dose of the lead in the device (without any possibility of dose accumulation inside the body), any health impact is estimated to be insignificant. This can also be inferred from the findings of Dong et al., 2020; Panthi et al., 2021 in which the researchers observed the direct inhalable emission from the broken devices to be inconsistent and/or below the detection limit of the sampling filters.

However, there can be potential human health risk of the consumers due to the accidental dermal and oral exposure to the lead upon the breakage of PeLED and PeW. But since this dermal and oral exposure during the use of these devices is entirely accidental in nature, it also falls out of our scope because we focus only on the regular potential exposure scenarios in this study. Nevertheless, we acknowledge that the accidental exposure scenarios should be considered for the future in which not only the substance(s) release amounts are to be considered but also to which degree(s) the perovskite remains intact when the device breaks.

In addition, the HSS assessment could only calculate emissions for chemical elements (e.g. Pb) for EoL phase, unlike for production or use phases in which emissions of all kinds of substances (e.g. compounds, elements, chemical groups etc.) could be calculated. Therefore, the elemental composition of the waste stream has to be known to calculate the emissions arising during the EoL. This inherent limitation of the HSS tool is due to the ecoinvent waste tool which itself provides only elemental emissions from the different EoL treatments (e.g. incineration, landfill). The HSS identified landfilling and incineration to be critical focal points of Pb metal emission which accounts for approx. 82% of total Pb emission across the whole life cycle. This underlines the importance of ensuring a proper recycling process for PbD for them to be sustainable. The enforcement of the waste electronics and electric equipment (WEEE) regulation since 2012, requiring that all WEEE is collected separately for recycling, is a promising start, but a clear recycling process should be put in place to recover the materials present in the devices and avoid the lead emissions. In fact, recycling aspect is one of the parameters which has been deemed critical by EU Ecodesign directive for improving the environmental aspects of energy harvesting and consumption devices (EU Directive 2009/125/EC, 2009). Ease for reuse and recycling can possibly be ensured through, for example, use of standard components, time necessary for disassembly, complexity of tools necessary for disassembly, use of component and material coding standards for the identification of components and materials suitable for reuse and recycling (including marking of plastic parts in accordance with ISO standards), use of easily recyclable materials, etc.

In light of the enforcement of the WEEE directive and growing concerns about sustainable product development, more recent studies show a growing attention to the development of innovative recycling and reusage methods for perovskite based materials, in particular with the aim to limit the lead metal emissions that can arise during the use phase and, if not properly treated, during EoL. Most of the studies reviewed so far, focus on the recycling of PePV (Binek et al., 2016; Chen et al., 2021; Chhillar et al., 2019; Liu et al., 2021). Liu et al. (2021) reviewed proposed technologies to recover different (or several) components of the perovskite solar cells (Electrodes, lead, perovskite film, electron transport layer, glass, absorber layer, etc.). Dissolution with the employment of different solvents (DMF, chlorobenzene, eutectic solvents, etc.) is the most forthcoming technique that can be applied to recover different components of the solar cell, including the lead and the perovskite layer, thus significantly reducing the Pb emissions during EoL. A more recent publication, (Schmidt et al., 2023), demonstrated a lab scale lead recovery process based on the use of hot water, without further solvent treatment. Furthermore, multiple studies (Binek et al., 2016, Kim et al., 2016; Chhillar et al., 2019) have successfully demonstrated the reuse of the recovered materials for the manufacturing on new perovskite cells, obtaining good energy conversion efficiencies. These results are extremely encouraging but, as underlined by Liu et al. (2021), such recycling technologies are currently under development and are not yet applied at large scale. For this reason, there are currently no data available quantifying the emissions to different compartments for the relevant recycling processes. Therefore, in the analysis and calculations of the emissions arising from the EoL of the PbD, recycling has been considered but it was not possible to calculate the relative emissions to different environmental compartments. Recent studies also indicate that e-waste is still disposed of in residual waste, and the small e-waste ends up in residual waste bins: in particular the average value of small electronic equipment that reaches the residual waste in the Netherlands, UK, France and Belgium is 59% (Rotter et al., 2016). For this reason, it is important to consider also incineration and landfilling as plausible EoL treatments for the PbD.

While there is a surge of research activity in exploring alternative perovskite materials, the state-of-the-art still requires Pb^{2+} as the B-site cation in the perovskite crystal structure (Ju et al., 2018). However, the Restriction of Hazardous Substances Directive (RoHS) directive bans the use of Pb and Pb compounds in the luminaire applications, like PeLED, to meet the high safety, health, and environmental protection requirements on the extended single market in the European Economic Area. Unless there is an exemption for LED and related luminaire products group from the RoHS directive to use Pb and Pb compounds on the grounds of their use in specific amalgamated compositions (e.g. PbBiSn–Hg, PbSn–Hg) or some socio-economic or political reasons, the RoHS framework can hinder the development of Pb-based PeLED.

4.4. Tier 3 assessment

From devices design point of view, one may approximate the *IS* values to be equal to 2.55×10^{-4}, 1.53×10^{-4} and 3.96×10^{-4} DALY per unit surface (m^2) of perovskite in PePV, PeLED and PeW respectively. During the tier 3 level assessment of the occupational risks, we observed that all estimated exposure concentrations for relevant compounds were lower than their corresponding OEL which signifies occupational risk to be unlikely for a worker population due to the inhalation of released substances in the indoor air at lab production scale. However, the released mass, *m*, and calculated *CF* are mainly based on the substance-intrinsic properties (e.g. vapor pressure) and assume a "passive" release from the product. For the occupational indoor air situation, we know that this is not the case and a lot of release/exposure scenarios (or process categories) depend on the activity energy too, rather than only on the substance properties. This is a clear deficit of the USEtox model. Thus, onsite experimental measurement data are always needed to be certain before completely ruling out occupational risk likeliness.

It should be noted that the *IS* values, reported in this study, correspond to the production of 10 cm^2 of perovskite surface (representing lab-scale production). The *IS* values will increase in case of higher crystal surface (e.g. 100 cm^2). Therefore, a new risk assessment will be needed for a perovskite crystal surface area other than 10 cm^2. Stanaway et al., 2018 evaluated global burden of disease and *IS* for environmental and health risks caused by the exposure to lead, in 195 countries and territories from central and eastern Europe, central, south, southeast and east Asia, north Africa, middle East and Oceania. These risk factors were estimated to contribute to 1 million deaths in 2017 approx., which correspond to 24 million DALY. If the estimated IS values from this study were to be compared with 24 million DALY, they are very low. The maximum *IS* value for all three PbD combined is equal to 8.42×10^{-7} DALY. To make an impact equal to 24 million DALY, the total perovskite crystal film surface would mount to 2.85×10^4 km^2 approx. (=10 cm^2 × 24 × 10^6 DALY/8.42 × 10^{-7} DALY) which would contain an approximate total of 5.7×10^4 metric tons of perovskite crystals (=2.015 g/m^2 x 2.85×10^4 km^2). Although producing this much amount of perovskite crystals is highly unlikely within the current scope of the assessment (restricted to TRL 5), it can be a realistic scenario upon devices' production upscaling to a mass level in future, especially considering the current global silicon wafers mass production scale to be 9 million metric tons approx. (Statista, 2023) for conventional photovoltaic cells in 2022. Therefore, for a large production scale or a technology scale-up of the PbD, environmental and human health risks are expected to be significant (e.g. 24 million DALY and 1 million deaths per year). Thus, the innovators need to consider alternatives to the material design in their methodology to make it safe to the human health before the perovskite-based technology becomes large enough to be comparable with current silicon wafers production. Such alternatives include, for example, substitution of Pb and Cs halides with tin metal without compromising with high efficiency and stability of the device (Cao and Yan, 2021), chemical absorption of Pb upon leaking (Li et al., 2021), replacing the use of hazardous solvents like DMF with DMSO (Küffner et al., 2021) which has 100 times lesser health impact, perovskite-structural change by replacing Pb^{2+} with an aliovalent metal cation (Yang et al., 2017).

4.5. Next steps

The assessed potential impacts of chemical compounds, which provide *CF* as substance-specific measures of relative impact potential, will be used in a comparative context of LCA as a next step. Compounds like Pb and Cs halides, LCS of EoL and environmental compartment of water which have been expected to be elements of potentially high concern upon upscaling, will be integrated in the LCA. This will help to obtain accurate results on the full spectrum of environmental impact of the PbD.

5. Conclusion

The presented tiered approach in this work proved to be a useful way to implement SSbD from an early stage of the PbD development. Its flexibility in the use of available knowledge and data proved to be a key aspect for its applicability to the PbD. While the LICARA Innovation Scan and HSS tools can be used by industry directly, they need expertise to do the tier 3 assessment. Amid the existing concerns regarding their toxicity and environmental impacts, our findings suggest that they are a promising innovation but the current state of technology suffers from consistently moderate benefits with several potential risks. More focus during the device development is needed to some specific technology benefits related aspects like having a controlled (easy-to-tailor) perovskite synthesis process, higher lifetime of use and better certainty of devices use efficiency, especially PeLED, to ameliorate its economic appeal in the market.

Our assessment estimated that although the lead metal is being emitted throughout the entire life cycle of the devices, the vast majority of long-term emissions occur during the EoL (approx. 82% of the total emissions), mainly to the ground water compartment. The high emissions of lead after landfill and incineration underline the importance of ensuring a proper recycling and reusage process for PbD. The use phase became a relevant focal point only when there is a breach in the encapsulation layer and the perovskite crystals get exposed to moisture.

Emission of several hazardous solvents and compounds was also estimated to take place during the production phase of PbD. Most of it is released to wastewater, with relatively lower amounts of release to the air at a pilot production scale (due to the protective measures put in place during synthesis and manufacturing of the perovskites). Considering this, it can be stated that the exposure of the workers to the emissions of toxic substances arising during the production stage seemed to be limited which was also confirmed within the tier 3 assessment in which the estimated worker exposure concentrations were observed to be much lower than the respective OELs.

The risk posed during each of the three LCS was quantified during tier 3 assessment. It was observed that for a pilot scale production, limited to 10 cm^2 of perovskite surface, the estimated impact scores were much lower than the estimated impact score of the conventional environmental and occupational risks caused by the lead contamination of air, water and soil. However, upon devices' production upscaling to mass level (e.g. 5.7×10^4 metric tons per year), we expect human health risks to be comparable to more than 8 million deaths per year. This aspect will be dealt in more detail in a separate publication where a technology scale-up scenario will be studied through an LCA. Nevertheless, based on current estimations, the product developers are urged to consider the suggested alternatives to the material design and reusage in their methodology to make it safer to the human health upon technology scale-up.

Declaration

During the preparation of this work, the authors did not use any generative AI and AI-assisted technologies in the writing process.

CRediT authorship contribution statement

Neeraj Shandilya: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Lia de Simon:** Writing – review & editing, Formal analysis. **Bernice Scholten:** Writing – review & editing, Validation, Investigation, Formal analysis. **Tom Ligthart:** Writing – review & editing, Validation, Project administration. **Susan Dekkers:** Writing – review & editing, Validation. **Eugene van Someren:** Writing – review & editing, Software. **Wouter Fransman:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Neeraj Shandilya reports financial support was provided by European Innovation Council Fast Track to Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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