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REVIEW

REVISED The critical issue of using lead for sustainable massive production of perovskite solar cells: a review of relevant literature [version 2; peer review: 2 approved]

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Abstract
This work aims to review the most significant studies dealing with the environmental issues of the use of lead in perovskite solar cells (PSCs). A careful discussion and rationalization of the environmental and human health toxicity impacts, evaluated by life cycle assessment and risk assessment studies, is presented. The results of this analysis are prospectively related to the possible future massive production of PSC technology.

Keywords
Perovskite Solar Cells, Environmental Assessment, Toxicity, Life Cycle Assessment, Metals, Lead, Sustainability, Photovoltaics

This article is included in the Perovskites collection.

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REVISED **Amendments from Version 1**

The Authors would like to thank the Reviewers for the time and effort dedicated to reviewing our paper. Version 2 contains the following changes in response to their constructive comments:

- Some wordings were improved to avoid misunderstandments, like in sections "Availability, viable alternatives and recyclability" and "LCA for environmental assessment of Pb in PSCs". Also some typos were corrected along the text

- The section entitled "Encapsulation as a viable solution to facilitate commercialization" was enriched commenting on a very recent work on this issue that was added in the bibliographic list

- The bibliographic list has been enriched with further and very recent references.

Any further responses from the reviewers can be found at the end of the article

Introduction

As part of the European Green Deal, the European Union (EU) has set the ambitious goal of reducing 55% of its greenhouse gas (GHG) emissions by 2030 and becoming the first continent in the world to be completely climate neutral by 2050[1,2]. To achieve this challenging goal, significant changes will be required in the energy mix of most of the EU countries to reduce dependency on fossil fuels and their consequent GHG emissions. The two other related objectives, namely increasing energy efficiency to 36% and increasing renewable energy share to 38.5%, will be essential to achieve the target defined above. Renewable energy sources are those that renew themselves naturally at rates that are equivalent or higher than the rates of their use, such as solar energy, wind energy, hydropower, marine (tide, wave, ocean) and geothermal energy. They prevalently contribute to electric power and minimally to thermal request. In sharp contrast with all the other fuels, renewables have already shown their resilience to the coronavirus pandemic crisis[3]. The share of renewables in the energy use of the 27 EU member states was approximately 19.7% at the end of 2019, very close to the 20% target originally established for 2020[4,5].

On the other hand, the share of renewables in the worldwide electricity supply reached 27% in 2019[6], 7% below the EU for the same year (i.e., 34%)[4], which shows that Europe is indeed ahead in the energy transition. Although technologies exploiting renewable energy sources are not always intrinsically ecofriendly, renewable energy is unquestionably important to ensure a sustainable society, in which both citizens and industries can benefit and develop while respecting the replenishing rate of natural resources. In this regard, the 7th Sustainable Development Goal (SDG) defined by the United Nations (UN) for 2030 is "Ensure access to affordable, reliable, sustainable and modern energy for all", stating a clear goal of increasing the share of renewable energy in the total energy usage[7,8]. Among the renewables, solar energy is especially important, given the expected increase as part of the decarbonization process, for the energy mix both in EU and in the world. Novel photovoltaic (PV) technologies will play a crucial role in this process, and one of the most promising emerging PV technologies to be recently developed is hybrid halide perovskite solar cells (PSCs).

PSCs have enormously advanced the research and development of innovative PV technologies in the last decade. The power conversion efficiency (PCE) of the cells overcame the record value year by year, reaching 25.5% for single-junction PSC, 24.2% for tandem configuration coupling of the PSC technology with copper indium gallium selenide (PSC/CIGS), 29.5% for the PSC/silicon tandem[9], and 17.9% for the perovskite solar module (PSM)[10]. The extremely high PCE, together with the availability of cell and module configurations, and the low cost of most raw materials and manufacturing techniques, were the pillars of research and development of PSC technology looking for industrialization and high competitivity on the PV market.

However, some not negligible drawbacks need to be overcome to allow PSCs to take the decisive step towards commercialization and thus enter the PV market. The long-term stability and rapid degradation of some components[11], the choice of suitable materials and manufacturing procedures for massive industrial scale-up[12], and environmental sustainability[13] are still open issues that companies and the scientific community are trying to address.

Concerning environmental sustainability, several researchers pointed out the problem of lead (Pb), employed in the crystal configuration of the best performing PSCs. Pb is highly toxic for humans and ecosystems and, if absorbed by living organisms, it negatively affects many internal organs, including the brain, and can bioaccumulate within tissues[14].

What makes it extremely dangerous for living organisms' health is the high mobility and great diffusion potential in the environment that the Pb-containing compounds have. This is due to Pb's chemical-physical characteristics and its widespread usage until the recent past[14]. For these reasons, the World Health Organization states that there is no safe level of Pb exposure[15], and throughout the RoHS Recast (RoHS2) Directive[16], the European Union is pushing for its removal and substitution from a range of electrical and electronic equipment. However, due to its particular characteristics and the scarcity of suitable substitute materials, Pb is still far from being replaced[17]. Regarding PV applications, although the RoHS2 Directive excludes solar panels from the restrictions (unless they are building or product integrated), as a precaution PSCs should respect 0.1% Pb content as the maximum concentration value tolerated by weight in "homogeneous material". In this context, the ambiguity of the definition of "homogeneous material" represents a critical point, especially for a perovskite-based device that is characterized by several nano or microlayers made of different materials stacked on top of each other[16,18].

Thus, the toxicity of Pb is one of the most relevant issues to address for safeguarding the environmental sustainability of future industrial production of PSCs. So far, many researchers have investigated the potential toxicological risks caused by the leakage of Pb during the life cycle of PSCs and modules[19–24]. At the same time, life cycle assessment (LCA) methodology has been applied to several PSC configurations to evaluate the eco-profiles of the technology[25–39] and understand better which could be the relevant environmental hotspots along the whole PSC life cycle in addition to those related to the use of Pb-based compounds.

Therefore, the concerns regarding the high toxicity of Pb-based compound used in PSCs, and the possible mass production limitations related to the current legislation, are still open issues for which a widespread consensus among the scientific community and manufacturers has not been reached yet[17].

This work aims to review all aspects connected with the sustainability and environmental assessment of Pb employed in PSCs to highlight the significant issues that should be taken into account to guarantee safe industrial development and massive exploitation of this technology. To do so, we first describe the physico-chemical properties of Pb, why it is pivotal for the PSC development and what are the potential risks for humans and the environment. Afterward, we outline the major outcomes of environmental analysis studies (LCA, toxicological and risk assessment) on PSCs, focusing on the toxicity-related environmental impacts. Next, we present the most recent mitigation and encapsulation techniques developed and published in last years, and finally, we outline the main end-of-life concerns and potential future recycling techniques.

Pb in PSCs

Conventional Pb-based perovskites show a distinctive crystal structure featuring the ABX_3 pattern where A is an organic or inorganic cation (usually methylammonium, formamidinium or cesium), B is Pb, and X is a halide (usually iodine or bromine). Perovskite is the PSCs' photoreactive compound, and it cooperates with several other materials and compounds in the cell to convert light into electricity (Figure 1).

The peculiarities of this crystal structure are the main factor that leads to the astonishing photoconversion efficiency PSCs have been showing so far. They are related to several optoelectronic parameters such as bandgap, absorption coefficient, carrier diffusion lengths, trap density, shallow defects and exciton binding energy[40]. For this reason, despite several attempts to replace Pb with other metals[40–42] such as tin (Sn), germanium (Ge), bismuth (Bi), antimony (Sb) or indium (In), no viable, effective and compelling alternative has been found yet.

From an operational perspective, the highest efficiency recorded for a Pb-free PSC is 10.9%, reached with a Sn-based perovskite[43,44]. Sn has a similar electronic configuration to Pb, and it seems to be the most promising candidate to replace Pb in perovskite for PV applications. However, low PCE and concerns about the environmental impact of Sn-based perovskite[21,24] have slowed down the development of Sn-based PSCs so far. In this context, several researchers are addressing their attempts and effort in the direction of investigating and examining in depth the potential risk of using Pb in PSCs.

Toxicology issues

Hailgnaw *et al.* analyzed Pb leakage in case of damage and exposure to rain of one Pb-based PSM[19]. Due to the high mobility and the potential solubility in water of Pb-based compounds originating from the perovskite (including also lead iodide, PbI_2, that, despite its moderate solubility in water, can release not-negligible quantities of the metal over time), they showed almost all the Pb leaked from the module, generating relevant pollution in all the environmental compartments (i.e., water, soil, and air) in the surroundings of the PSM installation. The authors stated that the concentration of Pb in the soil could increase by about 70 ppm, where the typical range of concentration for natural uncontaminated soil is <10–30 ppm, and 50–200 ppm in urban areas[19].

Babayigit *et al.* assessed the toxicity of the PbI_2 compound by measuring the statistically derived dose descriptors LC50 (i.e., lethal concentration for 50% of the population) and EC50 (the effect concentration for 50% of the population) in a population of zebrafish[21,22]. The authors revealed that both death and adverse impacts on the organisms occurred at a low concentration of PbI_2 in water. The synergistic effect of the exposure to Pb-based compounds and the decrease in pH caused by the formation of hydrogen iodide (HI) was crucial in obtaining these results.

Another valuable contribution for evaluating the toxicity of Pb-based compounds comes from Li *et al.*, which experimented with the uptake of Pb-based perovskite in mint plants[23]. The

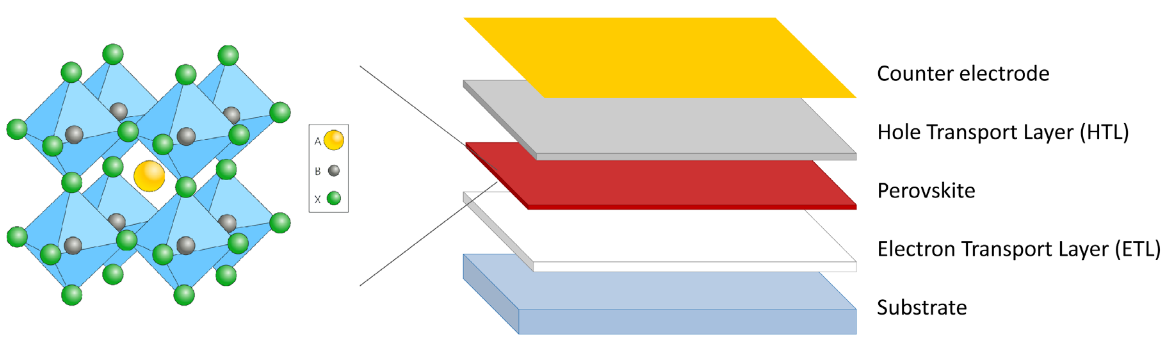

Figure 1. Crystal structure of perovskite (on the left) and conventional configuration of a perovskite solar cell (on the right).

authors measured the amount of Pb in roots, stems, and leaves of plants grown in contaminated soil. They found an increase of 10% in the amount of Pb in soil caused an increase of Pb content in plants higher than 100%. Furthermore, the presence of organic cations of the perovskite (methylammonium in this case) has a remarkable effect on the uptake.

Benmessaud *et al.* evaluated the cytotoxicity of Pb-based perovskite contamination in several human cells, highlighting the onset of different damaging effects, from a reduction in cell reproduction to cell death[45].

Comparison with other sources of Pb emissions

Despite the need for a deepened, detailed, and all-encompassing investigation of the toxicity-related issues, the potential risk and damage to humans and ecosystems associated with pollution by Pb-based compounds seems to be sufficiently documented. Besides that, the appraisal of environmental implications connected to large production of PSCs with a prospective approach can help to determine the eco-profiles of electricity produced by this technology, thus being an essential contribution to appropriate assessment of the whole issue.

Fabini attempted to quantify the Pb content in PSCs that would be required to supply the electricity mix in the US, comparing this value with the amounts of Pb-based compounds emitted by other sectors[20]. Results are reported in Table 1.

Apart from Pb emissions generated by automotive fuels before tetraethyl lead ($Pb(C_2H_5)_4$) was removed as an additive in gasoline, all other Pb emissions sources are still relevant and present in 2021. Given that only a small percentage of Pb employed in PSCs could be directly emitted into the environment, the analysis shows that potential pollution caused by future large-scale production of PSCs may be lower than or analogous to other current Pb emission sources. In this framework, the environmental compartment into which emissions flow considerably affects the behavior and potential toxicity of Pb-based compounds. Direct emission into the air could lead to diffused pollution, also affecting other environmental compartments, such as soil or water, and thus, indirectly, food. It is well known that treatment and disposal of coal ash and blackwater are hazardous, and could lead to environmental disaster[20]. In contrast, Pb content in perovskite is in a solid form and, if adequately encapsulated, its mobility could be adequately limited, and the consequent emission into the environment could be very low.

Hauck *et al.* performed a LCA to analyze the prospective contribution that large-scale production and installation of PSCs could make to the transition toward an energy system based on renewable sources[25]. In their work, the electricity produced by PSCs/Si modules in a tandem configuration is compared with the electricity produced by the average European electricity mix. Despite some significant assumptions and approximations, the authors concluded that a substantial reduction of Pb-based compound and GHG emissions could be achieved by replacing conventional energy production technologies with PSCs.

Billen *et al.* followed a similar approach by applying LCA to calculate the environmental impact and toxicity potential of electricity produced by Pb-based perovskite PV and comparing them to the US electricity mix eco-profile[26]. The major outcomes show that the environmental footprint of the kWh generated by PSCs could decrease Pb emissions by a factor of 2–4. The authors state that the potential Pb emissions related to PSCs could be marginal compared to those caused by conventional energy production technologies. In this context, the emission of toxic compounds that could potentially occur during the manufacturing phase, together with the unlikely emission of the whole Pb content during end-of-life, could be offset in only two years of operation.

Availability, viable alternatives and recyclability

The availability of raw materials and metals is one of the main issues to address when evaluating the sustainability of energy-generating technologies and innovative devices for

Table 1. United States (US) lead (Pb) emission sources and hypothetical Pb content in perovskite solar cells (PSCs) to supply the entire US electricity sector. The emission values have been detected in the years reported in brackets, but they are still relevant in 2021. Data is taken from Fabini, 2015[20].

Lead Emission Source	Total Value (tonnes/year)	Compartment
Automotive fuel (1973)	$2 \cdot 10^5$	Airborne emissions
Aviation fuel (2011)	$4.40 \cdot 10^2$	
Metals processing (2011)	$1.20 \cdot 10^2$	
Electricity generation (2011)	$3.50 \cdot 10^1$	
Coal ash, blackwater (2011)	$5.90 \cdot 10^3$ - $9.30 \cdot 10^4$	Liquid & solid content
Electronic solder (2012)	$6.20 \cdot 10^3$	
PSCs to supply electricity	$1.60 \cdot 10^2$	Solid content

the exploitation of renewable energy sources[46]. Among all the metals that could be employed in PSC devices, Pb shows some advantages, one of the most convincing being the availability of its natural reservoirs[47–49] as shown in Figure 2, which is taken from the European Commission Raw Materials Information System (RMIS)[50].

The critical raw material (CRM) diagram in Figure 2 points out that Pb ores have good availability, especially compared with other rare metals. In addition to this, due to the high recycling rate, a significant source of secondary Pb comes from recycling procedures[48]. In 2016, in the US, the amount of recycled Pb was more than 80%, while in Europe it was around 60%[18,24].

The significant recycling rate of Pb allows for hypothetical end-of-life management of PSCs that could limit and hopefully totally ward off the disposal of Pb-based electronic waste in landfills[51]. As has already been done for conventional Si-based[52] and CdTe[53] panels, a strategic plan for PSC systematic recycling engaging producers, sellers, consumers, and electronic waste recovery companies needs to be implemented as soon as the commercialization of PSCs starts. In this regard, several authors have already explored and investigated the feasibility of the PSC recycling process[54,55], highlighting the high recycling rate of Pb[56] and the potential recovery of most to all of the PSC components[57–64]. Although these processes have been demonstrated at a laboratory scale and need to be scaled-up, the prospect of manufacturing PSCs with recovered materials, avoiding efficiency losses, has been already documented[51,65–68].

Analyzing the possible replacement of Pb with other metals, some critical issues need to be addressed. As reported above, metals identified and tested as a viable alternative for metal-based perovskite in PSCs are Sn, Ge, Bi, Sb and In[40]. Figure 2 shows that most of these metals' availability is lower than Pb. These elements are scarce or even very rare, and they are employed for other uses. Roughly comparing annual production, it can be noted that the total amount of some alternative metals produced would not be sufficient to be employed in PV device manufacturing[24,49,69].

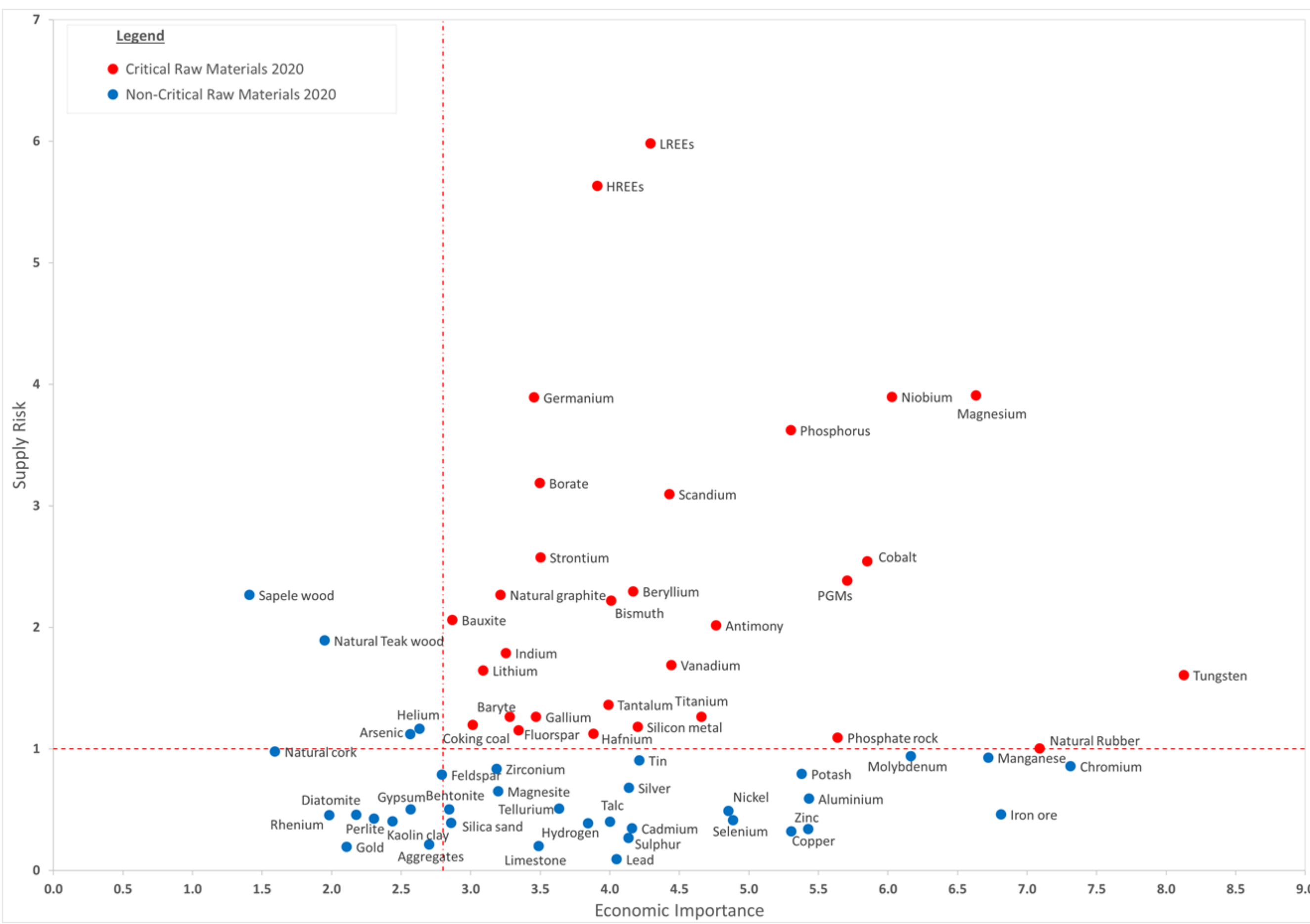

Figure 2. Critical Raw Materials list 2020 (Reproduced from "European Commission, Study on the EU's list of Critical Raw Materials (2020)"[70]).

The potential replacement elements should fulfill some crucial performance standards to be competitive with Pb. In addition to the already mentioned natural availability and ease of recycling, alternative metals should form a stable perovskite structure that exhibits outstanding optoelectronic properties and excellent PCE, they should be characterized by a low-cost supply chain and manufacturing procedure, and they should satisfy some commercial requirements, such as long-term stability and scalability[40].

Moreover, together with these stringent criteria, issues related to the whole life cycle of metals and their relative environmental sustainability must be considered. Nuss *et al.* performed a cradle-to-gate LCA of metals, illustrating the numerous interconnections among the manufacturing procedures and assessing the related environmental burdens[71]. One of the major outcomes of the study deals with the common sources and extraction procedures characterizing some elements. This aspect substantially influences the market availability and cost of some metals, whose production is commercially attractive only as a by-product of other metals[24]. From the environmental assessment perspective, among all metals, Pb displays one of the lowest impacts for all the environmental categories and indicators considered by Nuss *et al.* (i.e., GHG emissions, cumulative energy demand, terrestrial acidification, freshwater eutrophication, and human toxicity)[71]. In addition to this, the authors state that for some metals, the mining and concentration and the subsequent purification and refining steps exhibit approximately similar environmental burdens. These steps are also a major contributor to the environmental profile of the whole metal's life cycle[71]. Thus, the impact could be strongly reduced using secondary recycled Pb and implementing a thorough end-of-life strategy for PSC technologies.

LCA for environmental assessment of Pb in PSCs

The LCA methodology has been extensively applied to assess PSCs manufacturing's environmental impact and operational phase. Many different configurations of cells and modules employing several raw materials and chemical compounds and requiring various manufacturing procedures and deposition techniques have been analyzed in recent years[17–29]. To highlight the main potential environmental hotspots of PSCs, we performed a critical review and in-depth harmonization of LCA studies published (2019)[36] in the frame of the H2020 Project "ESPResSo". The major outcomes and results of the study are consistent with those reported in similar papers published more recently[27,29], and they can be summarized as follows.

The main hotspots in terms of materials employed for PSCs production are gold (used as back contact), the conductive solar glass, and the electron transport material (ETM) due to raw materials consumed during the synthesis. Regarding the manufacturing procedures, the back contact deposition, the ETM deposition and the glass substrate preparation show remarkably high environmental impacts due to their direct energy consumption[36]. Some manufacturing techniques have been found to be better than others for bringing PSCs to the industrial production scale with competitive deposition efficiency (e.g., ink-jet printing, slot-die coating, spray-coating)[27], and a global consensus on the replacement of gold as the material for back contact has been achieved[36].

Concerning the toxicity issues of PSCs, and the use of Pb-based compounds in particular, nearly all of the studies come to similar conclusions[17–29]. From an LCA perspective, the Pb and Pb-based compounds' burden on the environmental profile of PSCs can be considered substantially negligible. This is due to two main factors: i) the limited environmental impact that the production of Pb ore displays in LCA analysis[71], and ii) the exiguous amount of Pb in PSCs and the relative contribution to the global environmental footprint of devices, which is some orders of magnitude lower than those of other materials and processes required in the manufacturing procedure. However, despite the relatively low overall burden, the presence of Pb contributes highly to the toxicity-related categories[36]. This outcome can be explained through the discussion of the so-called characterization factors (CFs) of metals that are applied in the life cycle impact assessment step as weighting factors to aggregate life cycle emissions into scores for human health and ecosystem health impacts.

Figure 3a, b and c show the CFs of Pb in comparison with those of other heavy metals Values are derived from the most updated version of the Environmental Footprint (EF) method, which includes the USEtox model[72] for the evaluation of the potential toxicity of substances (the most highly recommended[73,74] impact assessment method).

Examining the characterization factors reported in Figure 3a, b and c, it is clear that Pb could generate non-negligible impacts and could be a potentially serious risk if it was emitted into the environment. For example, concerning the human toxicity non-cancer impact category relative to the soil and air compartments, the potential toxicities of Pb results are extremely high, especially if the Pb-based compounds are emitted in agricultural soil or indoor air. Moreover, Pb exhibits high potential toxicity for all air sub-compartments in the same category.

These outcomes agree with and strengthen those reported by studies focusing on toxicity modeling and risk assessment of Pb-compound emissions from PSCs[19–24], suggesting that the evaluation of potential toxicity of Pb-based PSCs could be still an open question. The main risk is underestimating the potential damage of local emissions and danger associated with small-scale pollution during the manufacturing process, use phase and end-of-life management. The point is that since the toxicity of a metal depends on several physico-chemical parameters such as oxidation state, ligands, solubility, morphologies, characteristics of the environment, and many others, the effect on biological systems should not be assumed or taken for granted[75]. Therefore, there is a further need for reliable measurements and empirical tests to improve knowledge of the toxicity of Pb-based PSCs.

For this reason, it is important to specify that the application of LCA for the evaluation of toxicity of specific metal-based compounds might not be exhaustive and might lead to results

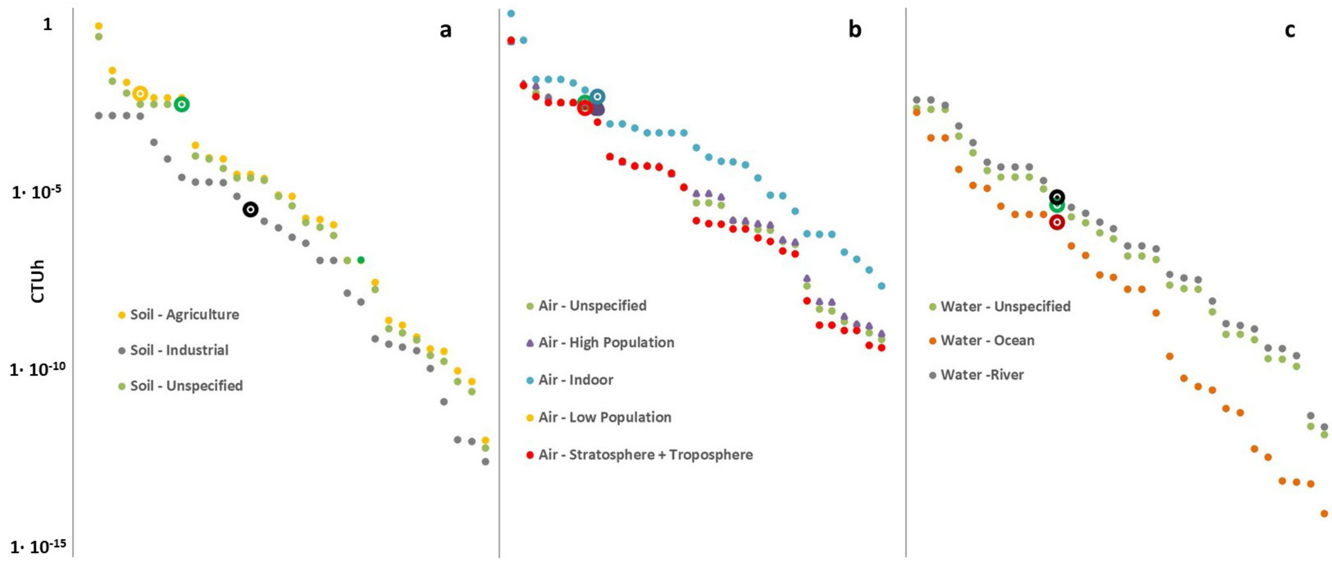

Figure 3. Plot of the toxicity-related characterization factors of heavy metals including lead (larger dots in the chart) for the impact category human toxicity non-cancer effect, relative to the environmental compartment soil (**a**), air (**b**) and water (**c**).Characterization factors are expressed in comparative toxic unit for humans (CTUh). Data is taken from the Environmental Footprint Life Cycle Impact Assessment Method[72,76].

with relatively high uncertainty. This is due to the inherent uncertainty of the USEtox model related to the lack of some physico-chemical parameters used to model the fate, exposure, and the potential toxicity of many metal-based compounds[72].

Encapsulation as a viable solution to facilitate commercialization

The most promising solution to mitigate the risks associated with Pb emission and leakage during the use and end-of-life phases is the physical encapsulation of PSCs and PSMs. Encapsulation is a standard procedure that uses different materials to cover and protect the laminated module from external agents. This procedure allows enhancement of the module's stability by limiting the oxidation and degradation of materials, and recent development demonstrates that physical encapsulation could also reduce Pb-based compounds' emission by sequestrating most of the Pb in the PSCs[77–79].

In recent studies, the encapsulated modules have been subjected to various stress tests, such as: i) mechanical shattering followed by water soaking[77]; ii) fire simulation[78]; and iii) mechanical damage followed by simulated rainfall[79], and, definitively, all studies came to similar conclusions.

The limitation of Pb leakage from shattered and soaked PSCs in water was substantial, exhibiting percentages of sequestration efficiency higher than 96% of the total Pb mass for all test conditions (i.e., different water temperature, pH, and soaking time). In addition to this, the PCE of the PSCs encapsulated with Pb-adsorbing films showed no appreciable differences compared with the non-encapsulated PSCs[77].

The results of the fire simulation tests outlined that glass encapsulation of the PSCs could avoid the formation of Pb-based compounds that are soluble in water, while facilitating the formation of Pb-based compounds that dissolved into the softened glass, thus limiting their emission into the surrounding environment. The monitoring of air emissions proved that the maximum simulated value of Pb emissions did not exceed the safety standards set by the European Commission[78].

The encapsulation with epoxy resins and the subsequent exposure of PSCs to different weather conditions showed a remarkable reduction in Pb-based compound leakage. The most promising encapsulation method under the most severe rainfall simulation (i.e., acid rain) exhibits a reduction in Pb-leakage of more than two orders of magnitude, also thanks to the high temperatures that the device could tolerate under outdoor conditions[79].

Recently Chen and co-authors[80] showed the effectiveness of a a low-cost mesoporous sulfonic acid-based lead-adsorbing resin that, when incorporated into PSCs as a scaffold, immobilizes lead ions inside it even if PSCs are exposed to rainwater. Introducing the insulating scaffold not only does not decrease the device efficiency, but also can be scaled up to large-area modules

Conclusion

The environmental sustainability of PSCs and the issues related to the toxicity of Pb in perovskite have started to be extensively addressed in the scientific literature. Based on the studies published so far, it can be inferred that the topic should be approached from as many perspectives as possible due to the inherent uncertainty associated with the models describing the environmental impact of Pb compounds.

From the toxicological point of view, it seems clear that Pb and Pb-based compounds employed and eventually released by PSCs are extremely dangerous and toxic for living organisms. Strong efforts should be put into the further investigation and characterization of fate, exposure and potential toxicity of all Pb-based compounds that are used and could potentially be emitted during the whole life cycle of PSC devices.

On the contrary, from the LCA perspective, Pb shows a quite limited burden on PSCs' environmental profile, mainly due to the small impact of the metal's production process. According to the main outcomes of LCA studies on PSCs, the replacement of some raw materials, the reduction of some chemical compounds' consumption, the improvement of energy requirements, and the implementation of a safe end-of-life phase are the crucial environmental hotspots that need to be addressed to accomplish industrialization and mass production. However, more detailed and in-depth LCA studies focusing on the life cycle of Pb-based compounds employed are necessary to evaluate the real sustainability of Pb-based PSCs. From this point of view, it would be beneficial to expand on the LCA models to customize the analysis for the specific conditions characterizing the investigated systems. Moreover, it should be considered that it is not the chosen life cycle impact assessment method that gives validity to the result of a LCA analysis, but the accuracy and awareness with which the results obtained are discussed, analyzed and contextualized by the operator.

At the same time, widening the perspective to mitigate risks along the whole value chain, for the technology to have a chance of entering the PV market firmly, manufacturing companies should put effort to i) guarantee the safety of the PSC manufacturing phase work environment, ii) develop reliable encapsulation techniques to prevent Pb leakage during the transportation and use phases, and iii) implement harmless and controlled end-of-life management procedures.

Data availability

No data are associated with this article.

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General Comments
This paper is a very well put together manuscript which meticulously captures the current thoughts on Pb use in perovskite solar cells and will benefit the field. We have provided minor comments/corrections that may be useful. It is well balanced and discusses the benefits and drawbacks of the use of lead in a logical and comprehensive fashion.

Introduction
Statement in paper: "Renewable energy is unquestionably important to ensure a sustainable society, in which both citizens and industries can benefit and develop while respecting the replenishing rate of natural resources."

Whilst the reviewers of course agree with this statement it may be worth noting that renewable energy technologies are not inherently sustainable (but are considerably much better than fossil fuel based alternatives) from an environmental perspective unless sustainability and end-of-life issues are mitigated/planned/designed for. This is mentioned later in the introduction as a challenge for PSCs but it is of course a challenge for all PV technology.

Statement in paper: "At the same time, life cycle assessment (LCA) methodology has been applied to several PSC configurations to evaluate the eco-profiles of the technology[25–37] and understand better which could be the relevant environmental hotspots along the whole PSC life cycle in addition to those *related to the use of Pb-based compounds."*

This is a comprehensive list of PSC LCA studies, and the conclusions actually point to a number of differing environmental hotspots. A recent conclusion worth noting from Tian *et al* LCA shows us that the use of functionalised glass substrates and precious metals in electrodes in particular are in most environmental impact categories the major contributors owing to the high impacts embedded in these materials form their production. Conclusions show these impacts can be significantly reduced through a circular economy approach to substitute precious metals and capture the glass for reuse in new modules. The embedded impacts in materials are higher than those of the production process itself, although where thermal processes for materials deposition and curing are used, this incurs the majority of the process impact. These are all things that really need to be addressed to make this technology truly sustainable, and actually differ from the conclusions of many other LCAs that have looked predominantly at lab scale fabrication and extrapolated. In light of this we would recommend adding Tian, X., Stranks, S.D., You, F., 2021. Life cycle assessment of recycling strategies for perovskite photovoltaic modules. Nat. Sustain. 1–9. https://doi.org/10.1038/s41893-021-00737-z

Another relevant reference, although not LCA, to add may be
Kadro, J.M., Hagfeldt, A., 2017. The End-of-Life of Perovskite PV. Joule 1, 29–46.
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They make comment on the issue of supply bottlenecks for solar glass substrates and a number of the other issues you touch on in this paper.

Statement in paper: "Regarding PV applications, although the RoHS2 Directive excludes solar panels from the restrictions, as a precaution PSCs should respect 0.1% Pb content as the maximum concentration value tolerated by weight in "homogeneous material"."

This is true, however the exemption will not apply if the PV is product integrated, and so respecting the RoHS limit will unlock this important application also. This could be very important in the context of powering IoT devises, many of which will be important to achieve the sorts of energy efficiency measures required to meet emissions targets also.

Reference 22

We are unsure what reference this makes to consideration of the leakage of Pb issue?

Statement in paper: "Next, we present the most recent mitigation and encapsulation techniques developed and published recently, and finally, we outline the main end-of-life concerns and potential future recycling techniques."

No need to say most recent and recently in same sentence.

Availability, viable alternatives and recyclability

Statement in paper: "In this regard, several authors have already explored and investigated the feasibility of the PSC recycling process [52,53]*, highlighting the high recycling rate of Pb*[54] *and the potential recovery of most to all of the PSC components* [55–57]*."*

With regard to references 55-57, there is a significant body of literature with including attempts to recycle PSCs which does show recovery of most to all of the cell components is possible in addition to the reference cited here. I would suggest that addition of additional references here so to cover the breadth of this knowledge to the same extent that the authors have done (commendably) for LCA earlier in the paper would strengthen the paper.

Statement in paper: "Although these processes have been demonstrated at a laboratory scale and need to be scaled up, the prospect of manufacturing PSCs with recovered materials, avoiding efficiency losses, has been already documented[49]."

Binek's paper [49] shows the potential for reusing the FTO substrate with no efficiency loss, however this is the only component of the cell (although very important from LCA and cost point of view) that was reused without loss in device efficiency. The paper specifically states results lower PCE in devices made from recovered perovskite precursor solutions. Although we agree with the statement that using recovered materials without efficiency loss has been demonstrated, the reference only shows this to be the case for substrates. I think a quick review as suggested in the comment above will show more research which has managed to reuse more cell components including the perovskite and ETLs without loss in efficiency which you could add here to support this statement.

Statement in paper: *"Analysing the possible replacement of Pb with other metals, some critical issues need to be addressed. As reported above, metals identified and tested as a viable alternative for metal-based perovskite in PSCs are Sn, Ge, Bi, Sb and In38. Figure 2 shows that most of these metals' natural availability is lower than Pb."*

Although it is true that the natural availability of these metals is lower than Pb, that is not necessarily what Figure 2 shows specifically. As it is a criticality analysis, it takes into account other factors within supply risk in addition to natural abundance and production including geopolitical factors, global supply and demand, supply concentration, and rate of import in the EU all of which may affect to the materials for the EU, but when combined do not necessarily reflect the natural availability picture alone. The authors go on to state that production rate may be an issue (which implies that natural abundance itself may not be the nature of the bottleneck but the rate at which they can be delivered to the global market), although it is expected that total demand from all sectors for some of these metals will exceed known reserves in coming decades. There are some papers that have examined this, including:
Valero, Alicia, Valero, Antonio, Calvo, G., Ortego, A., 2018. Material bottlenecks in the future development of green technologies. Renew. Sustain. Energy Rev. 93, 178–200. https://doi.org/10.1016/j.rser.2018.05.041

LCA for environmental assessment of Pb in PSCs
Statement in paper: *"The main critical raw materials employed for PSC production are gold (used as back contact), the conductive solar glass, and the electron transport material (ETM) due to the organic compounds consumed during the synthesis."*

From the references stated in the previous paragraph, it is not clear to me what organic CRM compounds are used in the synthesis of ETLs and how these are critical, or even how they contribute to the lifecycle impacts outlined in the studies mentioned in the previous paragraphs. It may be a confusion in the language. The previous paragraph states that this paragraph summarises the environmental hotspots, which certainly gold and the substrates are, but now we seem to be talking about critical raw materials. Perhaps it is confusing to talk previously in the paper about CRMs and now perhaps we are talking about materials critical to overall environmental impacts, and if so, we would suggest care with the use of the term critical here, and perhaps use the term 'significant' instead. Also, it could be made clear what organic materials used in ETM synthesis are significant? From reading the authors previous paper and other references, curing of the ETMs is significant due to energy demand of these thermal processes, and perhaps volatilisation of solvents in this process may also be significant to environmental impacts? Clarification of this would also be helpful to the reader, because the ETMs themselves are generally inorganic oxides or is this specific to all organic ETM?

Encapsulation as a viable solution to facilitate commercialization
While of course not all topics can be covered it may be worth noting/commenting on the work on resin layers to absorb lead/prevent leakage to the environment? e.g., Chen, S., Deng, Y., Xiao, X. *et al.* Preventing lead leakage with built-in resin layers for sustainable perovskite solar cells. *Nat Sustain* 4, 636–643 (2021) https://doi.org/10.1038/s41893-021-00701-x This could be in addition to encapsulation if needed.

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Is the topic of the review discussed comprehensively in the context of the current literature?
Yes

Are all factual statements correct and adequately supported by citations?
Yes

Is the review written in accessible language?
Yes

Are the conclusions drawn appropriate in the context of the current research literature?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Perovskite PV, applied photochemistry, circular economy, sustainability and critical raw materials

We confirm that we have read this submission and believe that we have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Author Response 15 Oct 2021

Riccardo Basosi

General Comments

This paper is a very well put together manuscript which meticulously captures the current thoughts on Pb use in perovskite solar cells and will benefit the field. We have provided minor comments/corrections that may be useful. It is well balanced and discusses the benefits and drawbacks of the use of lead in a logical and comprehensive fashion.

- ***Response:*** We express our sincere thanks for the efforts of the Reviewers in the evaluation of our manuscript. We are very grateful for the positive and constructive comments, which have been very helpful in preparing an improved revised version of the manuscript that we hope now fully meets the criteria for indexing.

Introduction

Statement in paper: "Renewable energy is unquestionably important to ensure a sustainable society, in which both citizens and industries can benefit and develop while respecting the replenishing rate of natural resources."

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- ***Response:*** We fully agree with the Reviewers and we have implemented the text accordingly.

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They make comment on the issue of supply bottlenecks for solar glass substrates and a number of the other issues you touch on in this paper.

- ***Response:*** We agree with the Reviewers' suggestion and we have implemented the bibliographic list with the work by Tian and co-authors. We have added also a Nature Sustainability "News and Views" article referred to that work. Concerning the work by Kadro and Hagfeldt, this paper has already been cited in the manuscript in section "Availability, viable alternatives and recyclability".

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- ***Response:*** We fully agree with the Reviewers and a reference to this issue has been made in the manuscript

Reference 22 - We are unsure what reference this makes to consideration of the leakage of Pb issue?

- ***Response:*** We thank the Reviewers for having highlighted this typo. We have removed such reference from the text.

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Although it is true that the natural availability of these metals is lower than Pb, that is not necessarily what Figure 2 shows specifically. As it is a criticality analysis, it takes into account other factors within supply risk in addition to natural abundance and production including geopolitical factors, global supply and demand, supply concentration, and rate of import in the EU all of which may affect to the materials for the EU, but when combined do not necessarily reflect the natural availability picture alone. The authors go on to state that production rate may be an issue (which implies that natural abundance itself may not be the nature of the bottleneck but the rate at which they can be delivered to the global market), although it is expected that total demand from all sectors for some of these metals will exceed known reserves in coming decades. There are some papers that have examined this, including:
Valero, Alicia, Valero, Antonio, Calvo, G., Ortego, A., 2018. Material bottlenecks in the future development of green technologies. Renew. Sustain. Energy Rev. 93, 178–200.
https://doi.org/10.1016/j.rser.2018.05.041

- ***Response:*** We thank the Reviewers for having highlighted this point that, actually, created a misunderstanding. We fully agree with Reviewers' comment, thus we have modified the text erasing the adjective "natural" and we added the suggested reference.

LCA for environmental assessment of Pb in PSCs
Statement in paper: *"The main critical raw materials employed for PSC production are gold (used as back contact), the conductive solar glass, and the electron transport material (ETM) due to the organic compounds consumed during the synthesis."*

From the references stated in the previous paragraph, it is not clear to me what organic

CRM compounds are used in the synthesis of ETLs and how these are critical, or even how they contribute to the lifecycle impacts outlined in the studies mentioned in the previous paragraphs. It may be a confusion in the language. The previous paragraph states that this paragraph summarises the environmental hotspots, which certainly gold and the substrates are, but now we seem to be talking about critical raw materials. Perhaps it is confusing to talk previously in the paper about CRMs and now perhaps we are talking about materials critical to overall environmental impacts, and if so, we would suggest care with the use of the term critical here, and perhaps use the term 'significant' instead. Also, it could be made clear what organic materials used in ETM synthesis are significant? From reading the authors previous paper and other references, curing of the ETMs is significant due to energy demand of these thermal processes, and perhaps volatilisation of solvents in this process may also be significant to environmental impacts? Clarification of this would also be helpful to the reader, because the ETMs themselves are generally inorganic oxides or is this specific to all organic ETM?

- ***Response:*** We thank the Reviewers for having highlighted this point that, actualy, created a misunderstanding. We have substituted "critical raw materials" with "hotspots in terms of materials" to clarify better this point and implemented the text concerning the environmental load characterizing the ETM production.

Encapsulation as a viable solution to facilitate commercialization

While of course not all topics can be covered it may be worth noting/commenting on the work on resin layers to absorb lead/prevent leakage to the environment? e.g., Chen, S., Deng, Y., Xiao, X. *et al.* Preventing lead leakage with built-in resin layers for sustainable perovskite solar cells. *Nat Sustain* 4, 636–643 (2021) https://doi.org/10.1038/s41893-021-00701-x This could be in addition to encapsulation if needed.

- ***Response***: We thank the Reviewers for the reference to this interesting work that has been added and commented in the manuscript.

Competing Interests: No competing interests were disclosed.

Reviewer Report 04 June 2021

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This is a very clear and well written review on ALL ASPECTS connected with the sustainability and environmental assessment of Pb employed in PSCs. This very useful literature analysis starts from the physico-chemical properties of Pb and its potential risks for humans and the environment. Afterward, the major outcomes of LCA, toxicological and risk assessment on PSCs, are presented focusing on the toxicity-related environmental impacts. Then, the most recent mitigation and encapsulation techniques are discussed and finally the main end-of-life concerns and potential future recycling techniques outlined.

The topic of this review is timely and has been discussed comprehensively in the context of the current literature. Many factual statements have been reported and adequately supported by correct citations. The language is clear and appropriate. The conclusions fit well in the context of the current research literature.

The paragraphs Pb in PSCs clearly states how Pb is fundamental for the high performances of the PV device as till now, no viable, effective and compelling alternative has been found. However the analysis of the literature regarding the toxicology issues (well documented) as well as the leakage from perovskite solar modules points out the critical aspects of its use versus other Pb sources. For this reason Table 1 (from ref.19) has been correctly selected and commented. Thus claiming that a substantial reduction of Pb-based compound and GHG emissions could be achieved by replacing conventional energy production technologies with PSCs.

The discussion on LCA for environmental assessment of Pb in PSCs is very well conducted and the general output clearly suggests that the evaluation of potential toxicity of Pb-based PSCs could be still an open question: more detailed and in-depth LCA studies focusing on the life cycle of Pb-based compounds employed are necessary to evaluate the real sustainability of Pb-based PSCs. Of course the availability of suitable data along the whole value chain (not only materials but also design of the cells, technology, encapsulation, etc.) will offer the possibility to assess the real potentiality and sustainability asset of this innovative technological approach.

Few really minor remarks:

Page 3
"In sharp contrast with all the other fuels, renewables have already shown their resilience to the coronavirus pandemic crisis."

- We agree with the authors, but an adequate reference or a more specific explanation in the text could be added.

Page 4

"The highest efficiency recorded for a Pb-free PSC is 9.6%, reached with a Sn-based perovskite..."

- We agree with the sentence however a novel record (10.9%, Chen *et al.* (2020)[1]) and a recent review on the topic can be useful for the reader (e.g., Nasti & Abate (2020)[2]).

Page 6

"Nuss *et al.* performed an LCA of metals..."

- Maybe rephrasing as, "Nuss *et al.* performed a cradle-to-gate LCA of metals", is more informative for the reader

Page 7

"The main critical raw materials"

- Here, the simple use of "critical materials" without "raw" could be more easy and general.

References

Refs: 8 ,9

- Year missing: is that made with the idea to keep the reference updated?

A list of the used abbreviations (even if all of them have been indicated in the text) could help the readers, especially those not completely familiar to the field.

References

1. Chen M, Dong Q, Eickemeyer F, Liu Y, et al.: High-Performance Lead-Free Solar Cells Based on Tin-Halide Perovskite Thin Films Functionalized by a Divalent Organic Cation. *ACS Energy Letters*. 2020; **5** (7): 2223-2230 Publisher Full Text

2. Nasti G, Abate A: Tin Halide Perovskite (ASnX3) Solar Cells: A Comprehensive Guide toward the Highest Power Conversion Efficiency. *Advanced Energy Materials*. 2020; **10** (13). Publisher Full Text

Is the topic of the review discussed comprehensively in the context of the current literature?

Yes

Are all factual statements correct and adequately supported by citations?

Yes

Is the review written in accessible language?

Yes

Are the conclusions drawn appropriate in the context of the current research literature?

Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Material synthesis and developing of innovative photovoltaics

We confirm that we have read this submission and believe that we have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Author Response 15 Oct 2021

Riccardo Basosi

We express our sincere thanks for the efforts of the Reviewers in the evaluation of our manuscript. We are very grateful for the positive and constructive comments. We have taken into account all their remarks in preparing an improved revised version of the manuscript that we hope now fully meets the criteria for publication in Open Research Europe.

Page 3
"In sharp contrast with all the other fuels, renewables have already shown their resilience to the coronavirus pandemic crisis." We agree with the authors, but an adequate reference or a more specific explanation in the text could be added.

- ***Response***: We have added a reference to contextualize better this assertion.

Page 4
"The highest efficiency recorded for a Pb-free PSC is 9.6%, reached with a Sn-based perovskite..."
We agree with the sentence however a novel record (10.9%, Chen *et al.* (2020)[1]) and a recent review on the topic can be useful for the reader (e.g., Nasti & Abate (2020)[2]).

- ***Response***: We thank the Reviewers for this suggestion and we have implemented the text accordingly.

Page 6
"Nuss *et al.* performed an LCA of metals..."Maybe rephrasing as, “Nuss *et al.* performed a cradle-to-gate LCA of metals”, is more informative for the reader.

- ***Response:*** We have modified the text accordingly.

Page 7
"The main critical raw materials"- Here, the simple use of “critical materials” without “raw” could be more easy and general.

- ***Response:*** We agree with the Reviewers that the term “raw” could have raised some misunderstanding, thus we have changed the expression “main critical raw materials” in “main hotspots in terms of materials”

References
Refs: 8 ,9- Year missing: is that made with the idea to keep the reference updated?

- ***Response:*** Yes, our intention is to refer to the NREL charts that are continuously updated A list of the used abbreviations (even if all of them have been indicated in the text) could help the readers, especially those not completely familiar to the field. Actually we have formatted the manuscript according to the article guidelines given by the publishing platform. This is the reason why an abbreviation list is not present in the manuscript.

Competing Interests: No competing interests were disclosed.