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PeroCUBE – High-Performance Large Area Organic Perovskite devices for lighting, energy and Pervasive Communications

Deliverable 7.2

Identification of main release sources of perovskites in PeroCUBE devices

WP 7 – Human health risk assessment and life cycle assessment

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Executive Summary

This deliverable presents a tier-1 assessment of the emissions of the substances from perovskite-based devices to different workplace, consumer and environmental compartments (including air, water and soil) over the devices' entire life cycle. It is the output of T7.2 and includes a Hotspot Scan of the potential sources of human and/or environmental exposures.

Need for the Deliverable

The overall objective of WP7 is to assess the potential human health risks and to provide a life cycle assessment to balance the risks and benefits of the application of perovskites in lighting and energy harvesting applications. These risks mainly arise from the release of hazardous substances during the production, use or disposal of the perovskite-based devices. Following the tier-0 qualitative assessment (D7.1) in which certain 'red flags' related to the potential risks and lower benefits (social or economic) were identified along the life cycle of the perovskite-based devices, a tier-1 assessment is now needed to further refine and identify the release hotspots in a quick manner. Such tiered approach allows a pro-active approach towards the elimination of any potential risk at an early stage of product development and thus enables a better product design or gives guidelines for an improved value chain design.

Objectives of the Deliverable

The objectives of this deliverable include:

- presentation of the concept, methodology and results of the Hotspot Scan of perovskite-based devices.
- further development of an online Hotspot scan tool to automatically produce hotspot scan workflow diagrams by simply answering a set of product and process relevant questions.
- identification of perovskites, lead and other hazardous substances release hotspots along the life cycle of perovskite-based devices using Hotspot Scan tool.

The devices which are considered for the hotspot scan are same as D7.1, i.e. perovskite-based photovoltaic cells (PePV), perovskite-based light emitting diodes (PeLED) and perovskite-based light fidelity system (PeLiFi).

Outcomes

The hotspot scan of the perovskite-based devices estimated that the vast majority of emissions (or release or losses) to different environmental compartments (air, water and soil) occurs during the end-of-life stage of the devices' life cycle (over 80% of the emissions). It was particularly relevant and valid for lead metal, thus indicating lead emission and end-of-life stage as relevant focal points for human and environmental exposure. For perovskite-based crystals and other hazardous substances used during the synthesis of the perovskite crystals (e.g. Lead nitrate, Lead halide, Methylammonium halide, DMF, precursor ink), main losses or release to the environmental compartments were estimated to occur during the production stage.

When the end-of-life stage was further scanned in detail, most of the emissions (>95%) were estimated to occur to the water compartment (wastewater, surface water or ground water). When incinerated, a considerable proportion of the lead (>50%) was estimated to be retained in the incineration ashes. When landfilled, nearly 100% of the lead contained in the waste is estimated to leach to the surface and ground waters. The high emissions of lead during landfill and incineration underline the importance of ensuring a proper recycling process for perovskite-based devices. Current recycling processes to dispose of the perovskite reaching the end-of-life stage have been observed to be rather immature/insufficient and thus come with a lack of available data.

The production stage, on the other hand, was estimated to account for 10% and 7-9% of the whole life cycle emissions of PePV and PeLED respectively. The emission occur dominantly to the wastewater (sewage). Relatively lower amounts were estimated to be released to the air (due to the protective measures put in place during synthesis and manufacturing of the perovskites) and even lower to the soil. Considering this, it can be stated that the potential exposure of the workers to the toxic substances arising during the production stage seems to be limited.

The emission of the lead from perovskite crystals during the use of the perovskite-based devices by the consumers was mainly accounted by the run-off/leaching of lead ions. Such emission was estimated to be lowest among all three life cycle stages (approx. 5% of the whole life cycle emissions) for perovskite-based devices.

PeLiFi (or PeLED) may affect human skin and vision, but it is believed that with the increased device efficiency, there will be lesser exposure of the consumer with light and thus not a major concern. The use of the PeLiFi (or PeLED) can be made safer with the minimization of the blue light emission from the device.

The development of the online Hotspot Scan tool is also reported which is built upon the generic structure of the LICARA Innovation Scan tool (reported in D7.1). The online tool assists users to determine release factors based on available relevant sources of information and automatically produce hotspot scan workflow diagrams by simply answering a number of product- and process-relevant questions. The public release of the tool and further improvements are forecasted in the near future.

Next steps

The next steps will include moving towards a higher tier (tier-2) quantitative assessment of human health risks by gathering information on exposure data (from production process in T4.1) and toxicological data (from scientific literature) related to human health impact over the entire life cycle of the perovskite-based devices. In case of lack of data, exposure models or developed alternatives will be used to extract exposure distributions for various relevant scenarios that could represent life cycle.

1 Introduction

The objective of WP7 is to assess the potential human health risks and to provide a life cycle assessment to balance the risks and benefits of the application of perovskites in lighting and energy harvesting applications. To achieve these goals, a tiered approach is followed, going initially from a qualitative approach (with relatively low input needs and higher uncertainty) to a full quantitative life cycle assessment (LCA) at the end of the project, when the applications will be better defined.

The first task in the WP7, i.e. task 7.1, was to qualitatively assess the benefits and risks of perovskite-based photovoltaic cells, light emitting diodes (PeLED), light fidelity system (PeLiFi) and wearable[1] compared with their conventional technological counterparts. The assessment was based on a qualitative approach (tier-0) using the LICARA Innovation Scan tool (https://diamonds.tno.nl/#licara). It was found that the aforementioned perovskite-based devices consistently exhibited low to moderate risks and moderate benefits over their entire life cycle. These low risk and moderate benefit scores put the devices in a transit 'yellow zone' of LICARA Innovation Scan, which means that these perovskite-based devices are promising developments and have the potential to be sustainable over their entire life cycle. However, they needed additional benefits and even lower risks for them to lie in the LICARA Innovation Scan's 'green zone' which implies a clear go-ahead with their further development in the innovation value chain. Use of hazardous lead halide compounds and volatile solvents like Dimethylformamide (DMF) during the production of perovskite-based devices was also a concern that was identified and reported. Their potential emission during any of the life cycle stages may hinder the devices' safety and technological sustainability along their innovation value chain.

As a next step, task 7.2 focuses on the identification and quantification of such harmful emissions to different workplace, consumer and environmental compartments (including air, water and soil) over the devices' entire life cycle to highlight potential sources of human and/or environmental exposures. This process is called the Hotspot Scan. It is a tier-1 assessment and uses sources like scientific papers, Best Available Techniques reference documents, (specific) environmental release categories (spERC/ERC) defined for the EUSES risk assessment used for REACH, Waste Electrical and Electronic Equipment (WEEE) directive, and expert judgement. During the hotspot scan the life cycle stage(s) and environmental compartment(s), to which an emission may occur (i.e. hotspots or focal points), are identified and the amount of emission is quantified. In addition, the potential transformation(s) of the perovskite-based devices' components are also identified for more information on the devices' degradation due to ambient environmental and operational conditions. This enables a better product design or gives guidelines for an improved value chain design.

The hotspot scan builds upon the experience gathered during task 7.1 regarding the production methods and intended use conditions of the perovskite-based devices. The perovskite-based devices considered for the hotspot scan are the same as included in D7.1, i.e.

- **Perovskite-based photovoltaic (PePV)**: PePV is a type of solar cell or a photovoltaic that uses organo-metallic compounds to produce electricity from sunlight through the photovoltaic effect. The perovskites used in this project are various lead halide compounds. The PePVs act as energy harvesting devices, i.e. devices which are able to capture energy from external sources (e.g. sunlight) and make it available for power applications.

[1] The feasibility, technical requirements and specifications of perovskite-based wearable could not be determined by the time T7.1 was executed due to which its risk-benefit assessment was decided to be excluded for any further assessment and hence was not covered in T7.1.

- **Perovskite-based light emitting diodes (PeLED)**: PeLED utilize lead halide perovskite as a direct bandgap semiconductor for electroluminescence in red, green and blue spectra of the visible light range with high-colour purity and low-cost light emission. They have an optical bandgap that can be tuned in the visible to infrared regions, which makes them very promising for a range of optoelectronics applications.
- **Perovskite-based Light Fidelity system (PeLiFi)**: A PeLiFi system is a bidirectional communication device that consists of one PeLED to simultaneously transmit light and data from the server and another PeLED as photo detector (i.e. router) to receive the data and provide it to the user (working with a laptop). This is possible because of the ability of the PeLED to emit light as well as absorb light in a specific wavelength.

2 Methodology

2.1 Hotspot Scan

The Hotspot Scan, or HSS, determines the "hotspots" (i.e. critical or risk prone stages) during life cycle of a product where emissions of a substance (compounds, elements, chemical groups etc.) to air (indoor and outdoor), water or soil can occur. 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, (e.g. 1000 kg or 1 ton of perovskite in PePV or PeLED) and the mass of the substance flows before and after the use phase (i.e. production phases and end of life phases) are all defined relative to this reference value. A reference value of 1000 kg is selected because it is the threshold quantity of a substance beyond which the substance manufacturer or importer in the European market has to submit a REACH registration dossier to ECHA unless the substance is exempt.

The present HSS tool was originally developed in the EU FutureNanoNeeds project (Boukris et al. 2014) with the goal to predict where in the life cycle of a nanomaterial-based device the main releases of the nanomaterial would occur and to which environmental or occupational compartments. In this project, this concept has been adapted to be applicable to hazardous substances used in the perovskite-based devices to be developed in PeroCUBE. Figure 1 provides, as an example, a schematic overview of the life cycle stages and main release and emission routes of (potentially) hazardous nanoparticles from a relevant device; the same principles apply to the emissions of other (hazardous) substances.

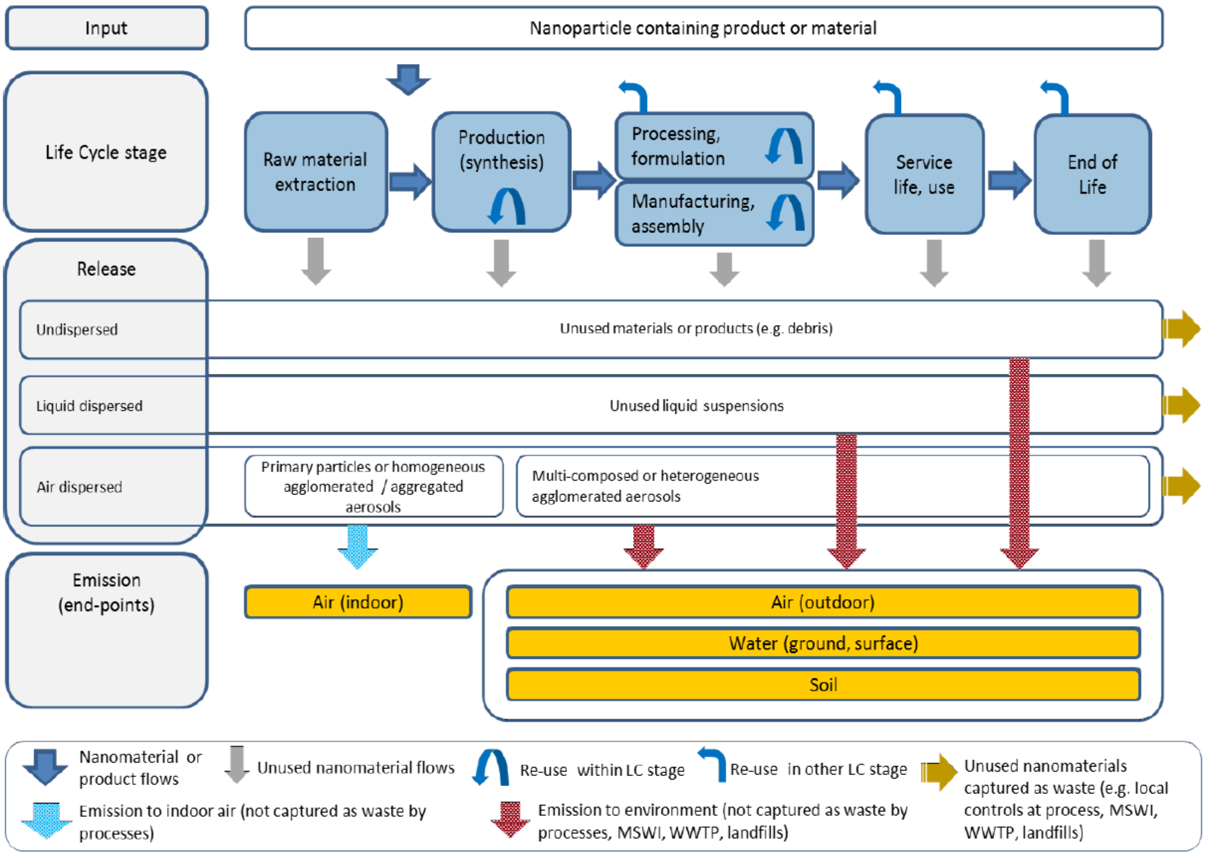

Figure 1: Illustrative example of a framework showing the main emission routes during the life cycle of a nanomaterial-based device (Boukris et al. 2014). For this study hazardous substances used in a device are the focus.

The approach of life cycle thinking is important to minimize the human health and environmental burdens associated with products or product portfolios throughout their entire life cycle and value chain. These human health and environmental burdens can be assessed by means of Life Cycle Assessment (LCA). However, performing a full LCA can be a challenging task due to the large amount and specificity of data required that, especially for products in the developmental phase, are hardly available in this early stage of product development. The HSS instead, provides an intermediate (tier-1) assessment focusing only on the flows of substances (e.g. elements, compounds, product parts, etc.) which pose high (or unknown) risks (i.e. substance of concern). The HSS focusses on the different life cycle stages of a product, from the production phase via the use phase -which is the reference point- to the end of life, analyzing mass flows of hazardous substances for all the processes that the product (in the present case, perovskite-based device) undergoes during its life cycle. Time comes in as factor as some products may have a longer service life than others, e.g. a couple of years for a wearable device and over a decade for a photovoltaic panel. During the service life or use phase, release of the hazardous substance may be intentional, e.g. a solvent in an ink, or unintentional, e.g. perovskites from a leaking PV panel. The use of the HSS leads to the identification of the focal points in the life cycle stages where significant (hazardous) release/emissions can occur to the different compartments and thus recommends further improvements on the product development to lower any negative impacts on human health and/or the environment.

The HSS thus deals with hazardous substances, and especially those present in the use phase. To determine the hazard level of a substance, we've used the REACH dossiers available at the European Chemicals Agency (ECHA, https://echa.europa.eu/) and PubChem (https://pubchem.ncbi.nlm.nih.gov/). Certain perovskites have been listed as a pre-registered substances, however data on hazardous properties or hazard statements are not yet available. Lead-based perovskites are water soluble and thus can give rise to the release of lead ions. Use of perovskites in PV, and the degradation products, was found to have non-negligible hazard potentialities by Bae et al. (2019). The use of lead and its compounds have been restricted due to its hazardous properties, human and eco-toxicity, in EU regulations like RoHS Directive, the one on the Restriction of Hazardous Substances in Electrical & Electronic Equipment (EU 2011). Their use in energy harvesting applications (e.g. PV) has had RoHS exempt status, since 2011. Lead compounds may damage the unborn child and are suspected of damaging fertility, are very toxic to aquatic life, very toxic to aquatic life with long lasting effects, harmful if swallowed, harmful if inhaled and may cause damage to organs through prolonged or repeated exposure (ECHA, 2021). Further details on the hazardous substances present in the life cycle of the products under study is found in section 3.1.

The HSS is applied for one hazardous substance at a time, thus, carrying out sequential HSS for all substances identified in the life cycle of the product. Still, doing this for all the substances present at any stage of the product's life cycle, would become a highly energy and data intensive task, thus vanishing the efforts of carrying out a "quick" scan to give an overview of the most concerning substances and emissions. Furthermore, a complete inventory of the emissions is carried out during the LCA of a product and the HSS is not a substitution of an LCA. Therefore, the HSS follows a certain stepwise methodology, as shown in Figure 2.

1. Substance identification

- All the substances present at the use stage of the product (and at the prior life cycle stage) are identified.
- Certain selection boundaries over the identification of the substances are established to ensure that the entire HSS process does not become too time consuming.

2. Substance prioritization

- Hazardous (or bio-persistent) substances with unknown emission levels (at any product life cycle stage) are prioritized.
- Substances with known negligible emission levels are excluded from the prioritization.

3. HSS execution

- The prioritized substances are selected one at a time.
- An individual HSS is performed for each prioritized substance.
- If the prioritized substance is present in only one life cycle stage, for instance production, the HSS is limited to only production stage.
- If more than one life cycle stage, for instance production, use and end-of-life, are concerned by the presence of the substance, then HSS includes all life cycle stages.

Figure 2: HSS methodology

The risk of a substance is the hazard times the exposure, a high hazard but no exposure thus poses no risks, a medium hazard and high exposure (of workers or the environment) certainly poses a risk. For the hazard part of this BASF has developed a method, implemented in their SEEBalance tool, (Landsiedel et al. 2002), based on the risk phrases of a substance. This method was translated to the current GHS hazard statements by TNO. The higher the hazard the higher the given toxicity potential (ranging from 0 to 1000). For the Hotspot scan we only use the hazard statements with a potential of 300 and higher for Human toxicity and eco-toxicity, physical hazards like flammability are not accounted for. The hazard statements which are relevant for the HSS are provided in the Annex Table A1. Substances of Very High Concern (SVHC) will always be a priority for the Hotspot scan and Lead is an SVHC. Substances with the following hazard properties may be identified as SVHCs :

- Substances meeting the criteria for classification as carcinogenic, mutagenic or toxic for reproduction (CMR) category 1A or 1B in accordance with the CLP Regulation.
- Substances which are persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) according to REACH Annex XIII.
- Substances on a case-by-case basis, that cause an equivalent level of concern as CMR or PBT/vPvB substances.

While performing HSS for end-of-life stage (if applicable), the emissions can only be calculated for chemical elements (e.g. Pb, Ag,...) unlike HSS for production or use stages in which emissions of all kinds of substances (e.g. compounds, elements, chemical groups etc.) can be calculated. Therefore, the elemental composition of the waste stream has to be known to calculate the emissions arising from the end-of-life stage. This inherent limitation of the HSS tool arises from the fact that it relies on the ecoinvent[2] waste tool which provides only elemental emissions from the different end-of-life treatments (e.g. incineration, landfill).

Once the HSS is performed for a substance, it helps to identify:

- Relatively large substance flows leaving the product system, e.g. waste flows (e.g. waste product to recycling or waste flows to WWTP) or leaching potential (e.g. corrosion sources during the use phase);
- Points indicating changes in substance flows (compared to conventional flows);
- High potential for (human) exposure due to high concern activities, e.g. high energy coating process;
- Points known or envisaged to be sensitive for human exposure or the environment, e.g. higher flows into a sewage plant may be of less importance than flow changes near to possible points of human exposure or sensitive environments;
- Significant knowledge gaps for scenarios, e.g. all process steps involved in devices recycling.

2.2 Life cycle

This section presents the relevant life cycle stages of a perovskite-based device (e.g. PePV, PeLED). A schematic overview is shown in Figure 3.

[2] https://www.ecoinvent.org/

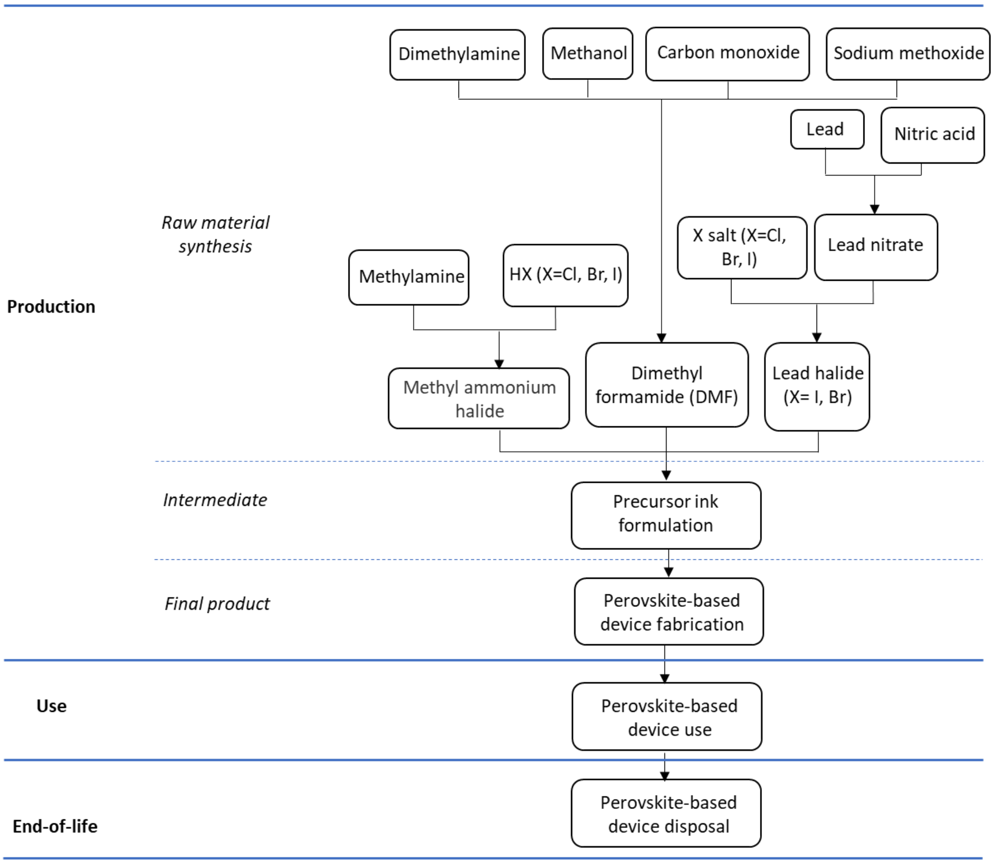

Figure 3: Life cycle stages of a perovskite-based device

The life cycle is considered to start from the device production stage which in itself consists of devices fabrication after raw materials synthesis and precursor ink formulation. Once the devices are fabricated, they are used, for instance within domestic settings of a house, for energy harvesting and energy emission purposes. Based on the life time of the device, they are used for a certain period of time by the consumers and finally are disposed of after their use. The following sections give a detailed overview of the different life cycle stages of the perovskite-based devices.

2.2.1 Production phase

Raw material synthesis

The three main substances that are needed for the synthesis precursor ink are methylammonium halide: CH_3NH_3X (X= I, Br, Cl), Lead halide: PbX (X= I, Cl, Br) and dimethylformamide, DMF: $(CH_3)_2NC(O)H$.

There can be three compounds which can be used as **methylammonium halide** during ink formulation:

- Methylammonium iodide (CH_3NH_3I) is an organic halide which is considered to be synthesized by combining equimolar amounts of methylamine (CH_3NH_2) and hydrogen iodide (HI) at 0 °C and stirring continuously for 2 h to obtain precipitated white solid form which is then washed multiple times to remove excess solvents. It is followed by evaporation of the white solid at 60-80 °C for one day to yield methylammonium iodide solid crystals (Upadhyaya et al. 2018).

- Methylammonium bromide (CH_3NH_3Br) and methylammonium chloride (CH_3NH_3Cl) are also considered to be synthesized in a similar way as CH_3NH_3I but instead using HBr and HCl respectively.

In case of **lead halide**, there can be three compounds which can be used during ink formulation:

- Lead iodide (PbI_2) is a salt that is considered to be synthesised via a precipitation reaction between potassium iodide KI and lead nitrate $Pb(NO_3)_2$ in a 2:1 molar ratio in water solution (Surabhi et al. 2014).
- Lead chloride ($PbCl_2$) is considered to be synthesised as a white precipitate by adding an aqueous solution of NaCl or HCl to lead nitrate solution in a 2:1 molar ratio (Perry and Phillips 1995).
- Lead Bromide ($PbBr_2$) is a white powder which is considered to be synthesised from treating lead nitrate $Pb(NO_3)_2$ with sodium bromide NaBr (Fry et al. 2020).

The ink formulation to be used for the perovskite-based device manufacturing may have different halide 'X' elements (or combination) depending on the type of device, for instance, as shown in Table 1.

Table 1: Presence of halide in each perovskite-based device

Device	Halide (X) element used during ink formulation
PePV	I or Br or both
Red PeLED	I or Br or both
Green PeLED	Br or Cl or both
Blue PeLED	Br or Cl or both

Dimethylformamide (DMF) is an organic solvent which is considered to be synthesized by the carbonylation of dimethylamine using sodium methoxide as a catalyst in the presence of carbon monoxide in methanol at 2–10 MPa and 353–373 K (Weissermel and Arpe 2008).

Intermediate precursor ink formulation

It is considered that both ***methylammonium halide*** and ***lead halide*** are dissolved in 3:1 molar ratio in ***DMF*** and stirred at room temperature for 8-10 h to obtain the perovskite precursor ink (Jung et al. 2019). There are several commercial grades of the precursor ink which are available in the market or synthesized in laboratories depending on the type of halide groups to be used.

Device fabrication

To fabricate perovskite-based devices, specific blends of perovskite precursors are incorporated in ink formulations which, during the process of production of perovskite-based devices, convert to lead halide perovskite in the form of a thin film layer. The perovskite thin films in perovskite-based devices are "synthesized" from (commercially) available perovskite precursor ink at the moment of printing (i.e. in-situ synthesis of perovskite crystalline thin films).

The deposition or printing technique is selected depending on the substrate onto which the perovskite thin film is to be deposited. For instance, the deposition of the perovskite film on flexible and rigid substrates takes place by roll to roll (R2R) and sheet to sheet techniques respectively. These are also the two precursor ink processing methods which are considered for this work.

In general, the bulk density of the deposited perovskite crystalline film is estimated to be in the order of 4.03 g/cm^3 for PePV. Considering a 500 nm-thick layer of perovskite crystalline film, the surface density of the film is equal to 2.015 g/m^2. Since the molar content of lead 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 PeLEDs, the average film thickness is much lower and estimated to be around 40 nm which corresponds to a surface density of 0.17 g/m^2 for the perovskite film and 0.06 g/m^2 for the lead in the film. However, the composition and thickness of the perovskite film are susceptible to change for PeLEDs over the course of the project. Therefore, the estimated density values for PeLEDs are only tentative.

The residual solvents left after the manufacturing are blow dried inside a ventilated oven and generated vapours are entrapped inside an activated carbon filter which is disposed-off by a specialized company.

The solvents and perovskite-based inks are handled inside fume hoods and the operating worker (varies from 1 to 2 in numbers at a time) is equipped with gloves, safety glasses, protective jackets and full face respirators.

One “source” of waste derives from a small amount of left over ink (i.e. the ink left after the printing process) present in the ink reservoir of the printer (~50 ml). The excess amount of ink is needed to (i) ensure enough supply of the ink during printing and (ii) guarantee a smooth printing process at the current production scale. At the moment it is not foreseeable if this waste stream will occur also at industrial scale and, if yes, in what amounts. For this reason, the disposal of the left over ink and emissions arising from this have been excluded from the current calculations of HSS but will be included in the full LCA (i.e. T7.3) if necessary.

Another source of waste is represented by the trimmings derived from cutting the PePV and PeLED from the roll. In some cases, there could be some irregular ink traces in the edges of the film roll that are trimmed off. The perovskite crystals in the trimmings are only present when a PePV (or PeLED) cell is printed continuously through the roll (and therefore the trimming procedure will have to cut through the perovskite layer), but in several occasions, the roll can contain several separate cells (i.e. discontinuous printing mode) and therefore the trimmings will be perovskite free. It is estimated that approximately 3% of the final roll (i.e. the output of the R2R production process) is trimmed and disposed of as solid waste. Still, the amount of perovskite thin film present on these trimmings is at the moment uncertain and estimates are not available. It is expected that only small portions of the trimmings will be contaminated with the perovskite thin film. Due to the fact that the trimmings never get in the material flow along the life cycle of the perovskite-based devices and it is highly uncertain to estimate the amount of perovskite crystals present in the trimmings, they have also been excluded from the calculations of the HSS and will be included in the full LCA, when more data on the production process will be available.

2.2.2 Use phase

Perovskite-based photovoltaics

The lifetime or usage of PePV is mainly affected by its hygroscopicity and ion migration (Meng et al. 2018). The hygroscopicity or moisture absorption of perovskite crystals is related to the environmental factors and can be induced by the relative humidity in the air or rainfall. The encapsulation of the perovskite crystals, e.g. by using titania and alumina layers, 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 of the crystals result in lower leaching concentrations of the crystals components compared with non-encapsulated crystals, it does not fully prevent leaching, especially under weak acidic conditions (Panthi et al. 2021). In addition, the possibility of the breakage of the encapsulation layer due to its mechanical damage cannot be ruled out due to the lack of stability studies on the encapsulation layer(s) under standardized conditions (Meng et al. 2018). The mechanical damage in the encapsulation layer and thus the perovskite run-off/leaching can be brought up by constant weathering and frequent mechanical impact, for example, by hails. Hailstorms are frequently experienced in several parts of the world, including Central Europe, southern Australia, certain parts of western Europe, India and China.

Upon run-off (with or without encapsulation layer breakage), the perovskite crystals start degrading and decompose 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 (Wu et al. 2020). The resultant lead halide compound(s) may further leach to soil, sewage and fresh water compartment and thus lead to its exposure to the whole ecosystem (Ligthart 2006; Panthi et al. 2021; Su et al. 2020). In the scarcity of the studies on the aspect of leaching of hazardous compounds from the perovskite-based devices, it is critical to consider the leaching scenario as one of the potential release mechanisms of perovskite crystals and the composing lead compounds in the environment during the use phase of the perovskite-based devices, at least until sufficient knowledge becomes available. For a worst case scenario, Hauck et al. 2017 estimates that approx. 20% of the perovskite film area gets damaged which results in susceptibility of methylammonium lead iodide and resulting lead and iodine ions for run-off. Based on the experiments by Hailgenaw et al. 2015, all this lead would also be emitted. So, worst case scenario can be can be estimated for 20% of perovskite becoming fully exposed to the rain water. Hailgenaw et al. 2015 observed that almost entire lead content in the perovskite crystals get released (60 to 93%) when the perovskite film is exposed to the simulated rain water with a certain pH value (pH= 4-6). With an encapsulation layer present in the perovskite-based devices, the losses of the perovskite crystals will be much lesser and assumed to be 5% to represent real life conditions.

Another factor affecting the usage of the perovskite-based devices is the halide ion migration across the interface with anode (silver layer). Under an external bias, lead halide starts to be formed at the anode side which may lead to the electrode corrosion with time and thus leads to the perovskite-based devices degradation (Dong et al. 2020). It is believed that the ion migration is rather related to the operational instability of the devices which has a direct impact on the devices lifetime and it does not contribute to any substance release from the device into the environment. Therefore, it has been kept excluded from the present HSS analysis.

Perovskite-based LED

When the PeLED is used inside the controlled and moderate environment or ambience of a consumer household, it is believed that, unlike PePV, PeLED is not subjected to any harsh weather or mechanical damage. Consequently an indoor use of the PeLED is believed to not impart the release of any substance during the use phase. On the other hand, when used outdoors, it is subjected to the same weather or mechanical damage as a PePV and thus leaches the same amount of lead in the city ecosystem per square meter as PePV.

2.2.3 End-of-life

As explained in section 2.4.2, three different EoL routes have been considered for the perovskite-based devices: recycling, landfilling and incineration. While the recycling technology is not well established and no information is available on the emissions arising from such a process, the ecoinvent tools provide the emission factors for the elements contained in the waste treated. In this case the focus has been also been posed on lead, in agreement with the considerations made in the previous paragraphs.

2.3 Compositions of perovskite precursor ink and thin film

Besides the manufacturing processes described above, in order to complete the HSS it is necessary to have detailed information of the final composition of the perovskite inks and thin film. This information was provided by the partners and it is summarized in the paragraphs below.

2.3.1 Precursor ink

The mass of each element present in one kilogram of perovskite precursor ink is shown in **Table *2*** for PePV and three different PeLEDs (green, blue and red). Separate elemental compositions of the precursor ink were received from CSEM and Uni Oxford.

For PePV, the two received compositions (one from CSEM and one from Uni Oxford) were almost the same, with slight differences in the mass fractions of the constituting elements (max std dev= 17 g observed for Iodine). The exceptions were bromine and barium which are absent in the composition list of Uni Oxford but present in that of CSEM.

For Green PeLED, four separate compositions were received (three from CSEM and one from Uni Oxford). Again there were small differences in the mass fractions of the constituting elements (max std dev= 24 g observed for carbon). One of the three CSEM's ink compositions exceptionally contains 0.2 g of lithium.

For Blue PeLED, only one composition was received from CSEM.

For Red PeLED, two separate compositions were received (one from CSEM and one from Uni Oxford). On the same pattern as for previous devices, the two compositions had slight differences in the mass fractions (max std dev= 33 g observed for carbon). CSEM uses same 0.2 g of lithium in the formulation of precursor ink for red PeLED which Uni Oxford does not.

Table 2: Elemental composition of 1 kg of precursor ink used for the fabrication of perovskite-based devices

Elements	Mass (kg)			
	PePV	**Green PeLED**	**Blue PeLED**	**Red PeLED**
Oxygen (without O from H_2O)	0.1287	0.2260	0.1836	0.1842
Hydrogen (without H from H_2O)	0.0604	0.0830	0.0694	0.0852
Carbon	0.2779	0.3974	0.2756	0.4070
Sulphur	0.0497	0.0773	0.3679	0.0590
Nitrogen	0.1074	0.1355	0	0.1528
Bromine	0.0128	0.0385	0.0260	0.0328
Iodine	0.2230	0	0	0.0438
Chlorine	0	0.0030	0.0101	0
Caesium (or Barium)	0.0071	0.0266	0.0334	0.0135
Lead	0.1329	0.0342	0.0338	0.0512
Lithium	0	0.0003	0.0002	0.0003

For the purpose of harmonization and based on the high degree of similarity between the different compositions, they were combined by taking an average composition so that there is one precursor ink composition per device, as shown in Table 2. This choice is justified by the fact that the compositions supplied by the partners at this moment are not definite and are bound to change in the future as the project progresses.

2.3.2 Perovskite thin film

After being deposited/printed on a substrate (rigid/flexible), the wet precursor ink yields a solid thin film composed of perovskite crystals. The elemental mass fractions of constituting elements in different perovskite-based devices are shown in Table 3 for 1 kg of the crystals.

For PePV, two separate compositions were received from CSEM and VTT. Also in this case, the compositions received were very close to each other (max std dev= 35 g for iodine). For green PeLED, three compositions (all from CSEM) were received which were also similar to each other (max Std Dev= 39 g of bromine with the exceptions of chlorine and caesium present in the second and third compositions respectively). For blue and red PeLEDs, only one composition was received for each device (from CSEM).

Multiple compositions are combined by taking an average composition so that there is one perovskite film composition per device, as shown in Table 3. Clearly, there is an elevation in the content percentage of lead in the crystals in perovskite thin film with respect to the content in the ink.

Table 3: Elemental composition of the 1 kg of perovskite crystals in perovskite-based devices

Elements	Mass (kg)			
	PePV	**Green PeLED**	**Blue PeLED**	**Red PeLED**
Hydrogen (without H from H_2O)	0.0066	0.0105	0	0
Carbon	0.0158	0.0251	0	0
Nitrogen	0.0368	0.0586	0	0
Chlorine	0	0.0457	0.0782	0
Bromine	0.0452	0.4425	0.2938	0.2445
Iodine	0.5315	0	0	0.2330
Caesium (or Barium)	0.0358	0.2225	0.2444	0.2033
Lead	0.3283	0.4045	0.3810	0.3170
Lithium	0	0.0023	0.0026	0.0021

NOTE*: As mentioned earlier, the presence of lead in the PePV falls under the exemption (since 2011) within RoHS directive which restricts the use of hazardous substances like lead in in electrical and electronic equipments. However, for PeLED, the RoHS directive may prove to be hindrance towards its development along the value chain.*

2.4 Other relevant information for HSS

2.4.1 Production and use phase

HSS is performed for the hazardous substances which pose unknown (high) risks because of their unknown emission/release information. Several information sources regarding emission from industrial products and process categories are however available to 'build' the unknown emission estimates of the prioritized substances. The most relevant sources are as following:

- The REACH regulation of the EU, has developed a tool, EUSES, to estimate the potential environmental risk of different chemicals. In the background report of EUSES (European Commission, 2004[3]), A-tables are provided for the emission factors (formally coined 'release factors'), that give the fraction that is emitted of a substance per specific type of process, industrial category and substance properties.
- Similarly, within REACH the "Environmental Release Category" ERC have been defined. These label the characteristics of use based on six aspects relevant from the environmental perspective, including those characteristics enabling mass flow analysis along the life cycle of a substance[4].
- A number of industry sectors have developed Specific Environmental Release Categories (spERCs) that include more detail of, for instance, the type of process used. They are available from the ECHA website[5].
- A library with risk management measures, called ECEL, determines the efficacy of diverse risk management measures in place at a workplace to reduce the indoor exposure. ECEL 3.0 is freely available as an online tool hosted as part of TNO's DIAMONDS platform at https://diamonds.tno.nl/#ecel.
- Other sources include the Dutch Emission Registration or the OECD's emission scenarios[6] or scientific literature reviews.
- Still, it could still be possible that the processes considered are not covered by the above sources and therefore an expert opinion is needed to estimate the emission factors for the hotspot scan.

To build or select the relevant emission estimates of prioritized substances from the aforementioned EUSES A-tables, certain substance and process specific properties are needed to be known. These properties are shown in **Table *4***.

Table 4: Relevant properties used for emission factors estimation from EUSES A-tables

Properties	Example
Industrial category	Chemical industry (code: 3), Electrical/ Electronic Industry (code: 4), etc.
Life cycle stage	Production, Industrial Use, Domestic use
Vapour pressure	Vapour pressure in Pa
Main category	Substances (other than intermediates) produced in a continuous production process (Code: 1b), Inclusion onto a matrix (code: 2), etc.

[3] European Commission. (2004). European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Background Report (Vol. 0, pp. 1–451).

[4] European Chemicals Agency. (2010). Use descriptor system. In Guidance on information requirements and chemical safety assessment (Version 2., p. 47). Helsinki, Finland.

[5] https://echa.europa.eu/search?p_p_id=echasearch_WAR_echaportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_count=1&_echasearch_WAR_echaportlet_doSearch=true&_echasearch_WAR_echaportlet_themeSearch=true

[6] OECD. (2014). Introduction to Emission Scenario Documents. Retrieved August 09, 2014, from http://www.oecd.org/chemicalsafety/risk-assessment/introductiontoemissionscenariodocuments.htm

Similarly, the properties which are needed to be known to select the relevant emission/release factors from the aforementioned spERCs are shown in Table 5.

Table 5: Relevant properties used for emission factors estimation from spERCs

Properties	Example
Industrial category	Coatings and Inks, Paints etc.
Life cycle stage	Formulation, use
Base	Organic Solvent, water-borne, etc.
Solute	Solid, liquid, etc.

2.4.2 End of Life phase

The calculations regarding the emissions rising from the end-of-life treatments are based on a set of tools created to calculate waste-specific inventories (i.e. a list of inputs and outputs) of different waste materials for different disposal technologies. This set of tools was developed by Gabor Doka[7] in several projects mandated by the ecoinvent organisation. The tools allow to create process inventories for advanced disposal technologies like municipal incineration and sanitary landfilling, but also for more rudimentary disposal technologies like open burning and open dumping. The underlying process models are built upon the existing models used for waste disposal in ecoinvent. The elements to be considered as being discharged into the environment during the end-of-life stage are based on the composition of waste taken in consideration (in this case the perovskite thin film that is integrated in the different perovskite-based devices).

Apart from information characterising the waste (elemental composition, heating values, degradability, burnabilities), the regionalisation (i.e. the differences in waste treatment according to the geographical location of the region where the waste is treated) requires that a range of different disposal sites are described using local parameters like climate – e.g. temperature, precipitation – and technical parameters like landfill height or gas collection rates (Doka 2020). Figure 4 gives an overview of the general process structure for the regionalised waste tools.

[7] https://www.doka.ch/home.htm

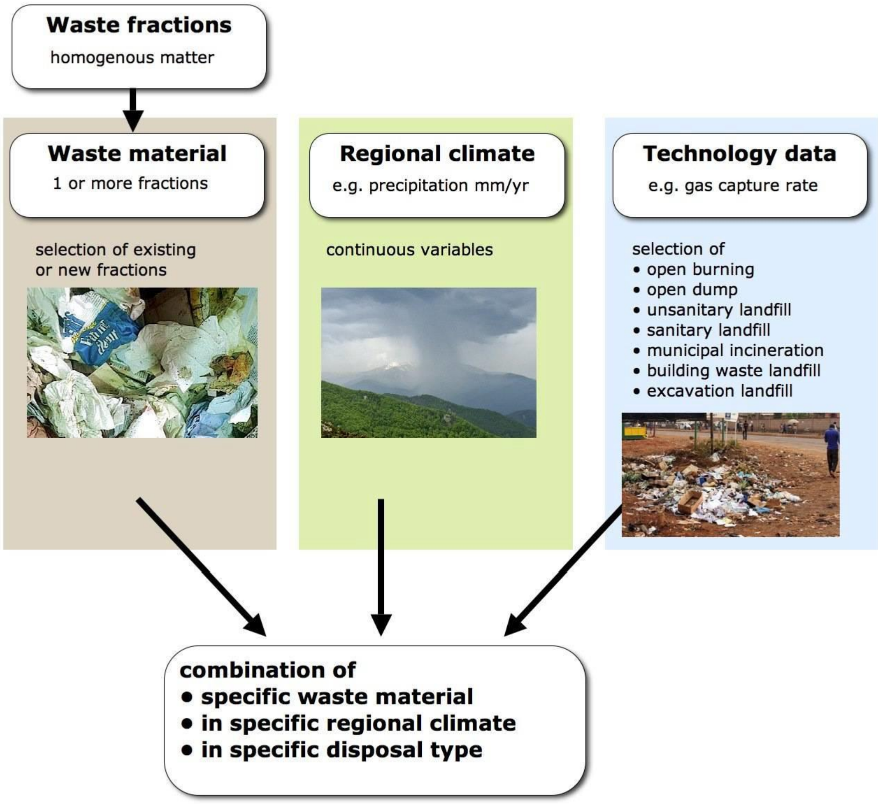

Figure 4: Overview of the general process structure for the regionalised waste tools (Doka 2020).

For the current scan, the tools regarding landfilling, waste incineration and treatment of wastewaters are considered. Assumptions are also necessary on the types of installations where the disposal of the perovskite-based devices are to take place. The end-of-life tools provide options and information for climate and installations for global, (i.e. averaged global data), Brazil, India, South Africa and Switzerland locations. For the purpose of this work, the chosen location is Switzerland as it offers the best proxy (i.e. only European country) for European waste disposal technologies and climate, albeit on the high-end of disposal technologies compared to other European countries.

It is expected that the perovskite-based devices are to be integrated in electronic equipment commercial products, such as screens, wearables (e.g. watches) and small portable electronic devices and therefore fall under the European WEEE directive. Since 2018, 'open scope' has been in place which implies that electrical and electronic equipments are *a priori* considered to be in scope in the European Union, unless specific exclusions apply. This further implies that, in practice, new products, such as clothes and furniture with electric functionality, can also fall under the WEEE directive (Adrian et al 2020). Still, in spite of this, it is to be expected that a considerable share of the small consumer products will end up in the general waste[8].

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 recycling methods for perovskite based materials, in particular with the aim to limit the emissions from lead that can arise during the use phase and, if not properly treated, during the end of life. Most of the studies reviewed

[8] As of 2017 only 59% of e-waste was recycled in northern Europe and only 53% in western Europe (Adrian et al 2020)

so far, focus on the recycling of perovskite-based PV (Binek et al. 2016; Chillar et al. 2019; Liu et al. 2021; Kim et al. 2016). 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 lead emissions during the end of life phase. Furthermore, multiple studies (Binek et al 2016, Kim et al 2016, Chillar 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., such recycling technologies are currently under developed 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 end-of-life of the perovskite-based devices, 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 NL, UK, FR and BE is 59% (Rotter et al. 2016). For this reason, it is important to consider also incineration and landfilling as plausible end-of-life treatments for the perovskite-based devices. According to the latest Eurostat data[9], 23% of the municipal waste is landfilled every year across the EU.

As the products developed in this project are fairly new in their innovation process and far from their large scale production, it is yet unsure in exactly what kind of commercial applications they will be applied and it is hard to estimate what exact recycling scenario could be applicable to the final devices or what emissions will arise from such recycling procedure. Consequently, the information retrieved for the end-of-life stage are considered to be equally relevant, valid and applicable to all perovskite-based devices (PePV or PeLED). Based on this, it is assumed that 41% of the perovskite-based devices will be recycled, 14% will be landfilled (i.e. 23% of the 59% found in the residual waste) and 45% will be incinerated.

[9] https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Municipal_waste_statistics#Municipal_waste_treatment

3 Results

3.1 Substance identification and prioritisation for HSS

Following the HSS methodology, as a first step, the substances present in the production and use phases of the life cycle of the perovskite-based devices are identified and the substance selection boundaries of the HSS are established to consider:

- In the production phase- (i) the substances which are directly used to formulate precursor ink (i.e. methylammonium halide, dimethyl formamide and lead halide), (ii) precursor ink (iii) lead and (iv) lead nitrate;
- Use phase- (i) lead and (ii) perovskite crystals;

The two substances in the use phase are also present in the end-of-life phase.

As a second step of the HSS methodology, selected substances are prioritized in Table 6. As mentioned earlier, a substance is prioritised if it is hazardous (based on acute or chronic health effects) for humans or environmental organisms and its emission level is unknown. This evaluation is made based on the available scientific evidence obtained through literature research. As shown in Table 6, prioritised substances consists of both elements and compounds in various physical states.

Table 6: Identification of the substances emitted from perovskite-based devices during their life cycle and their prioritisation for the performance of HSS

#	Relevant life cycle stage	Identified substance	Substance type	Prioritised for HSS? (Yes/No)	Reason for prioritisation/exclusion
1	Production to End-of-life	Lead	Metal element	Yes	Pb is known for its hazardous effect of acute toxicity to human health and environment, including reprotoxic effects in humans (i.e. causing interference in some way with normal human reproduction) and long-term adverse effects in the aquatic environment[10]. It is constantly present throughout the life cycle (Figure 3). Its release amounts during different life cycle stages are unknown and thus poses **unknown risk**.
2	Production	Lead nitrate	Solid compound	Yes	Hazardous effect of $Pb(NO_3)_2$ include acute toxicity to human health and environment, including reprotoxic effects in humans (i.e. causing interference in some way with normal human reproduction) and long-term adverse effects in the aquatic

[10] https://pubchem.ncbi.nlm.nih.gov/compound/5352425

					environment.[11] Its release amount is unknown and thus poses **unknown risk**.
3	Production	Methylammonium halide (X= Cl, Br, I)	Solid compound	Yes	Hazardous effects of CH_3NH_3X include irritation of eye, skin and respiratory tract[12]. Its release amount is unknown and thus poses **unknown risk**.
4	Production	DMF	Liquid compound	Yes	Hazardous effects of DMF to humans include allergy, asthma symptoms, skin damage and serious eye irritation. However, it does not show any significant hazardous environmental effects.[13] Its release amount is unknown and thus poses **unknown risk**.
5	Production	Lead halide	Solid compound	Yes	Hazardous effect of PbX_2 include acute toxicity to human health and environment, including reprotoxic effects in humans (i.e. causing interference in some way with normal human reproduction) and long-term adverse effects in the aquatic environment[14]. Its release amount is unknown and thus poses **unknown risk**.
6	Production	Precursor ink	Liquid compound	Yes	Both methylamine (CH_3NH_3) and phenethylamine ($C_8H_{11}N$) groups of the precursor ink are known for their acute toxicity and skin irritation effects. They can also be very toxic to aquatic life with long-lasting effects when released to the environment[15]. The release amount of the ink is unknown and thus poses **unknown risk**.
7	Production to End-of-life	Perovskite crystals	Solid compound	Yes	The presence of lead in the perovskite crystals induces inherent lead toxicity (human and environmental) to the crystals. The release amount of the crystals is unknown and thus poses **unknown risk**.

[11] https://pubchem.ncbi.nlm.nih.gov/compound/24924
[12] https://pubchem.ncbi.nlm.nih.gov/compound/519034
[13] https://pubchem.ncbi.nlm.nih.gov/compound/6228
[14] https://pubchem.ncbi.nlm.nih.gov/compound/24831
[15] https://pubchem.ncbi.nlm.nih.gov/compound/Phenethylamine

3.2 Execution of HSS

The following sections show the results obtained from executing the HSS for the prioritised substances (see Table 6) emitted from perovskite-based devices. The HSS is performed separately on each prioritised substance. The HSS takes the amount of substance present in the use phase as a reference, and the upstream and downstream processes are scaled in order to comply with this reference value. In the current case, the reference values is 1000kg of perovskite crystals in the thin film present in a perovskite-based device.

The percentages indicated in the graphs represent the release coefficients from that specific process for the substance under consideration and the quantities represent the amounts of emissions of that substance compared with the 1000 kg as reference.

3.2.1 Perovskite-based PV

Perovskite crystals flow

The flow of the perovskite crystals through the life cycle of the PePV is shown in Figure 5. The use phase is central in the hotspot scan and serves as the reference from which the upstream production stage and downstream end-of-life stage are calculated in order to ensure the production of 1000 kg of perovskite crystals applied in a PePV.

The air, water and soil are the three environmental compartments to which emission of the perovskite crystals are considered. The release or emission amounts in air includes emission to both indoor and outdoor air. A distinction between the two air types is made, however, during PePV fabrication because it is the only point when the information on the used engineering controls are known from the device fabricating partners in the project. The release or emission of the perovskite crystals to the second environmental compartment, i.e. water, consists of emission to waste (sewage) water reaching wastewater treatment plants (WWTP) during production phase. The sources of the HSS estimates are colour coded and shown as legend in Information on substance and process specific properties which were used to compile release factors from EUSES A-tables (see **Table *4***) are- Industrial code: 4; Life cycle stage: Industrial Use; Vapour pressure: >100 Pa; Main category: Inclusion onto a matrix (code 2).

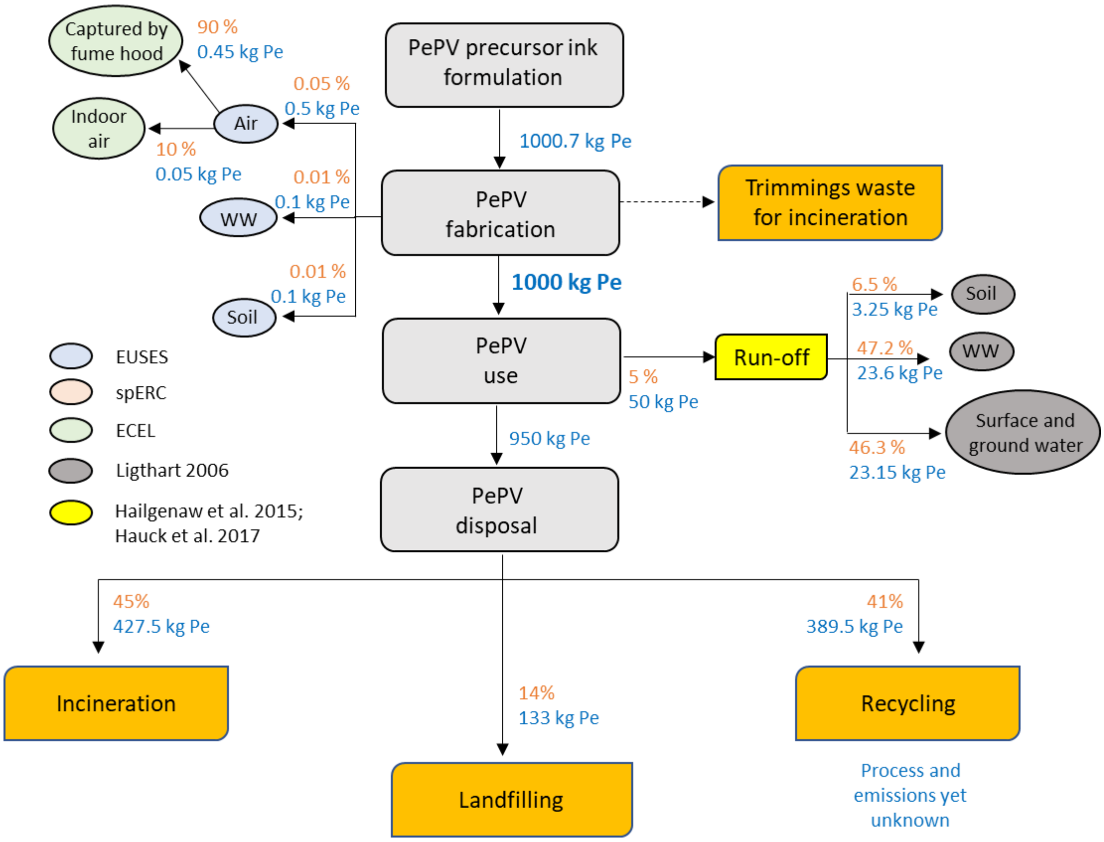

Figure 5: HSS of the perovskite crystals (Pe) release along the PePV life cycle; exclusion of the trimming waste is shown with a dashed arrow

As it can be seen from Figure 5, small losses of perovskite crystals occur during the production stage (0.7 kg) where most of the losses end up in the air (0.5 kg). The perovskite crystals (in the form of Pb^{2+} ions) run-off due to the localised breaches of the encapsulation during the use phase is estimated to amount to 50 kg over its entire service lifespan (5% of the 1000 kg perovskite crystals) which has been obtained on the basis of information extracted from Hailgenaw et al. 2015 and Hauck et al. 2017, and extrapolated from the lead run-off estimation in the following section. Out of 50 kg, 23.6 kg and 23.15 kg of Pe leach into the wastewater and fresh water (surface and ground water). The remaining amount, i.e. 3.25 kg of perovskite crystals leach into the soil.

At the end, 950 kg of perovskite crystals (out of 1000 kg present in the use phase) are to be disposed of during the end-of-life stage. Based on the information gathered from the scientific literature and public reports (section 2.4.2), highest amount of perovskite crystals are disposed of through incineration (45% of the perovskite crystals reaching end-of-life), followed by recycling through which 41% of the perovskite crystals reaching end-of-life are disposed of and the remaining 14% which accounts for the landfilling of the perovskite crystals reaching end-of-life. It is not possible to further estimate the losses of the perovskite to different environmental compartments during end-of-life because of the limitation of the ecoinvent tool which estimates only the elemental emissions (and not the emission of compounds like perovskite crystals).

Lead metal and lead compounds flow

The flow of lead metal during different life cycle stages is shown in the HSS depicted in Figure 6. As usual, the reference point of the hotspot scan is set at the use phase with 1000 kg of perovskite crystals containing 328.3 kg of lead. From this reference value, the quantities of lead necessary for the upstream production and downstream end-of-life processes are calculated, taking into account the loss of lead at every step. The sources of the HSS estimates are colour coded and shown as legend in Figure 6.

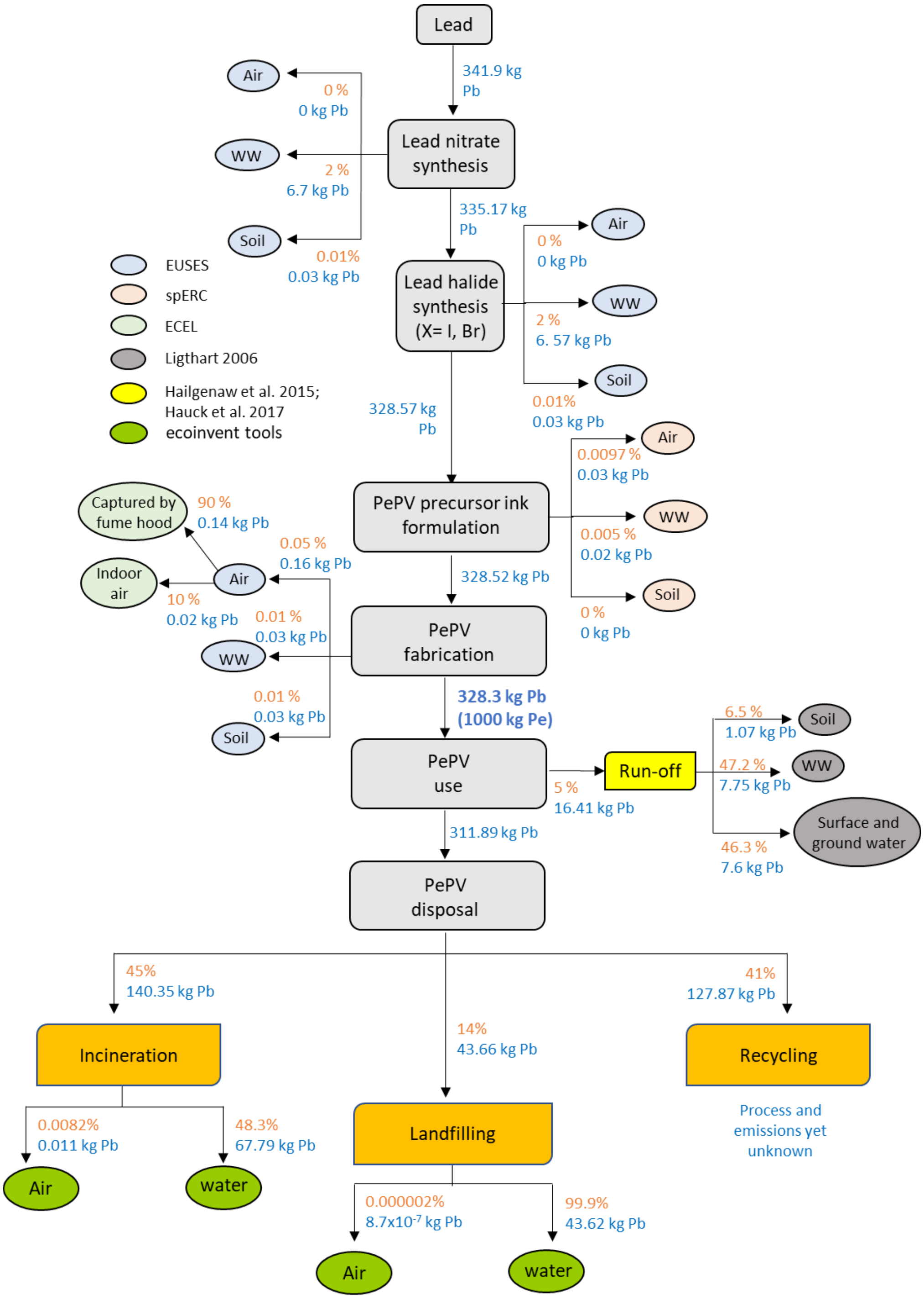

Figure 6: HSS of the lead metal (Pb) release along the PePV life cycle

The released amounts of lead metal in each environmental compartment is summarised in Table 7. 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. A distinction between the two air types is made, however, during PePV fabrication because information on the used engineering controls were known from the device fabricating partners in the project. The release or emission of the lead to the second environmental compartment, i.e. 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 both surface and ground waters as well as wastewater. For end-of-life stage, the release in water implies release in surface and ground waters. The third emission compartment (soil) encompasses the emissions generated during any life cycle stage which are disposed or leached to the ground.

Table 7: Estimates of lead release amounts to each environmental compartment for each life cycle stage for 1 ton of perovskite crystal used in PePV

LC stage/phase		Process	Lead release amounts (kg) in			
			Air#	Water	Soil	Total
Production	**Raw material synthesis**	Lead nitrate synthesis	0	6.7*	0.03	6.73
		Lead halide synthesis	0	6.57*	0.03	6.6
	Intermediate	Precursor ink formulation	0.03	0.02*	0	0.05
	Final product	PePV fabrication	0.16	0.03*	0.03	0.22
Use		PePV use	0	7.6^ 7.75*	1.07	16.41
End of Life	**PePV disposal**	Incineration	0.011	67.79^	0	67.8
		Landfill	8.7×10^{-7}	43.62^	0	43.62
		Total (kg)	0.2	140.08	1.16	141.44

#Includes release to both indoor and outdoor air
*Includes release to wastewater
^Includes release to surface water and ground water

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 perovskite the crystalline film in the PePV during printing over a specific substrate. There are four processes in the production phase which lead to the release of lead into the environment: lead nitrate synthesis; lead halide synthesis, precursor ink formulation and PePV fabrication (Table 7). Out of the four processes, the lead nitrate synthesis emits the highest amount of lead metal to the environment (6.73 kg), almost all amount to the wastewater (6.7 kg). A similar observation holds true for lead halide synthesis. In Table 8, the individual released amounts of the lead nitrate and lead halide (iodide and bromide) are also shown.

During the fabrication of PePV, the highest amount of lead is estimated to be released to air in Table 7 (0.16 kg). With the use of a fume hood as a worker exposure control measure, the release amount of lead to the indoor air is substantially reduced to 10% (0.02 kg) and the rest of the lead 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 lead emission to the environment but it is kept excluded from the scope of the current scan. The total lead emissions into the environment during the production phase amounts to 13.6 kg or approx. 10% of the total lead emission over whole life cycle.

Table 8: Estimates of release amounts of lead compounds to each environmental compartment during the production of 1000 kg of perovskite crystal used in PePV

Compound	Produced amount (kg)	Released amount (kg)			
		Air#	Water*	Soil	Total
Lead nitrate	547.04	0	10.94	0.05	10.99
Lead iodide$	746.46	0	14.92	0.07	14.99
Lead bromide$	594.25	0	11.88	0.06	11.94

Includes release to both indoor and outdoor air

* Includes release to wastewater

$ Either lead iodide or lead bromide is used during the PePV production

Use

During the use phase, the perovskite film can leach a total amount of 16.41 kg of lead over its assumed entire service lifespan (i.e. 5% of the lead 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% of the total lead 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 production phase amounts to approx. 12% of the total lead emission over whole life cycle.

End-of-life

An estimated total of 311.89 kg of lead reaches the end-of-life stage out of which 140.35 kg is estimated to be disposed of via incineration (approx. 45%) and 14% is disposed of via landfilling (43.66 kg). During incineration, it is estimated that 0.011 kg of lead is released to the air and 67.79 kg is released to the surface and ground waters. The latter represent approx. 48% of the total lead emission over the whole 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 lead (i.e. 43.62 kg) is leached to water which approx. 31% of the total lead emission over the whole life cycle. Therefore, the end-of-life stage accounts for approx. 79% of total lead emission. Considering this situation, it is essential to implement recycling strategies to recover the lead and avoid the heavy emissions generated by these end-of-life scenarios, in particular landfilling. In fact, even if in the case considered here only 14% of the perovskite thin film is disposed of by landfilling, approximately 100% or the lead contained in the device can leach to the water compartment.

Other substances flow

To select the relevant release factors and estimate the release amounts of methylammonium halide, DMF and precursor ink, the properties are shown in Table 9 which were used in EUSES A-tables (see **Table *4***) and spERCs (see Table 5).

Table 9: Information on substance and process specific properties used to compile release factors from EUSES A-tables and spERCs

Substance	Industrial Category	Life cycle stage	Vapour Pressure (Pa)	Main category		Used Table
				Code	Glossary text	
Methylammonium halide	3 (Chemical industry: Chemicals used in synthesis)	Production	<1	1b	Substances (other than intermediates) produced in a continuous production process	A1.1
DMF	3 (Chemical industry: Chemicals used in synthesis)	Production	100-1000	1b	Substances (other than intermediates) produced in a continuous production process	A1.1

Process	Industrial Category (IC)	Life cycle stage	Base	Solute	spERC	
					Code	Glossary text
Precursor ink	Coatings and Inks	Formulation	Organic solvent borne	Solid	CEPE SPERC 2.2a.v1 (CEPE M1)	CEPE 3 - Formulation of Organic Solvent Borne Coatings and Inks – Solids

The HSS estimates for respective release amounts of these substances are shown in Table 10. These substances are restricted to only 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 methylammonium halide (total release: 45.01 kg; dominant release in water: 44.79 kg).

Table 10: HSS estimates of release amounts of other substances (apart from perovskite crystals, lead and lead compounds) to each environmental compartment during the production of 1000 kg of perovskite crystals (with 328.3 kg Pb) used in PePV

Compound	Produced amount (kg)	Released amount (kg)			
		Air#	Water*	Soil	Total
Methylammonium halide (X= I or Br)	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

Includes release to both indoor and outdoor air
* Includes release to wastewater

Thus, from Figure 6 and Tables 7, 8 and 10 the release of prioritised substances is estimated to occur dominantly to the air and water compartments during the entire life cycle of PePV, with lower released amounts to soil.

3.2.2 Perovskite-based LEDs

Perovskite crystals flow

The HSS for perovskite crystals flow in the case of PeLED is same as PePV and thus follows the same release amounts as shown in Figure 5.

Lead metal and lead compounds flow

Figure 7 shows the release of lead metal during different life cycle stages for a green PeLED. The average content of lead in PeLED is generally greater than in PePV per 1000 kg of perovskite crystals in the perovskite thin film.

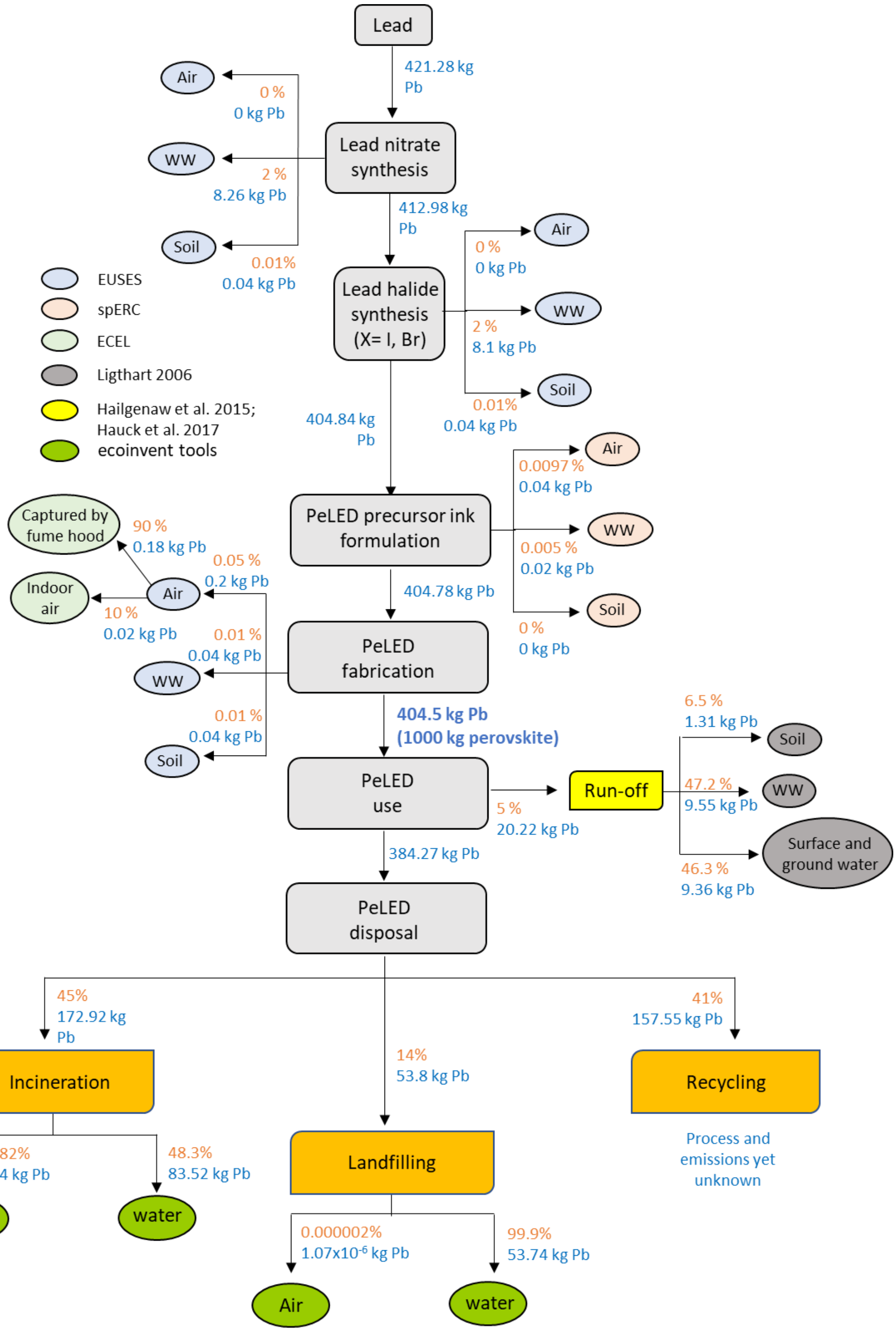

Figure 7: Hotspot scan of the lead release along the green PeLED life cycle

Depending on the colour of the PeLED, the content of the lead changes, as already shown in Table 2 and Table 3. The flow of the lead shown in Figure 7 is for producing 404.5 kg of lead in green PeLED which corresponds to 1000 kg of perovskite crystals. The release amounts of lead in each environmental compartment is shown in Table 11. The sources of information used during the building of the scan are colour coded and shown as legend in Figure 7. The environmental compartments and their implications are same as considered for PePV.

Table 11: Estimates of lead release amounts to each environmental compartment for each life cycle stage for 1000 kg of perovskite crystal used in green, blue and red PeLED

LC stage/phase		Process	Lead release amounts (kg) from green PeLED in			
			Air#	Water	Soil	Total
Production	**Raw material synthesis**	Lead nitrate synthesis	0	8.26*	0.04	8.30
		Lead halide synthesis	0	8.1*	0.04	8.14
	Intermediate	Precursor ink formulation	0.04	0.02*	0	0.06
	Final product	PeLED fabrication	0.2	0.04*	0.04	0.28
Use		PeLED use	0	9.36^ 9.55*	1.31	20.22
End of Life	**PeLED disposal**	Incineration	0.014	83.52^	0	83.53
		Landfill	1.07×10^{-6}	53.74^	0	53.74
		Total (kg)	0.25	172.59	1.43	174.27
LC stage/phase		**Process**	**Lead release amounts (kg) from blue PeLED in**			
			Air#	**Water**	**Soil**	**Total**
Production	**Raw material synthesis**	Lead nitrate synthesis	0	7.94*	0.04	7.98
		Lead halide synthesis	0	7.78*	0.04	7.82
	Intermediate	Precursor ink formulation	0.04	0.02*	0	0.06
	Final product	PeLED fabrication	0.19	0.04*	0.04	0.27
Use		PeLED use	0	8.82^ 8.99*	1.23	19.05
End of Life	**PeLED disposal**	Incineration	0.014	83.78^	0	83.79
		Landfill	1.07×10^{-6}	53.91^	0	53.91
		Total (kg)	0.24	171.28	1.35	172.88
LC stage/phase		**Process**	**Lead release amounts (kg) from red PeLED in**			
			Air#	**Water**	**Soil**	**Total**
Production	**Raw material synthesis**	Lead nitrate synthesis	0	6.6*	0.03	6.63
		Lead halide synthesis	0	6.47*	0.03	6.50
	Intermediate	Precursor ink formulation	0.03	0.02*	0	0.05

	Final product	PeLED fabrication	0.16	0.03*	0.03	0.22
Use		PeLED use	0	7.34^ 7.48*	1.03	15.85
End of Life	**PeLED disposal**	Incineration	0.014	84.47^	0	84.48
		Landfill	1.08×10^{-6}	54.36^	0	54.36
		Total (kg)	0.20	166.77	1.12	168.09

#Includes indoor and outdoor air
*Implies release to wastewater
^Implies release to surface water and ground waters

Production

The underlying processes constituting the production phase of PeLED (green, red or blue) are same as PePV, i.e. Lead nitrate synthesis; Lead halide synthesis, Precursor ink formulation and PePV fabrication (Table 11). For the PeLED (green, blue and red), the highest amount of release of the lead occurs during the synthesis of lead nitrate (8.30 kg for green PeLED, 7.98 kg for blue PeLED and 6.63 kg for red PeLED), followed by lead halide synthesis (8.14 kg for green PeLED, 7.82 kg for blue PeLED and 6.50 kg for red PeLED). For both processes, almost all of the lead release occurs to the water (Figure 7 and Table 11). In Table 12, the individual released amounts of the lead nitrate and lead halide (bromide and chloride) are also shown, for instance, for green PeLED.

Table 12: Estimates of release amounts of lead compounds to each environmental compartment during the production of 1000 kg of perovskite crystals used in green PeLED

Compound	**Produced amount (kg)**	**Released amount (kg)**			
		Air#	**Water***	**Soil**	**Total**
Lead nitrate	674.05	0	13.48	0.07	13.55
Lead bromide$	732.19	0	14.64	0.07	14.71
Lead chloride$	554.63	0	11.09	0.05	11.14

Includes indoor and outdoor air
* Includes release to wastewater
$ Either lead bromide or lead chloride is used during the green PeLED production

As shown by Table 11, the highest release of lead during the PeLED fabrication is estimated to be equal for both water and soil (0.04 kg for green and blue PeLED and 0.03 kg for red PeLED). The lead release to the air is much higher (0.2 kg for green PeLED, 0.19 kg for blue PeLED and 0.16 kg for red PeLED) and with the use of fume hood, the lead release amount to the indoor air is further reduced to a very low value (10%). The total lead emissions into the environment during the production phase amounts to 16.78 kg, 16.13 kg and 13.4 kg for green, blue and red PeLEDs respectively which are approx. 7-9% of the total lead emission over whole life cycle of the respective PeLEDs.

Use

There is no release estimated for PeLED during its use if it is used inside the controlled and moderate environment or ambience of a consumer household which inhibits any type of element or substance release. However, for outdoor uses, the lead run-off of 20.22 kg is estimated over its assumed entire service lifespan (i.e. 5% of the lead initially available in the use phase). Out of the 20.22 kg, 9.36 kg and

9.54 kg are estimated to leach into the fresh water (surface and ground waters) and wastewater respectively. Each of these fractions represent approx. 5% of the total lead emission over the whole life cycle (Table 11). The rest, i.e. approx. 1.31 kg, leaches into the 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. It is undoubtedly higher released amount than in production phase.
Similarly, the release amounts during the use phase of blue PeLED is estimated to be 19.05 kg (approx. 11% of the total lead emission over the whole life cycle). For red PeLED, the release amount is estimated to be 15.85 kg (approx. 9.4% of the total lead emission over the whole life cycle). Individual environmental releases for all three coloured PeLEDs are shown in Table 11.

End-of-life

The two main processes accounting for PeLED end-of-life are incineration and landfill, same as PePV. For green PeLED, for instance, an estimated total of 384.27 kg of lead reaches the end-of-life stage (Figure 7) out of which 172.92 kg is estimated to be disposed of via incineration (approx. 45%) and 14% is disposed of via landfilling (53.8 kg). During incineration, it is estimated that 0.014 kg of lead is released to the air and 83.52 kg is released to the water (surface and ground water). The latter represent approx. 48% of the total lead emission over the whole 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 lead (i.e. 53.74 kg) is leached to the water which represents approx. 31% of the total lead emission over the whole life cycle. Therefore, the end-of-life stage accounts for approx. 79% of total lead emission. Considering this situation, it is essential to implement recycling strategies to recover the lead and avoid the heavy emissions generated by these end-of-life scenarios, in particular landfilling.

Other substances flow

The production stage of the PeLED involves the release of the substances other than perovskite crystals, lead and lead compounds. They are thus same as those prioritised for PePV and with the same properties as shown in Table 9. Their respective release amounts are shown in Table 13, for instance, for green PeLED. The highest released amount is estimated for DMF solvent (154.49 kg) which is dominantly released in wastewater (146.44 kg). The second highest release is estimated for methanol (51.92 kg) which is dominantly released in air (32.05 kg), followed by methylammonium halide (44.15 kg). Thus, during the production phase of the PeLED, the release of prioritised substances is estimated to occur dominantly to the air and water compartments, with lower released amounts to soil.

Table 13: Estimates of release amounts of other substances to each environmental compartment during the production of 1000 kg of perovskite crystal used in green PeLED

Compound	Produced amount (kg)	Released amount (kg)			
		Air#	Water*	Soil	Total
Methylammonium halide (X= Br or Cl)	2196.57	0	43.93	0.22	44.15
DMF	7321.9	7.32	146.44	0.73	154.49
Precursor ink	11837.43	1.15	0.59	0	1.74

Includes release to both indoor and outdoor air
* Includes release to wastewater

3.2.3 Perovskite-based LiFi

As the manufacturing process of the PeLiFi device consists in the mounting of different PeLED devices and does not involve the production of different PeLEDs, it is reasonable to assume that there are no other emissions of substances or elements different than those arising from the PeLEDs. Similarly, the PeLiFi use phase occurs in the same way as PeLED. In addition, PeLiFi devices should be subjected to the WEEE directive, therefore similar consideration to the end-of-life of the other perovskite devices should apply. Based on these observations, the HSS of the PeLiFi device will follow the same flow as shown in Figures 5 and 7 and Tables 11-13.

In addition, PeLiFi uses visible light as data transfer medium. The three coloured PeLEDs, i.e. blue, green and red, operate in the wavelength spectrum ranging from 450 to 750 nm. This spectrum lies outside the wavelength spectrum of UV rays (280 to 315 nm) or X rays (0.01 to 10 nm) which are known for their ionization potential causing alteration to human DNA's molecular structure and thus are harmful to humans (Roy 2017). Thus, the visible light spectrum emitted by the PeLiFi (or PeLED) are free from such harmful effects.

Although there is no study dealing with human or environmental impact of PeLiFi (or PeLED), but in general, the probability is low that artificial lighting for visibility purposes induces acute pathologic conditions, since expected exposure levels are much lower than those at which effects normally occur, and are also much lower than typical daylight exposures (SCENIHR, 2012). Some studies carried out on LED show some mild negative effects. For instance, the production of skin pigmentation surrounded by erythema (skin redness) has been observed even by visible light emitted by LED but it disappears in less than 2 hours (Mahmoud et al., 2010). The other negative effect has been observed to be posed by the blue LED lights which are the most damaging light to human eyes. Fortunately, blue lights can only reach the retina if the LED is directly viewed (Ticleanu & Littlefair 2015). Exposure to blue light at night (independent of lighting technology) while awake (e.g. shift work) may, however, be associated with an increased risk of breast cancer and also cause sleep, gastrointestinal, mood and cardiovascular disorders. The intensity of the light is important in this case. Low light levels, e.g. 100 lx during night reading, may give an adverse health effect if blue light is used (SCENIHR, 2012).

The other possible hazard is if the LED is broken which may emit hazardous lead metal vapours. However, during a test of LED lights, only a small amount of heavy metal concentration was found which was estimated to be non-lethal (Sodhi and Johnson 2015).

4 DIAMONDS Hotspot Scan: an online tool

4.1 Rationale for building a tool

There are four reasons why we believe it is important to build upon our experience and expertise and develop the HSS into an online tool, i.e. :

1. ***The possibility to augment the classical written report with a digital version***
   To perform a HSS, a lot of information needs to be gathered from diverse tables in different documents (e.g. EUSES, spERCs), several calculations are needed to be done and all this information needs to be brought together and visualized to a user in a comprehensible manner. All of these tasks are time-consuming and prone to human errors. A substantial part of this work can be automated to systematically guide and assist the user and avoid unnecessary mistakes.
   Where a written report provides an excellent way to capture all important aspects into detail, a digital version augments this with a level of interactivity and with providing insight in the effects of design changes. Digitization also helps to create Hotspot scans in a systematic manner with a standardized format making it easier to compare different scans with each other.
2. ***Allowing Perocube members to make changes to the digital version and see the effects after the deliverable is finalized.***
   The HSS described in this deliverable is a one-time reflection on the current scenario. Over time, the scenario may change or underlying information may change. A digital version of the HotSpot Scan allows the Perocube members to keep the scan up-to-date or get insight on how the new situation effects the HSS outcome. Obviously, an expert opinion may still be advised as a digital version is never a replacement for an expert's manual advice.
3. ***Assist Perocube members as well as other users in performing new HotSpot Scans***
   The development of an online HSS tool that is available to the public will allow Perocube members as well as any other interested (industrial) user outside the Perocube project to get initial insights on possible focal points for completely different scenarios. It is, however, important to note that the currently developed version is still limited in scope and should be seen as a good starting point for future improvements in other projects.
4. ***Allow future projects to further develop and extend the HotSpot Scan***
   The LICARA Innovation Scan, developed in the previous task, was based on earlier developed versions that were initiated in previous projects. This allowed us to finalize the LICARA Innovation Scan into a mature tool. For the HotSpot Scan it is important to realize we are at the very beginning. By developing and sharing this first version, we intend to find future projects that are willing to bring the tool to further maturity.
5. ***Offer the community a portfolio of complementary tools to implement safe-by-design principles***
   The HostSpot Scan is not the only tool running on the DIAMONDS platform. It is a new addition to a broader vision to create a sustainable portfolio of complementary online tools that can help industry, academia and regulators in all kinds of safe-by-design aspects. In task 7.1 we

finalized the LICARA Innovation Scan (and LICARA nano Scan) allowing a qualitative (tier-0) approach to perform a risk-benefit analysis. The currently developed HotSpot Scan follows as a tier-1 assessment indicating important focal points. Some information for the HSS was obtained from our earlier developed online risk management measure library, called ECEL. There will be more online tools we are already working on in the area of risk assessment and exposure assessment, including a decision support system that connects all these tools and helps users in making safe-by-design choices.

4.2 Background modular approach

As part of deliverable D7.1, we developed the "LICARA Innovation Scan" as an online tool to assist in the execution of a tier-0 risk-benefit analysis. The LICARA Innovation Scan was deliberately built in a generic modular fashion. In essence, the LICARA Innovation Scan consists of a set of questions (captured in a Questionnaire Module), a set of algorithms (captured in a Script Module), a set of visualizations (captured in a Visualization Module) and an integrating component (captured in a Scan Module) that brings all components together. Due to this generic approach, it is possible to develop new online tools using the same building blocks.

Taken together, the execution of the tier-1 hotspot scan in this deliverable was assisted by the development of a follow-up online tool, called the Hotspot Scan. The Hotspot Scan was built upon the generic structure of the LICARA Innovation Scan. The Hotspot Scan assists users to determine release factors (based on available spERCs and release categories in EUSES) automatically to produce hotspot scan workflow diagrams by simply answering a number of questions. We intend to release the Hotspot Scan to the public and further improve the tool in future projects.

4.3 Sustainable Platform

After their initial development within a project, it always remains a challenge to keep an online tool properly maintained in the years after the project has been completed. To alleviate this, TNO has developed an online platform, called DIAMONDS, that can be used as a generic backbone for scientific tools. Tools developed on this generic backbone can become more sustainable as the overall maintenance is shared and tools can benefit from the generic building-blocks of the platform.

The DIAMONDS platform already offers the LICARA nanoSCAN and the LICARA Innovation Scan to the public. In addition, a library with risk management measures, called ECEL, is also available as a publicly available online tool on the platform. ECEL was used in this project to determine the efficacy of diverse risk management measures in reducing the exposure to humans. As part of this deliverable, we have now extended the library of online tools available to the public with the novel Hotspot Scan.

4.4 Structure of the tool

Figure 8 gives a schematic view of the structure of the tool. The main steps that a user goes through are indicated in three columns explained in the green boxes. One step is the gathering of information, outside of the tool, that is needed in the second step. In the second step, the user starts filling in answers to the questions asked by the tool. These are questions to:

a) define the steps in the life cycle workflow that are relevant for this product/substance, i.e. first we have a production step, then a formulation step, then use step and then an end-of life step. The tool allows maximally 7 steps to be defined.

b) Answer simple questions about the process to allow the tool to automatically suggest a SPERC or EUSES document and the corresponding specific release factors (in %).
c) Define the final release factor percentages by accepting the automatically suggested values (if it was possible) or fill in these percentages manually.

In the final step, the tool uses all provided information from the questionnaire and starts calculating all kinds of values, such as the actual amounts and aggregated percentages etc. These calculated values together with the information about the steps of the workflow are used to automatically build up result visualizations (based on standardized visualization templates). The user can inspect three kinds of outcomes, i.e. the life cycle workflow, the flows from waste to environment and the accumulation of all flows into each environmental compartment. These visualizations are discussed in more detail in the subsequent sections.

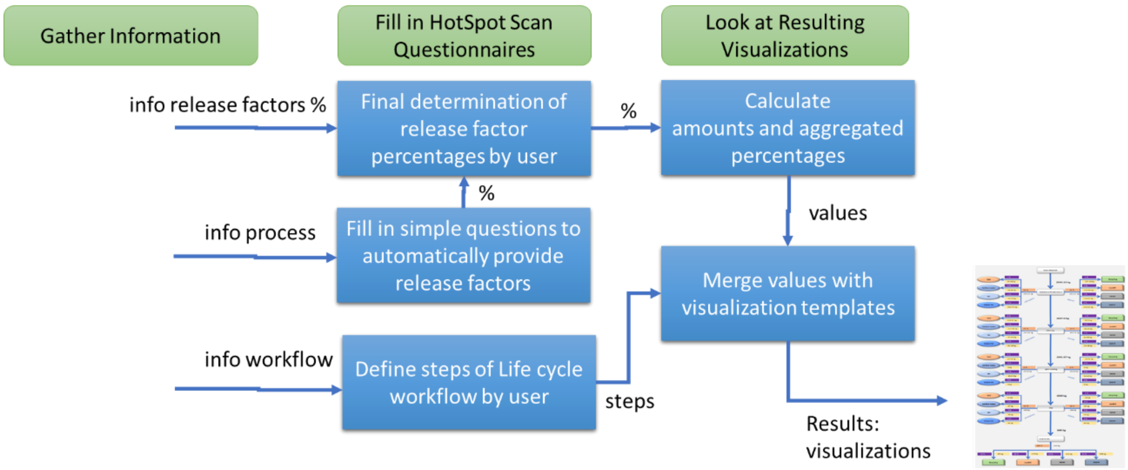

Figure 8: Schematic diagram of the structure of the Hotspot Scan tool

4.5 Resulting Implementation

4.5.1 Registration and login

On the initial landing page (https://diamonds.tno.nl/#hotspotscan) a black LOGIN/REGISTRATION button is available in the top-right corner. This button brings up a login page, which is depicted in Figure 9. Registered users can directly login, but first-time visitors need to register a DIAMONDS account. A link to the registration form is provided on the bottom-right of the login-page. After registration is completed, users get an email to confirm their registration after which they can directly login.

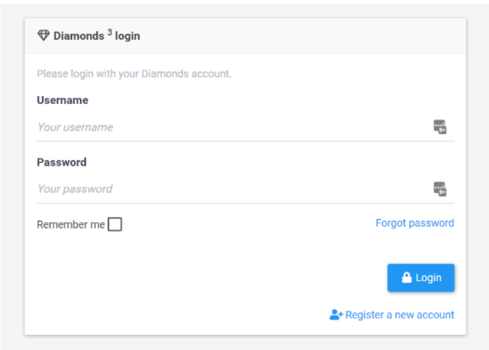

Figure 9: Screenshot of login with registration link.

Once logged in, users can choose between the available tools by clicking on one of the available tiles (see Figure 10). Users can simply click on the new Hotspot Scan tile (just below "Private projects") to start the Hotspot Scan. Note that both ECEL and LICARA Innovation Scan are also available under the "Publicly available tools" because they are already made freely available to the public. After the launch of the Hotspot Scan, its tile will also become available under "Publicly available tools" instead of "Private projects".

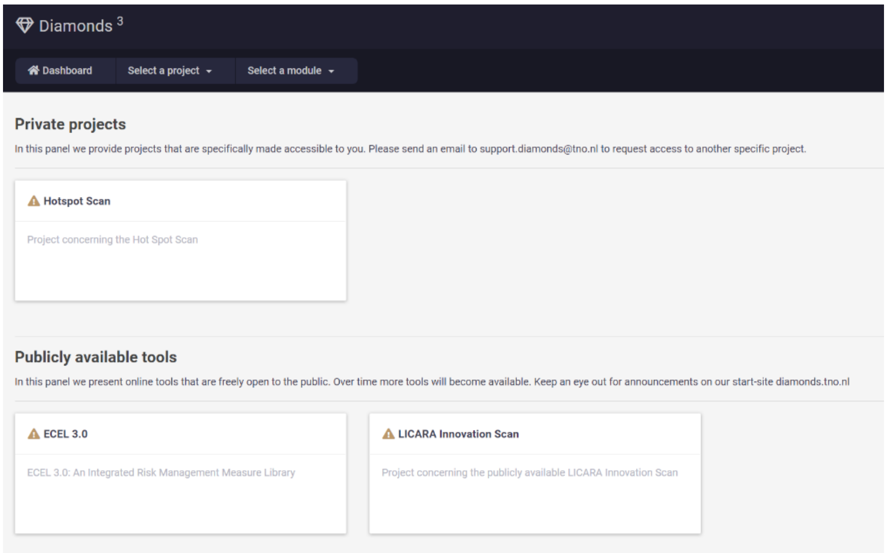

Figure 10: Screenshot of homepage shown directly after login. Users can click on any of the available tiles to start the corresponding tool. Besides the already available ECEL and LICARA Innovation Scan, the new Hotspot Scan is now also available.

4.5.2 Starting with defining a new scan

After choosing the Hotspot Scan tile, users start the Scan module and have the option to continue with the Hotspot Scan (by clicking on that tile) or bring up generic Help information via the "?Help" Tab (see Figure 11). In the future, different types of Hotspot Scans might become available as different tiles.

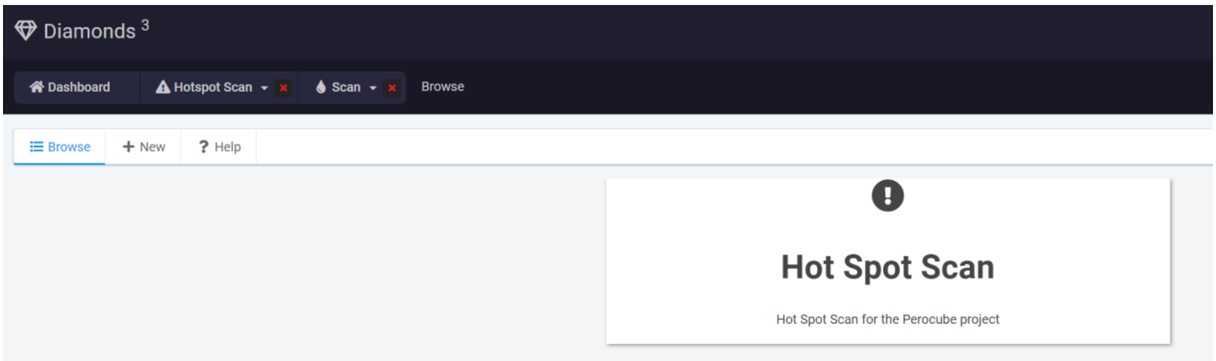

Figure 11: Screenshot of start of the Scan module, where users can choose which type of Scan to continue with (only "Hotspot Scan" is available) or read the help page via the ?Help Tab.

After this choice, the user is presented with all his/her previous runs that have been saved, as depicted in Figure 12. The user can decide to select one of the available previous runs or start a completely new run (via "> New Run" Tab between blue Summary Tab and "? Help" Tab). When starting a completely new run, the user can provide a name and this run will be saved. In future visits, this run will now also be available in the list of available runs. The subsequent experience is similar to having selected one of the available previous runs except that in the latter, the previously provided answers to the questions are loaded and presented as pre-filled answers in the subsequent pages.

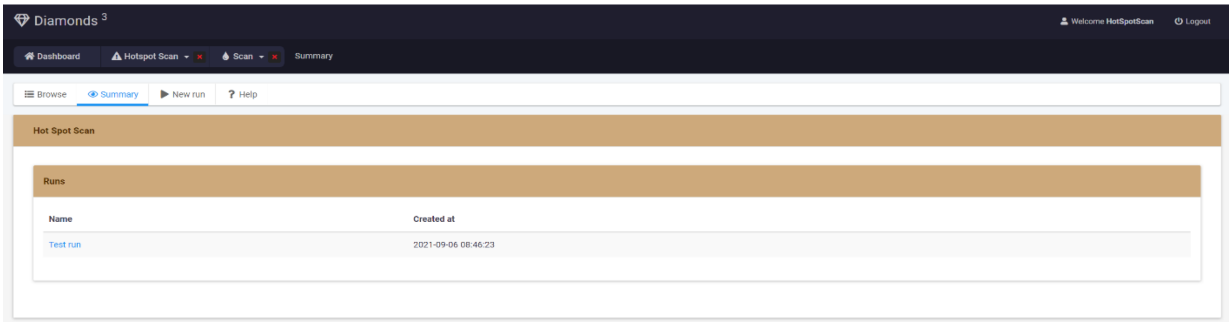

Figure 12: Screenshot of page with previously saved runs. The ">New run" Tab allows the possibility to start a new scan run. Alternatively, clicking on an existing run one can continue with that particular run.

Before starting the hotspot scan, introduction pages are presented to the user. These introductory pages can always be revisited at a later time by clicking on the "Hotspot Introduction" Tab. The introduction pages explain what the Hotspot Scan is (see Figure 13). Throughout the tool, users can choose to navigate through all pages in chronological order by using "<- BACK" or "SAVE & NEXT ->" buttons at the bottom. Alternatively, users can click on the top tabs to quickly navigate through the main components ("Hotspot Introduction", "Hotspot Scan", "Hotspot Result") and/or click the underlying subpages presented as numbered steps just below the top tabs.

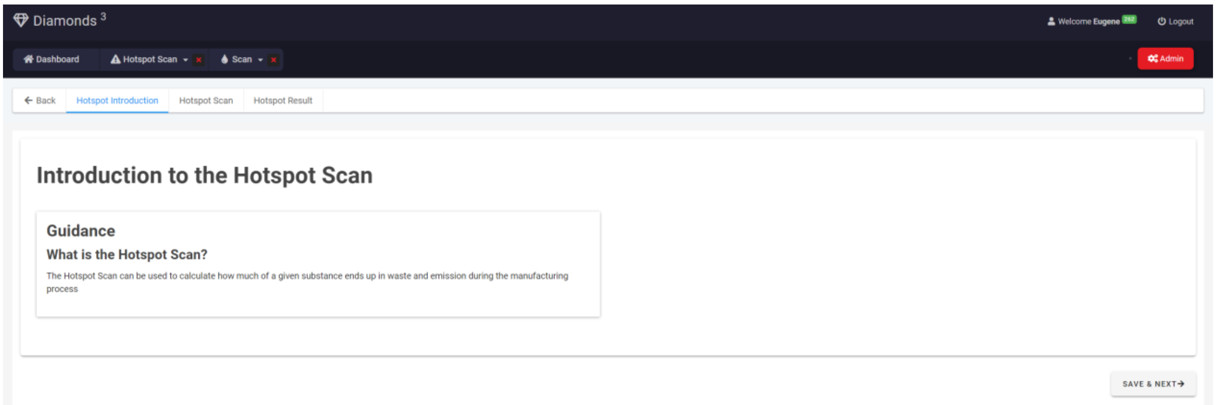

Figure 13: Screenshot of the first page of the introduction pages. This page provides basic introductory information about what the Hotspot scan is and how you can use it correctly. (Note to reviewer: This page still needs to be filled with in information)

After the introductory steps of the "Hotspot Introduction" component, follows the second "Hotspot Scan" component. This component guides the user through ten steps corresponding to seven potential phases in the life cycle of the product of interest and three steps concerning emissions in waste treatments. In each step, the user can fill in information for a number of questions with mostly predefined options and see their effect on the resulting scores for that particular phase. The user can then save the results and continue with the next step. Due to the modular nature, the user is also allowed to jump between steps as per his/her liking. The seven steps to describe life cycle workflow phased are:

- Step 1 “First production phase”. (this is the required phase in which the product is produced at the start of the workflow)
- Step 2 “Additional phase” (optional intermediate step, e.g. production, formulation etc.)
- Step 3 “Additional phase” (optional intermediate step, e.g. production, formulation etc.)
- Step 4 “Additional phase” (optional intermediate step, e.g. production, formulation etc.)
- Step 5 “Additional phase” (optional intermediate step, e.g. production, formulation etc.)
- Step 6 “Use phase” (this is the required phase in which the product is used)
- Step 7 “End of Life” (this is the required phase where the product reaches the end of life)

Step 1 represents the required start phase of the workflow, which is generally the first process of the production phase. Steps 2-5 are additional phases that are completely optional, which are generally production or formulation phases. Step 6 is the required use phase. Lastly, step 7 is the required end-of-life phase that represents the end of the life cycle.

In each step, the tool asks a number of simple questions with the aim to determine the release factors (the percentage of the product that is emitted to air, water, soil in this step) automatically from spERCs or EUSES. If no information about release factors are available or the user has its own information available, the user is able to provide these percentages manually. Future improvements of the tool will aim to increase possibilities for automatic determination of release factors. Figure 14 shows an example of a series of simple questions concerning the paint, oils & ink industry leading at the end to a specific SPERC and its relevant release factors.

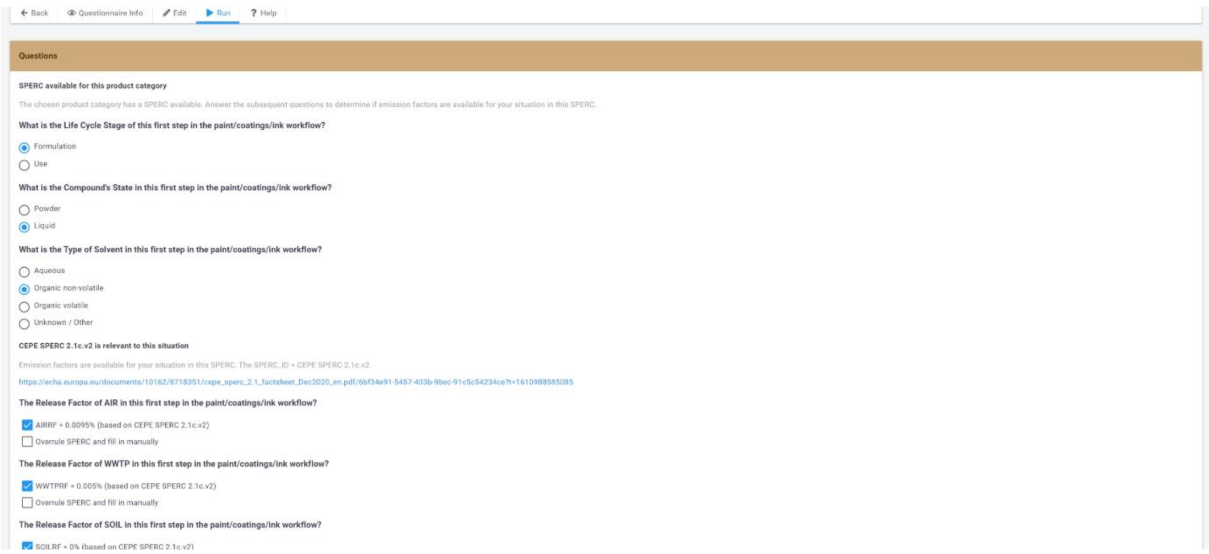

Figure 14: Screenshot of series of simple questions to automatically extract relevant release factors. This is an example relevant for the “paints, oils & ink industry”, which the user has chosen at the beginning (not shown). First the tool indicates there is a SPERC available for this industry. The user is then asked to provide information about the life cycle stage (here Formulation is answered), subsequently the user is asked about the state of the compound/substance (here Liquid is answered), then the user is asked about the type of solvent used (here organic non-volatile is answered). Given these answers, the tool indicates a particular SPERC is relevant and providing a url to that SPERC. Finally, the user is presented with the release factors and an option to use these values or provide manual alternatives.

If no information can be automatically retrieved, or the user wants to manually provide release factor percentages, this is possible as well. Figure 15 shows an example of a step with questions about the percentages of the product emitted to diverse emission- or waste compartments.

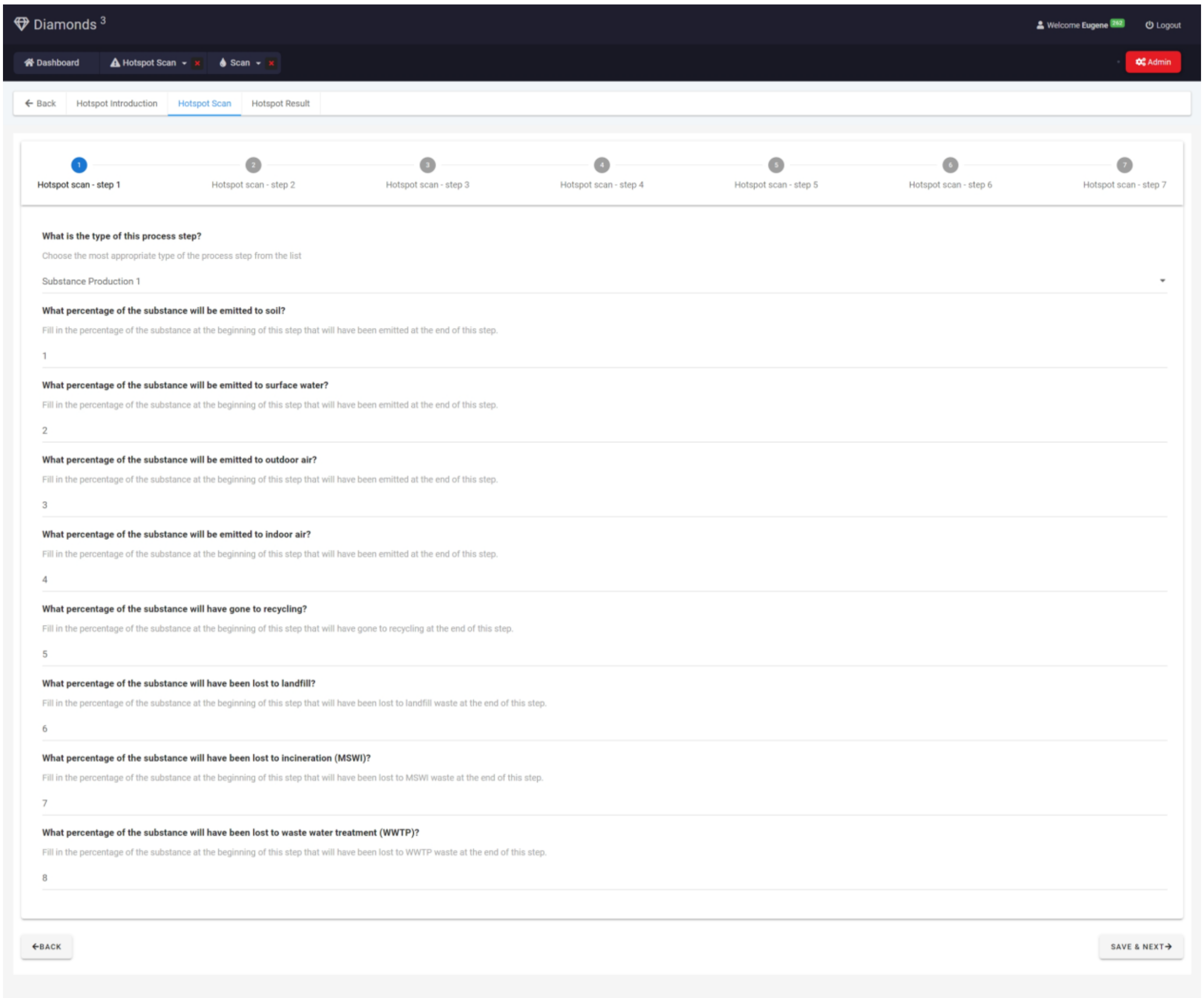

Figure 15: Screenshot of the first step of the production phase that represents the start of the life cycle. Shown are release factor questions that the user can fill in manually, representing the percentages of the product/substance that are lost to emission and/or waste.

Obviously, asking for these percentages is only necessary if they cannot be automatically derived from spERCs or EUSES information. Part of the product that ends up in waste treatment may still end up in the environment. The last three steps (step 8, 9 & 10) is concerned about obtaining those percentages (see also Figure 16).

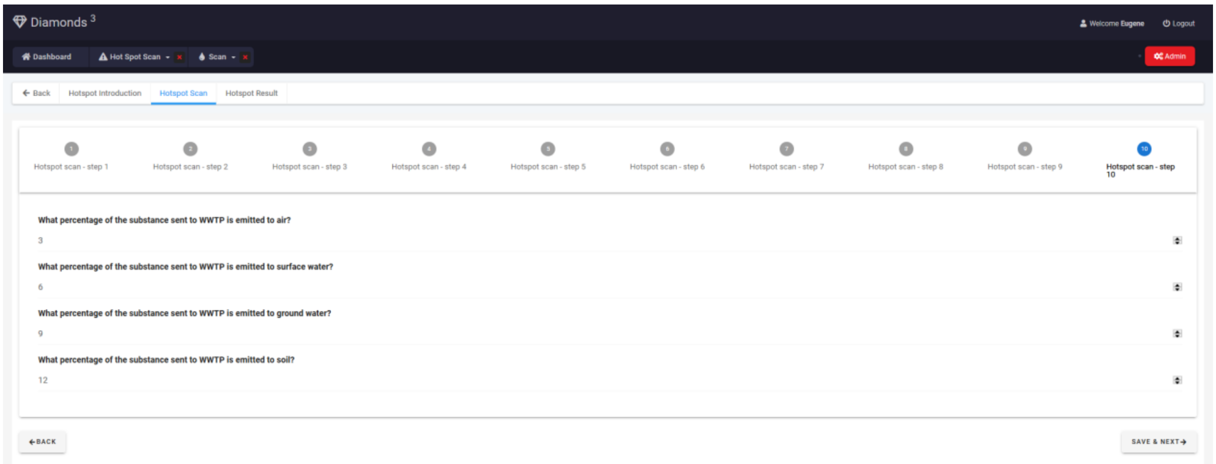

Figure 16: Screenshot of the last step asking the percentages of the product ending up in waste treatment (here WWTP) that are emitted air, water or soil.

When all pages are filled in, the user can inspect the results by clicking on the “Hotspot Result” Tab. All answers are processed and amounts and percentages are automatically calculated and presented in a hotspot visualization as depicted in Figure 17. From top to bottom, the visualization presents the different life cycle phases (that have been filled in by the user) from start of production at the top to use and end-of-life at the bottom. At each step it shows how much product is directly emitted and to which compartment (on the left) as well as how much product goes to waste treatment or recycling (on the right). The primary input of the tool are the actual steps of the workflow and the release factor percentages indicated in purple boxes. The tool takes 1000 kg as the reference amount of material going into the use phase and calculates all other amounts based on this reference point (using the provided release factor percentages).

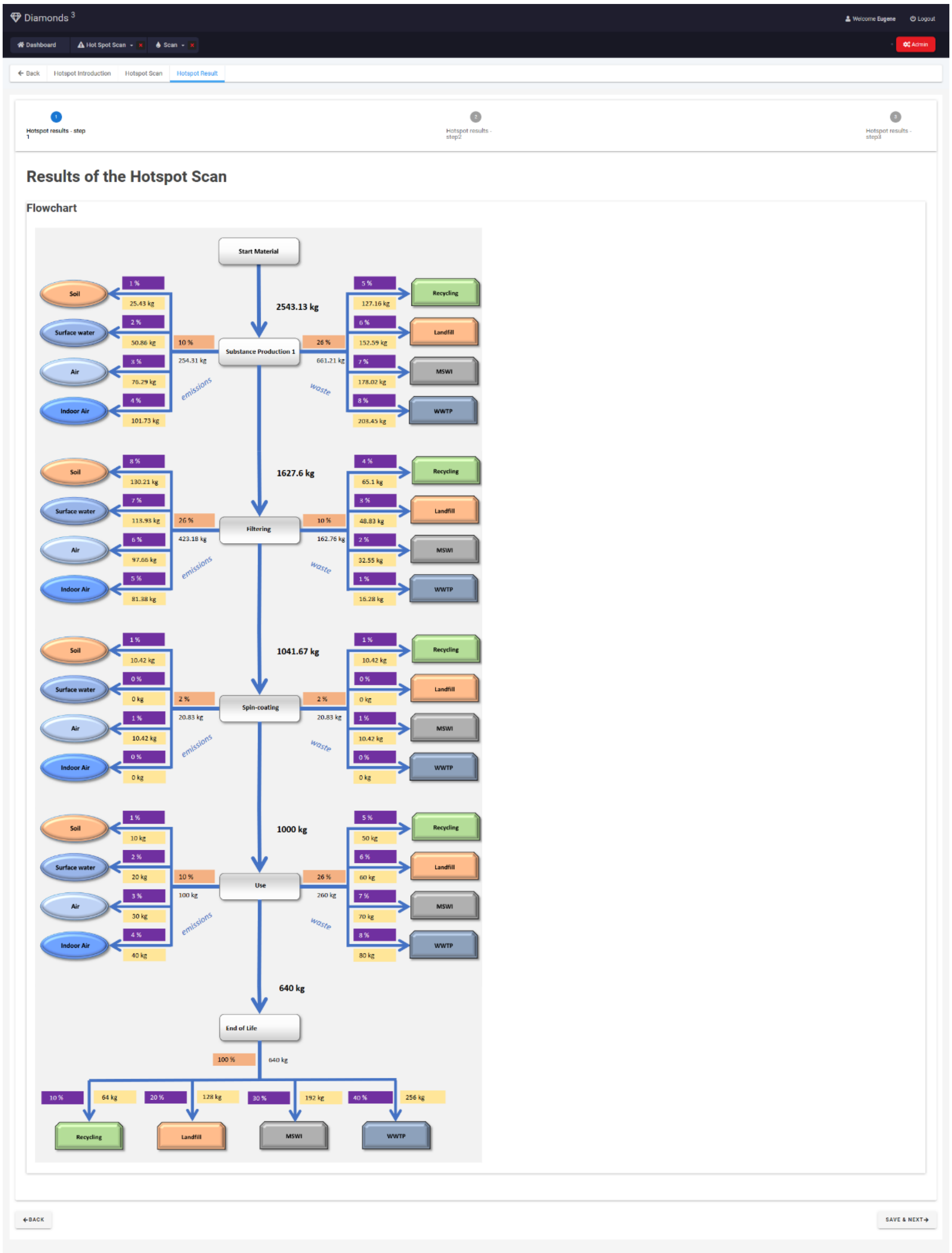

Figure 17: Screenshot of the hotspot visualization workflow plot available under the "Hotspot Result" Tab. Shown are all the steps for which the user has filled in answers. From top to bottom in the middle, the life cycle steps are represented from start till end-of-life. On the left, the percentages and amounts lost to direct emissions are shown. On the right, the percentages and amounts lost to waste treatments and/or recycling are shown. The tool automatically takes 1000 kg of product/substance at the start of the use phase and automatically computes the corresponding amounts of the diverse flows in upstream and downstream phases of the life cycle. Percentages are indicated in purple boxes for particular release factors and orange boxes for aggregated percentages. Amounts are indicated in yellow boxes for particular release amounts or without a box for aggregated amounts.

Besides the main workflow visualization, the tool also offers two additional perspectives. One visualization reflects how much of the product going to the waste treatment is still emitted to the environmental compartments (based on the answers provided in step 8, 9 and 10). The third perspective, visualizes how much of the product finally ends up in each environmental compartment (summing up all direct emissions from the individual steps as well as indirect emission via waste treatment). These two additional perspectives are illustrated on the left, respectively right of Figure 18.

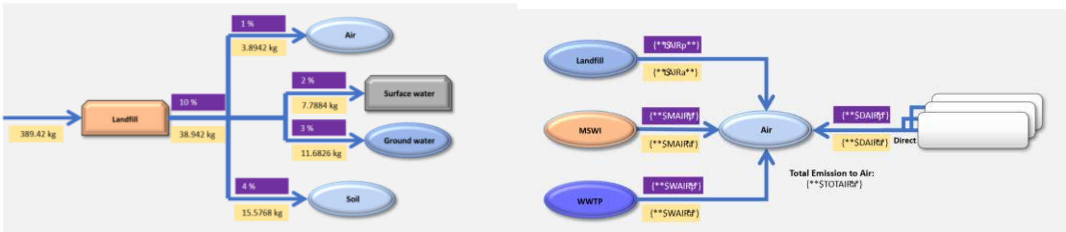

Figure 18: Two additional perspectives. Left panel: Screenshot of emission from waste treatment (here shown for Landfill) to environmental compartments. Right panel: Screenshot of total emission to one particular environmental compartment (here shown for Air) from direct emissions in all the workflow steps (indicated on the right) as well as via the different waste treatments (indicated on the left). (Note to reviewer this visualization will be improved, i.e. changing variable names, like {**$TOTAIRa*} to actual percentages)

4.6 Dissemination

To present basic background information about the tool for visitors that do not need to login, we have created a landing webpage at https://diamonds.tno.nl/#hotspotscan as depicted in Figure 19.

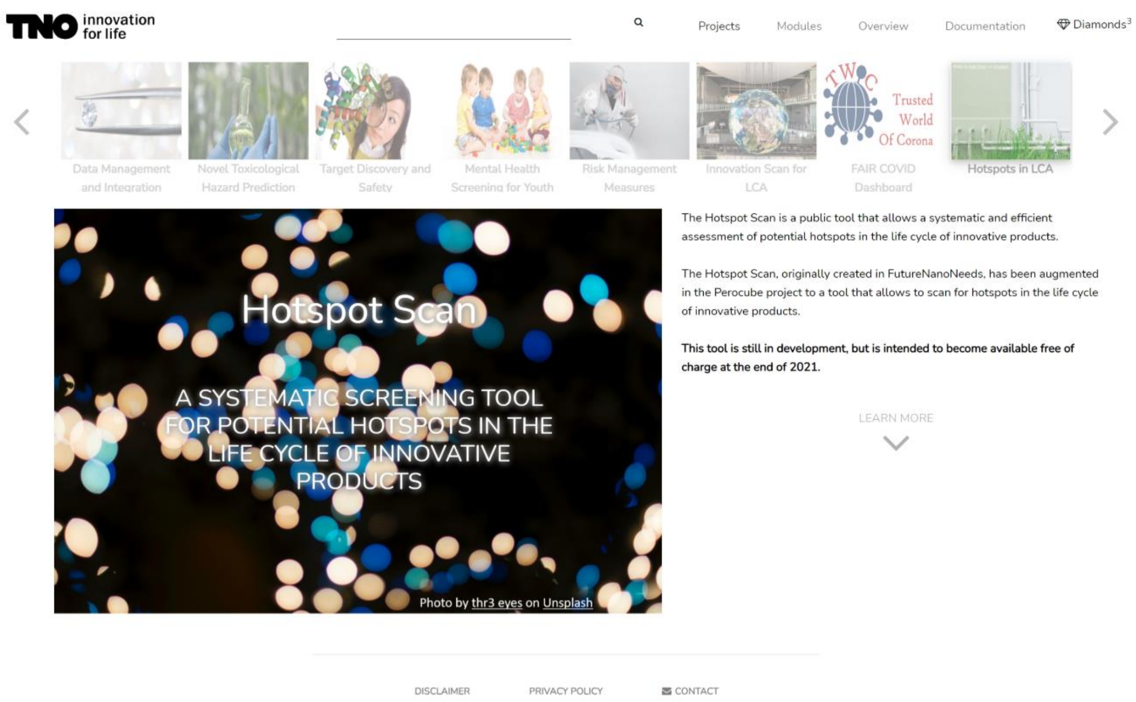

Figure 19: Screenshot of initial landing page with basic information about the purpose of the Hotspot Scan (for which no login is required) with url: https://diamonds.tno.nl/#hotspotscan.

This landing page provides basic information on the purpose of the tool. More detailed information for interested visitors is available, by clicking on the "learn more" link. Upon clicking on that link, more extensive background information is made available on a separate webpage as depicted in Figure 20.

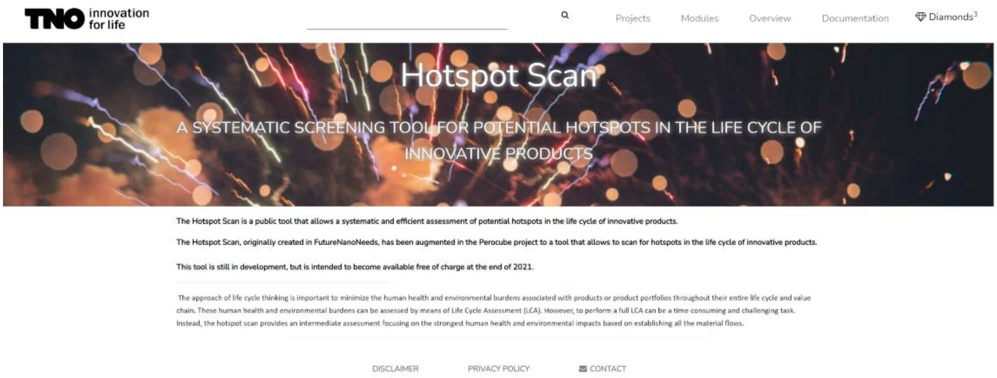

Figure 20: Screenshot of a webpage with more detailed background information (for which no login is required) for interested visitors. *(Note to reviewer: the content of this webpage will be extended)*

The tool will be launched and become publicly available in Q4 of 2021. At that time, account registration instructions will be published on the information page. In addition, a press release announcing the launch and other PR activities via the PeroCUBE dissemination channels (website, briefing) are anticipated.

5 Conclusions

The hotspot scan of the perovskite-based devices estimated that the vast majority of emissions to different environmental compartments occurs during the end-of-life of the devices' life cycle (approx. 80% of the emissions). The lead metal is constantly being emitted throughout the entire life cycle of the devices. It thus indicates lead emission and end-of-life stage as a major focal point for human and environmental exposure during the life cycle of the perovskite-based devices. In this case, emissions arising from landfill and incineration were considered while recycling was excluded due to the immaturity of the recycling processes (and consequent lack of data available) for this kind of devices. In both cases, (landfill and incineration) most of the emissions occur to the water compartment. While in the case of the incineration, a considerable proportion of the lead is retained in the incineration ashes, in the case of landfilling nearly 100% of the lead contained in the waste is estimated to leach to the water. The high emissions of lead during landfill and incineration underline the importance of ensuring a proper recycling process for perovskite based devices.

The enforcement of the 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 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.

Lead emissions during the production stage of the PePV and PeLED account for approximately 10% and 7-9% of their whole life cycle emissions. The production stage also includes the emissions of other toxic substances: lead nitrate, lead halide, methylammonium halide, DMF and precursor ink. These substances are used in the production stage of the perovskite crystals and are mostly emitted to the wastewater. Relatively lower amounts are released to the air (due to the protective measures put in place during synthesis and manufacturing of the perovskites) and even lower to the soil. Considering this, it can be stated that the exposure of the workers to the emissions of toxic substances arising during the production stage seems to be limited.

The emission of the lead during the use of the perovskite-based devices is mainly accounted by the leaching of lead ions upon the breach of the encapsulation layer. For PePV, such emission is estimated to be approx. 12% of the whole life cycle emissions (lowest among all three life cycle stages) over its entire service lifespan. For PeLED, it is estimated to be approx. 9-12% depending on the PeLED colour when used outdoors and subjected to severe weathering conditions over its entire service lifespan. When used indoors, the lead emission from PeLED is estimated to be non-existent.

PeLiFi (or PeLED) may affect under certain conditions human skin and vision, but it is believed that with the increased device efficiency, there will be lesser exposure of the consumer with light and thus not a major concern. The use of the PeLiFi (or PeLED) can be made safer with the minimization of the blue light emission from the device.

The RoHS directive bans the use of lead and lead 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 lead and lead 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 lead-based PeLED and PeLiFi.

The release focal points (i.e. hotspots), identified in the present hotspot scan, thus revealed that the perovskite-based devices have the potential to release hazardous elements/substances from within the devices to the environment (mainly in water) mainly during production and end-of-life stages. The use stage only becomes a relevant focal point when there is breach in the encapsulation layer and the perovskite crystals get exposed to the water. With these quantitative information on the exact release hotspots and the knowledge of the type of hazardous substances being emitted during different life cycle stages, the current tier-1 HSS further expands and refines the outcome of the tier-0 LICARA Innovation Scan of the perovskite-based devices in D7.1. The tier-0 scan deemed all life cycle stages to be equally prone to the hazardous substance release in general and assigned qualitative low to moderate risk scores to the development of the devices.

As part of deliverable D7.1, we assisted the execution of the tier-0 approach by development of an online tool available to the public, called the “LICARA Innovation Scan”. Likewise, the execution of the tier-1 hotspot scan in this deliverable was assisted by the development of a follow-up online tool, called the Hotspot Scan. The Hotspot Scan was built upon the generic technical structure of the LICARA Innovation Scan. The Hotspot Scan assists users to determine release factors based on available spERCs and automatically produce hotspot scan workflow diagrams by simply answering a number of questions. We intend to release the Hotspot Scan to the public and further improve the tool in future projects.

6 References

Adrian S, Drisse MB, Cheng Y, Devia L, Deubzer O, Goldizen F, et al. Quantities, flows, and the circular economy potential The Global E-waste Monitor 2020. [cited 2021 Jul 30]; Available from: http://ewastemonitor.info/wp-content/uploads/2020/12/GEM_2020_def_dec_2020-1.pdf

Bae, SY., Lee, S.Y., Kim, Jw. et al. Hazard potential of perovskite solar cell technology for potential implementation of “safe-by-design” approach. Sci Rep 9, 4242 (2019). https://doi.org/10.1038/s41598-018-37229-8

Binek A, Petrus ML, Huber N, Bristow H, Hu Y, Bein T, et al. Recycling Perovskite Solar Cells to Avoid Lead Waste. ACS Appl Mater Interfaces [Internet]. 2016 May 25 [cited 2021 Jul 6];8(20):12881–6. Available from: https://pubs.acs.org/doi/abs/10.1021/acsami.6b03767

Buchert M, Manhart A, Bleher D, Pingel D. Recycling critical raw materials from waste electronic equipment Commissioned by the North Rhine-Westphalia State Agency for Nature, Environment and Consumer Protection. Darmstadt; 2012.

Boukris E, Ligthart T, Koch R, Brouwer D. D3.7 Identification of main release sources of the next generation of nanomaterials. 2014.

Chhillar P, Dhamaniya BP, Dutta V, Pathak SK. Recycling of Perovskite Films: Route toward Cost-Efficient and Environment-Friendly Perovskite Technology. ACS Omega [Internet]. 2019 [cited 2021 Jul 6];4:11880–7. Available from: https://pubs.acs.org/sharingguidelines

Collins MK, Anctil A. Implications for current regulatory waste toxicity characterisation methods from analysing metal and metalloid leaching from photovoltaic modules. Int J Sustain Energy 2017; 36: 531–544.

Doka G. Updates to Life Cycle Inventories of Waste Treatment Services. Part II " Waste incineration ". 2013.

Doka G. Calculation manual for LCI calculation tools for regionalised waste treatment [Internet]. 2020 [cited 2021 May 31]. Available from: https://www.doka.ch/06_CalculationManualDoka2020.pdf

Dong Q, Lei L, Mendes J, So F. Operational stability of perovskite light emitting diodes. J. Phys.: Mater. 2020; 3: 012002.

ECHA. lead compounds with the exception of those specified elsewhere in this Annex https://echa.europa.eu/substance-information/-/substanceinfo/100.240.788. Retrieved 08 September 2021.

EU Directive 2009/125/EC. Establishing a framework for the setting of ecodesign requirements for energy-related products. EUROPEAN PARLIAMENT AND THE COUNCIL. 21 October 2009.

EU Directive 2011/65/EU. Restriction of the use of certain hazardous substances in electrical and electronic equipment. EUROPEAN PARLIAMENT AND OF THE COUNCIL. 8 June 2011.

Fry JN, Nombona N, Diale M. Synthesis and characterisation of methylammonium lead tri-bromide perovskites thin films by sequential physical vapor deposition. Physica B: Condensed Matter 2020; 578: 411884.

Hailegnaw B, Kirmayer S, Edri E, Hodes G, Cahen D. Rain on Methylammonium Lead Iodide Based Perovskites: Possible Environmental Effects of Perovskite Solar Cells. J. Phys. Chem. Lett. 2015; 6: 1543–1547.

Hauck M, Ligthart T, Schaap M, Boukris E, Brouwer D. Environmental benefits of reduced electricity use exceed impacts from lead use for perovskite based tandem solar cell. Renewable Energy 2017; 111: 906-913.

Jung M, Ji S-G, Kim G , Seok SI. Perovskite precursor solution chemistry: from fundamentals to photovoltaic applications. Chem Soc Rev 2019; 48: 2011-2038.

Johnson GT, Lewis TR, Wagner WD. Acute toxicity of caesium and rubidium compounds. Toxicology and Applied Pharmacology 1975; 32: 239-245.

Kim BJ, Kim DH, Kwon SL, Park SY, Li Z, Zhu K, et al. Selective dissolution of halide perovskites as a step towards recycling solar cells. Nat Commun [Internet]. 2016 May 23 [cited 2021 Jul 6];7(1):1–9. Available from: www.nature.com/naturecommunications

Kim K, Nam K, Kang W, Choi Y. Decision making framework for beneficial use of dredged sediment in the terrestrial environment based on environmental risk assessment and sediment characterization. J Korean Soc Environ Eng 2018; 40: 227–238.

Landsiedel, R., & Saling, P. (2002). Assessment of toxicological risks for life cycle assessment and eco-efficiency analysis. The International Journal of Life Cycle Assessment, 7(5), 261–268. https://doi.org/10.1007/BF02978885

Ligthart, T. N. Environmental performance of lead sheet and alternative weather-proofing products. TNO report 2006; Apeldoorn.

Liu FW, Biesold G, Zhang M, Lawless R, Correa-Baena JP, Chueh YL, et al. Recycling and recovery of perovskite solar cells. Mater Today. 2021; 43: 185–97.

Mahmoud BH, Ruvolo E, Hexsel CL, Liu Y, Owen MR, Kollias N, Lim HW, Hamzavi IH. Impact of Long-Wavelength UVA and Visible Light on Melanocompetent Skin. Journal of Investigative Dermatology 2010; 130: 2092–2097.

Meng L, You J, Yang Y. Addressing the stability issue of perovskite solar cells for commercial applications. Nature Communications 2018; 9: 5265.

Panthi G, Bajagain R, An Y-J, Jeong S-W. Leaching potential of chemical species from real perovskite and silicon solar cell. Process Safety and Environmental Protection 2021; 149: 115–122.

Perry DL, Phillips S.L. Handbook of Inorganic Compounds. CRC-Press 1995. 1st edition.

Rotter VS, Maehlitz P, Korf N, Chancerel P, Huisman J, Habib H, et al. Waste Flow Studies Deliverable 4.1 [Internet]. 2016 [cited 2021 Jul 30]. Available from: http://prosumproject.eu/sites/default/files/ProSUM D4.1 Waste Flow Studies_0_0.pdf

Roy S. Impact of UV Radiation on Genome Stability and Human Health. In Ultraviolet Light in Human Health, Diseases and Environment, Advances in Experimental Medicine and Biology. S. Ahmad (ed.) Springer International Publishing AG 2017; 207-219

SCENIHR. (2012). Health Effects of Artificial Light. https://doi.org/10.2772/8624

Sodhi A and Johnson J. Light Fidelity (LiFi) - The Future of Visible Light Communication. International Journal of Engineering Research and General Science 2015; 3: 117-128.

Su P, Liu Y, Zhang J, Chen C, Yang B, Zhang C, Zhao X. Pb-Based Perovskite Solar Cells and the Underlying Pollution behind Clean Energy: Dynamic Leaching of Toxic Substances from Discarded Perovskite Solar Cells. J. Phys. Chem. Lett. 2020; 11: 2812–2817.

Surabhi R, Bhat K, Batra A, Chilvery A, Aggarwal M. Synthesis, Purification, Crystal Growth and Characterization of Lead Iodide (PbI2) Purified by a Low-Temperature Technique. Adv. Sci. Eng. Med. 2014; 6: 1-5.

Ticleanu C, Littlefair P. A Summary of LED Lighting Impact on Health. International Journal of Sustainable Lighting 2015; 1: 3–4.

Upadhyaya A, Negi CMS, Yadav A, Gupta SK, Verma AS. Synthesis and Characterization of Methylammonium Lead Iodide Perovskite and its Application in Planar Hetero-junction Devices. Semicond. Sci. Technol. 2018; 33: 065012.

van Harmelen T, Zondervan-van den Beuken EK, Brouwer DHDH, Kuijpers E, Fransman W, Buist HBHBHB, et al. LICARA nanoSCAN - A tool for the self-assessment of benefits and risks of nanoproducts. Environ Int. 2016; 91: 150–60.

Weissermel K and Arpe H. Industrial Organic Chemistry: Important Raw Materials and Intermediates, Wiley-VCH Verlag GmbH & Co. KGaA, 2008, ch. 2

Wu M, Ladi NH, Yi Z, Li H, Shen Y, Wang M. Stability Issue of Perovskite Solar Cells under Real-World Operating Conditions. Energy Technol. 2020; 8: 1900744.

7 Annexure

Table A1: Hazard statements relevant for the Hotspot scan

Hazard	Statement	Hazard	Statement
300	Fatal if swallowed.	362	May cause harm to breast-fed children.
301	Toxic if swallowed.	370	Causes damage to organs.
302	Harmful if swallowed.	371	May cause damage to organs.
303	May be harmful if swallowed.	372	Causes damage to organs through prolonged or repeated exposure.
304	May be fatal if swallowed and enters airways.	373	May cause damage to organs through prolonged or repeated exposure.
305	May be harmful if swallowed and enters airways.	300/310	Fatal if swallowed or in contact with skin.
310	Fatal in contact with skin.	300/330	Fatal if swallowed or if inhaled.
311	Toxic in contact with skin.	310/330	Fatal in contact with skin or if inhaled.
312	Harmful in contact with skin.	300/310/330	Fatal if swallowed, in contact with skin or if inhaled.
313	May be harmful in contact with skin.	300/314/330	Fatal if swallowed, or if inhaled, causes severe skin burns and eye damage.
314	Causes severe skin burns and eye damage.	301/311	Toxic if swallowed or in contact with skin.
315	Causes skin irritation.	301/331	Toxic if swallowed or if inhaled.
316	Causes mild skin irritation.	311/331	Toxic in contact with skin or if inhaled.
317	May cause an allergic skin reaction.	301/311/331	Toxic if swallowed, in contact with skin or if inhaled.
318	Causes serious eye damage.	302/312	Harmful if swallowed or in contact with skin.
319	Causes serious eye irritation.	302/332	Harmful if swallowed or if inhaled.
320	Causes eye irritation.	312/332	Harmful in contact with skin of if inhaled.
330	Fatal if inhaled.	302/312/332	Harmful if swallowed, in contact with skin or if inhaled.
331	Toxic if inhaled.	303/313	May be harmful if swallowed or in contact with skin.
332	Harmful if inhaled.	303/333	May be harmful if swallowed or if inhaled.
333	May be harmful if inhaled.	313/333	May be harmful in contact with skin or if inhaled.

Hazard	Statement	Hazard	Statement
334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.	303/313/333	May be harmful if swallowed, in contact with skin or if inhaled.
335	May cause respiratory irritation.	315/320	Causes skin and eye irritation.
336	May cause drowsiness or dizziness.	400	Very toxic to aquatic life.
340	May cause genetic defects.	401	Toxic to aquatic life.
341	Suspected of causing genetic defects.	402	Harmful to aquatic life.
350	May cause cancer.	410	Very toxic to aquatic life with long lasting effects.
351	Suspected of causing cancer.	411	Toxic to aquatic life with long lasting effects.
360	May damage fertility or the unborn child.	412	Harmful to aquatic life with long lasting effects.
361	Suspected of damaging fertility or the unborn child.		