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Lead *vs.* tin in the preparation of metal halide perovskites: is this the real fight for the future of solar energy?†

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Metal halide perovskites (MHPs) have gained attention as a viable alternative to crystalline silicon solar cells, offering comparable power conversion efficiencies exceeding 26%. However, their large-scale adoption remains limited by several challenges, most notably, the reliance on toxic post-transition metals like lead. While efforts have been made to replace lead with less hazardous metals such as tin, a comprehensive evaluation of the environmental trade-offs has often been overlooked. This study presents, for the first time, a quantitative comparison of the environmental and human health impacts associated with lead and tin precursors in the fabrication of two benchmark perovskite active layers: $MAPbI_3$ and $MASnI_3$. The results show that tin accounts for 27.6% of the total manufacturing impact, compared to only 18.8% for lead. The endpoint single score analysis further highlights that tin is 1.6–1.8 times more impactful than lead. Based on the LCA data, a tin-based device would at least require a PCE of *ca.* 42% to match the environmental and PCE performance of its lead-based counterpart.

Broader context

Lead-based perovskites have attracted significant interest in the field of organic semiconductors since their development, achieving remarkable power conversion efficiencies exceeding 25%. Despite their high performance, concerns about their potential toxicity have driven the scientific community to explore alternatives, such as tin-based perovskites, often without conducting comprehensive environmental assessments. In this research article, we present a cradle-to-gate life cycle assessment comparing a lead-based perovskite ($MAPbI_3$) with its tin-based counterpart ($MASnI_3$), to determine which material poses a greater environmental impact. In brief, our study quantifies the somewhat unexpected limitations on the use of tin. For the preparation of a perovskite, tin accounts for 27.6% of the total manufacturing impact, compared to only 18.8% for lead. The endpoint single score analysis further highlights that tin is 1.6–1.8 times more impactful than lead. Based on the LCA data, a tin-based device would at least require a PCE of *ca.* 42% to match the environmental performance of its lead-based counterpart. These findings underscore the importance of conducting thorough sustainability evaluations rather than relying on assumptions. They also encourage the scientific community to investigate alternative metal halides and show how crucial the design of more efficient organic components is.

Introduction

In the modern era, driven by the ongoing depletion of fossil resources and growing environmental concerns, solar photovoltaic has become a significant technology for producing green electricity. As a result, nearly 5% of global energy is now produced through the photovoltaic effect. Currently, almost the entirety of this 5% comes from single crystalline silicon technologies which,[1] according to the National Renewable Energy Laboratory (NREL)[2] have achieved a record power conversion efficiency (PCE) of 26.1%. However, these technologies are not immune to notable drawbacks, including high production costs and environmentally harmful manufacturing processes.

As a result, over the past fifteen years, both academic and industrial efforts have largely focused on the development of perovskite solar cells (PSCs),[3] which have demonstrated impressive efficiencies and have now matched the performance of silicon-based ones.[4]

Chemically, a perovskite is a molecular entity (chemical formula ABX_3) constituted by two different cations (A and B) and an anion (X). Precisely, in metal halide perovskites, A is generally an organic or inorganic cation such as $CH_3NH_3^+$, $CH_2(NH_2)^+$, Cs^+, or Rb^+, B is a metal cation such as Pb^{2+} or Sn^{2+} and X is a halide anion such as Cl^-, Br^- or I^-.[5]

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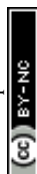
Unfortunately, despite their proficiency, metal halide perovskites (MHPs) are still far from widespread utilization as silicon-based photovoltaics, because of the easy degradation of the active layer primarily induced by high temperature, oxygen and moisture.[1]

In addition, there are other technical factors that limit their large-scale use, that is the need for a dangerous precursor, such as lead salts for their preparation, whose human health toxicity has been already stated by the World Health Organization.[6] For this reason, several endeavors have been devoted to substitute lead with other metals such as bismuth, antimony but mostly tin,[7] in the hope of the creation of a greener active layer.

To date, within the optoelectronic community, tin is regarded as the most sustainable alternative, primarily due to the remarkable stability demonstrated by perovskites containing tin, along with their optical bandgaps of 1.2–1.4 eV, closely aligning with the optimal bandgap of 1.34 eV for the Shockley–Queisser (SQ) limit under the AM 1.5 solar spectrum.[8]

Despite its promising features, tin presents toxicity and environmental concerns that cannot be overlooked. Over the past decade, several studies have highlighted its limitations compared to lead, revealing that it can be both a harmful element to ecosystems and a potential contributor to global warming.

These findings support the established understanding that the impact of a substance extends beyond its direct effects on human health, encompassing broader environmental consequences. Even compounds considered safe for humans can disrupt ecological balance and indirectly affect human well-being.

Krebs *et al.*[9] were among the first to demonstrate, through a cradle-to-grave analysis, that tin-based devices face notable drawbacks, including higher costs and limited availability. Moreover, their architecture often requires gold, which significantly increases the overall environmental impact.

Similarly, Yuan *et al.*[10] demonstrated that due to their lower efficiency, tin-based devices generate a higher environmental burden per kilowatt hour of electricity produced.

More recently, Troshin *et al.*[11] confirmed through combined *in vitro* and *in vivo* studies that tin and lead have comparable toxicological profiles, offering no clear biological advantage for tin.

In this scenario, the present manuscript aims to clarify which metal, lead or tin, has a greater impact in the synthesis of metal halide perovskites (MHPs), by examining their respective implications for human health, the environment, and chemical performance.

Unlike previous studies that assessed the tin *vs.* lead debate superficially and often focused on the entire device (where electrodes rather than the active layer dominate the environmental impact), this study offers a more targeted analysis of the metals themselves. It also underscores the often-neglected influence of organic components within the perovskite layer on the overall environmental footprint.

To achieve this goal, we conducted a life cycle assessment (LCA) study. This is a standardized and widely recognized approach for evaluating the environmental impacts of a process or procedure, such as chemical synthesis,[12,13] throughout its entire life cycle, from material requirements to product disposal.

The cradle-to-gate analysis herein reported focuses on data related to the chemical preparation of two benchmark active layers: methylammonium lead iodide (MAPbI$_3$), as synthesized by Miyasaka,[14] and methylammonium tin iodide (MASnI$_3$), as described by Snaith.[15]

Results and discussion

To introduce the topic, it is essential to first focus on the two synthetic procedures under consideration. Both the Miyasaka and Snaith protocols[14,15] involve synthesizing the active layers through the reaction between methylammonium iodide and a post-transition metal iodide, utilizing different solvents as reaction and processing media: lead iodide in γ-butyrolactone (GBL) for the Miyasaka protocol and tin iodide in *N,N*-dimethylformamide (DMF) for the Snaith protocol. Additionally, the perovskite solutions produced exhibits different concentrations, with 8 wt% in the Miyasaka method and 40 wt% in the Snaith procedure.

These differences in terms of solvent type and amount could profoundly falsify our evaluation, because their impact on the procedures could be higher or lower, consequently altering the impact of the other reactants.

For these reasons, we first compared the two solvents to determine their divergences in terms of human health and environmental benignity. This preliminary evaluation was performed through an endpoint-level characterization that offers us a single score value expressed in mPts.

The results shown in Fig. 1 suggest that GBL is slightly more impactful than DMF (δ 0.06 mPts). Despite the magnitude of the scores being almost similar, this difference, although limited, could mislead the study, and so the results derived from the analysis of the global impact.

Moreover, to accurately assess the differing impacts of lead and tin, and considering the points mentioned above, we decided to standardize the protocols by assuming that both were conducted using 40 wt% of the MHP precursor relative to the amount of solvent.
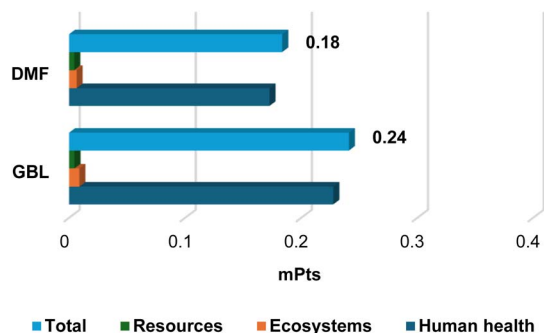

Fig. 1 Endpoint characterization of the solvents used in the procedures considered.

This assumption has also been corroborated by analysing the most recent protocols, where usually both MAPbI$_3$ and MASnI$_3$ are synthesized, independently by the solvent system adopted, in highly concentrated solutions that often exceeds 40 wt%.[16–18]

After defining our system boundary, we initially performed a midpoint analysis on the procedures under consideration, evaluating 18 impact categories. We assumed that both the procedures investigated utilized the same 60% by weight solvent, *i.e.* DMF (Fig. 2).

As can be observed, the impact derived from the metal halides is almost identical, with an average impact among the different impact categories of 26% for PbI$_2$ and 21% for SnI$_2$. On the contrary, the scenario is dominated by methylammonium iodide, which results in the most impactful component (average 58% in MAPbI$_3$ and 64% in MASnI$_3$). This, considering the synthetic procedure needed for its preparation, derives from the large volumes of toxic and volatile solvents adopted, such as diethyl ether.

In order to verify that switching from one solvent to another doesn't affect the impact of MAPbI$_3$ and MASnI$_3$, the same characterization was performed considering GBL instead of DMF (Fig. ESI-1†) for both the reference protocols.

As previously specified (Fig. 1), when modifying the reaction and processing media, the results change, with a general increment of the impact caused by GBL, and a general reduction

of the influence induced by the other constituents, even if the percentage impact over the total of both lead iodide and tin iodide remains almost unchanged (~25% and ~20%, respectively), while the methylammonium iodide footprint decreases to 55% in MAPbI$_3$ and to 61% in MASnI$_3$.

The plot thickens when considering the actual solvents utilized in the original procedures, that is GBL for MAPbI$_3$ and DMF for MASnI$_3$ because of the differences derived from the impact associated with different media, that affect the global evaluation. As stated above, this effect is most noticeable when evaluating the most impactful component, *i.e.* methylammonium iodide. In fact, as mentioned when considering only DMF or GBL as reaction solvents, the average impact of the two metal halides used over the 18 categories is generally constant, while the average effect induced by methyl ammonium iodide among the two procedures becomes sensitively different (55% in MAPbI$_3$ 40 wt% in GBL and 64% in MASnI$_3$ 40 wt% in DMF) (Fig. ESI-2†).

This corroborates the considerations and approximation made, confirming that evaluating the two procedures at the same concentration and with the same media is the best option to actually assess the impact derived from the whole procedure or from a particular component.

At this stage, considering the midpoint characterization did not lead to satisfactory and clear results, we performed an
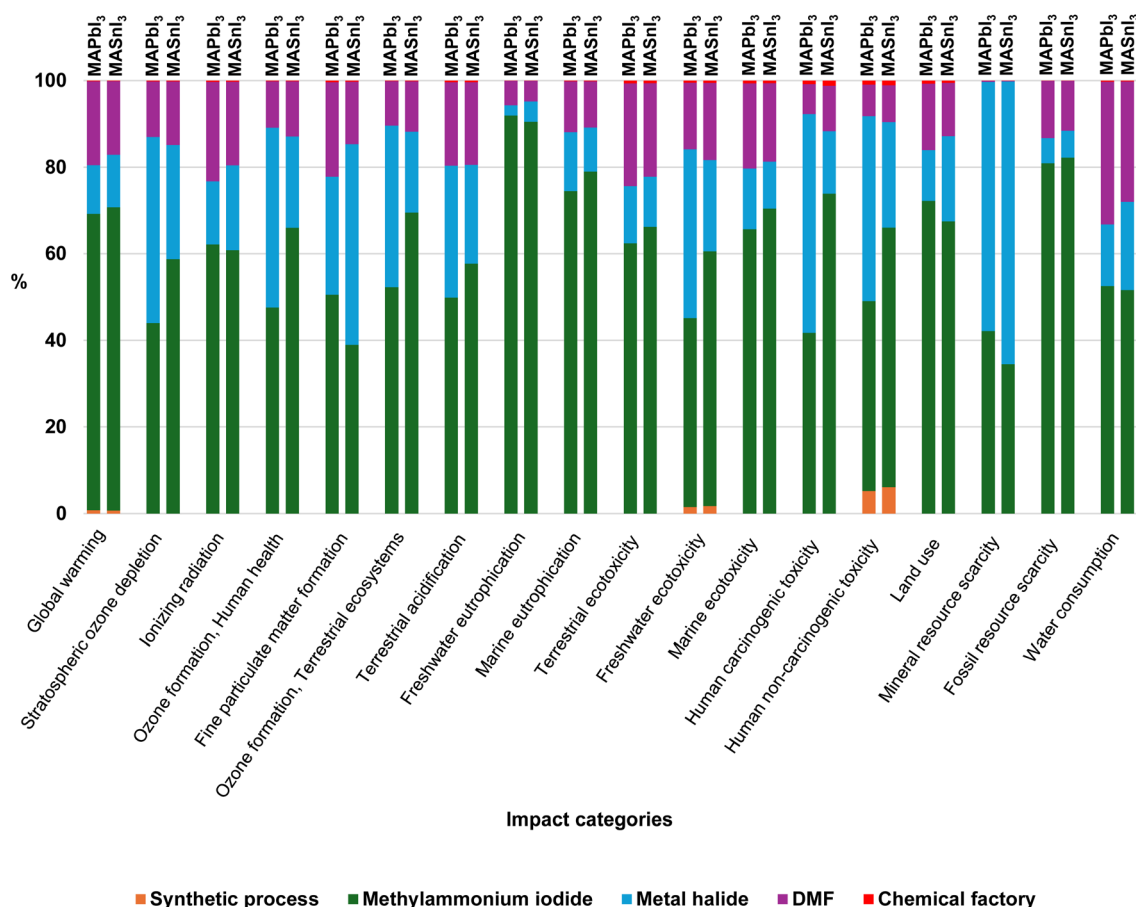

Fig. 2 Midpoint characterization for the synthesis of 1 g of MAPbI$_3$ and MASnI$_3$ 40 wt% in DMF.

endpoint characterization of the two routes analysed to definitively assess which among lead and tin iodide is the most impactful.

This calculation is a type of analysis which aims at collecting the 18 categories into three macro damage areas (*Human health, Ecosystems and Resources*). If the midpoint level looks at the impact along the cause-effect chain reflecting the changes induced in the environment caused by emissions or resource depletion, the endpoint looks at the consequences derived from the cause-effect chain.[19]

The endpoint characterization will finally give us a numerical score expressed in millipoints (mPts), which will represent

the overall impact of a certain process under investigation. The higher the score, the more impactful the process.

As reported in Fig. 3, the endpoint referred to in the synthesis of MAPbI$_3$ and MASnI$_3$ 40 wt% in DMF highlights that the use of tin is definitely not the best choice, as it is believed, to define a greener active layer. In fact, as plotted, the impact of MASnI$_3$ on the overall manufacturing step is higher (1.83 mPts) than the impact derived from the production of MAPbI$_3$ (1.45 mPts).

Indeed, the figure below shows that both footprints are primarily influenced by two impact categories: "*Global warming*" and "*Fine particulate matter formation*", accounting for
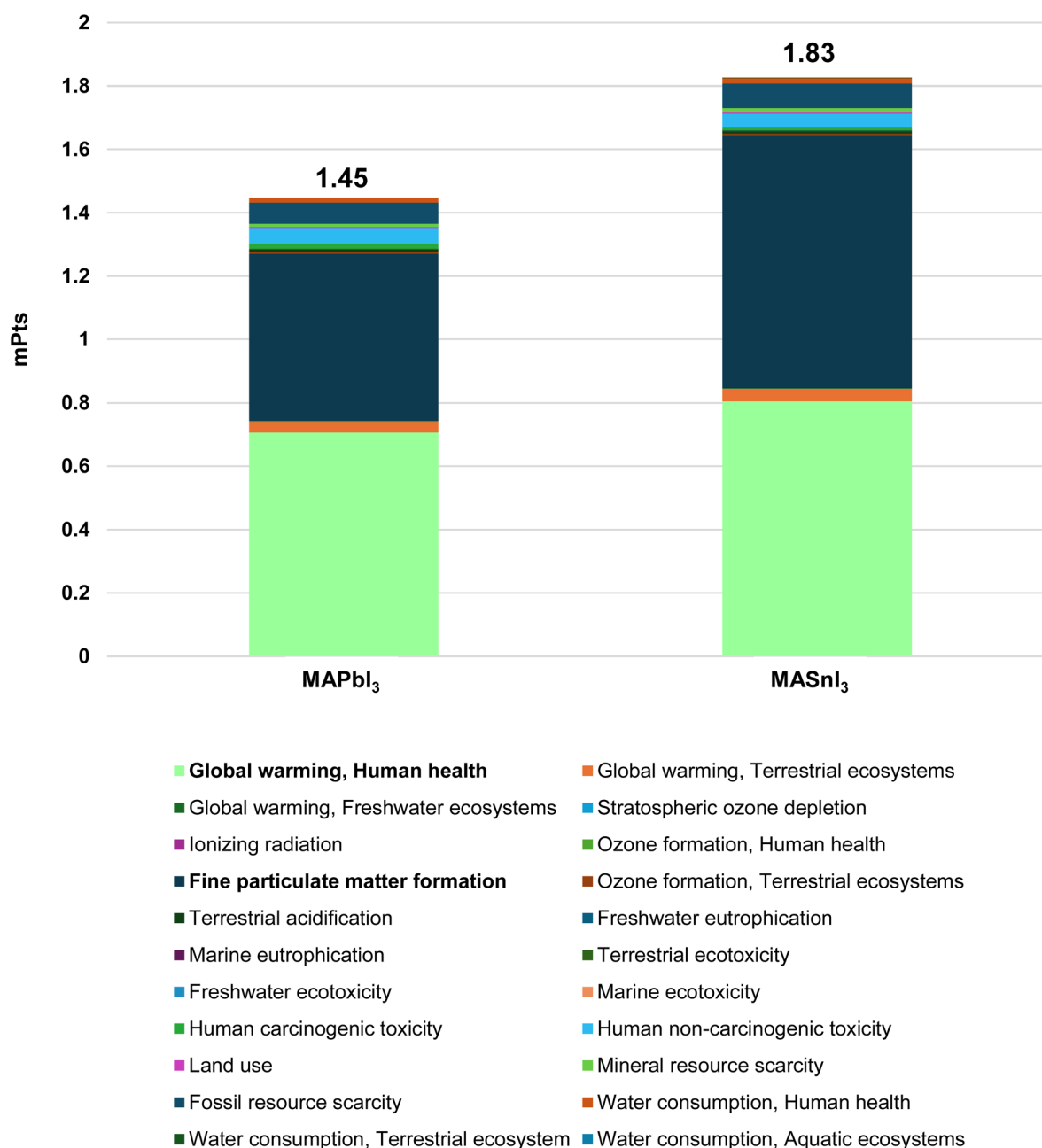

Fig. 3   Endpoint single score characterization for the synthesis of 1 g of MAPbI$_3$ and MASnI$_3$ 40 wt% in DMF.

approximately 90% and 87.6% of the total, respectively. While in the second category, the impact of metal halides was not negligible (see Fig. 2), for the first one the influence of both lead and tin iodide was limited if related to methylammonium iodide.

At first sight this could seem strange and inconsistent, however it indicates that the midpoint categories influence differently the endpoint result, having a different strain on it. Some categories, such as not surprisingly "*Global warming*" and "*Fine particulate matter formation*", deeply shape the endpoint characterization since both rising temperatures and the presence of particulate dust significantly affect human and environmental health.[20]

Further evaluations that confirm the data obtained and the supremacy of certain categories over others, can be achieved looking at the "*Mineral resource scarcity*" category. In fact, considering the midpoint analysis, we could assert that the metal halide has a great impact on the global assessment (see Fig. 2). In contrast, focusing on the endpoint level, the same category only mildly affects the final score (0.7% for MAPbI$_3$ and 0.8% for MASnI$_3$), since the event considered (mineral depletion) in this case does not have a sensitive consequence on the areas of protection. To provide deeper insight into the role of the metal halides considered, we also evaluated their contribution to the global assessment (Fig. 4).

In both procedures, approximately 91% of the impact is concentrated in the *Human health* damage area, with the remaining portion distributed between the *Ecosystems* and *Resources* areas. Specifically, the percentage contribution of lead iodide to the global single score during the manufacturing of MAPbI$_3$ is 18.8% (0.272 mPts), while for tin iodide in the synthesis of MASnI$_3$, it is 27.6% (0.503 mPts).

In particular, of this 27.6%, 20.3% (0.369 mPts) derives from the "*Fine particulate matter formation*" category, confirming the high impact of tin on both human health and the environment, while 5.3% (0.102 mPts) comes from the "*Global warming*" category.

Similar trends were observed when GBL was used as a solvent instead of DMF. In this case, the contribution of lead iodide decreases slightly to 17.8%, and tin iodide to 26.3%. This reduction can be attributed to the higher influence of GBL compared to DMF.

Chemically, this difference between lead and tin and so between lead iodide and tin iodide, arises from the synthetic routes used in their preparation. While lead iodide is synthesized directly from metallic lead and iodine, the synthesis of tin iodide typically involves a multi-step process starting with tin chloride, followed by an exchange reaction to yield tin iodide. This more complex route is, to the best of our knowledge, the primary reason for the greater environmental footprint of tin compared to lead.

The environmental impact of tin in the global assessment of the active layer, is consequently ~1.85 times higher than that of lead (approximately 0.27 mPts for lead and 0.50 mPts for tin). These values are obtained by the analysis of the footprint of a 1 g-functional unit, which includes the preparation of 1 g of MAPbI$_3$ or 1 g of MASnI$_3$. It should be noticed that the molecular weight (MW) of tin is smaller than that of lead (*i.e.* in 1 g, more millimoles of tin are considered). Therefore, if the assessment is made considering the millimols (mmol), for 1 g of active material, the number of mmol of tin is slightly larger than that of lead meaning that a larger quantity of tin iodide (1.88 millimoles) is used compared to lead iodide (1.61 millimoles).

As a result, when considering a hypothetical comparison on millimoles (1.61 for both metals), the impact of tin iodide
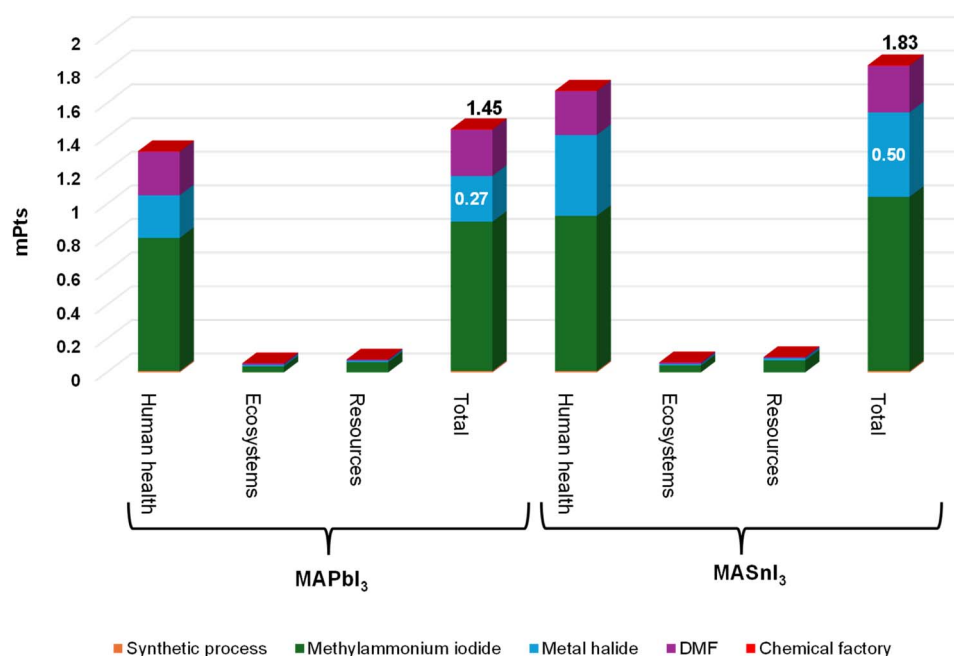

Fig. 4 Endpoint single score (mPts) characterization for the synthesis of 1 g of MAPbI$_3$ and MASnI$_3$ (40 wt% in DMF). Focus of the component contribution into the three damage areas.
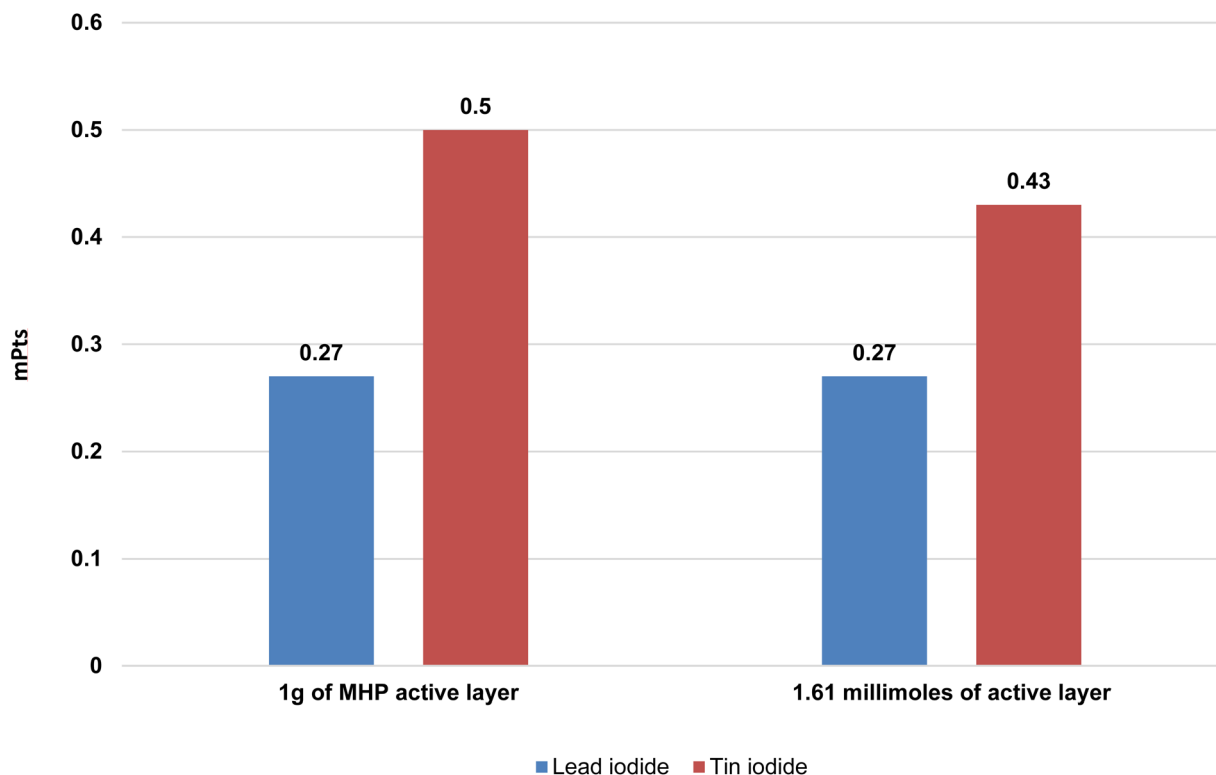
Fig. 5 Focus on the endpoint single score (mPts) contribution of the metal halides.

decreases to approximately 0.43 mPts. Tin is anyway *ca.* 1.6 times more impactful than lead.

It is worthy of note that for MAPbI$_3$, power conversion efficiency (PCE) is approximately 26% (Fig. 5),[21] while that for MASnI$_3$ is about 8%.[22]

Therefore, to balance the PCE and environmental impacts of MAPbI$_3$, MASnI$_3$-based devices should reach at least a PCE of *ca.* 42%, corresponding to the 1.6 times higher environmental impact.

If only the grams (Fig. 4) (and not the millimoles) are considered, for the manufacturing of a device to balance the lead environmental profile, a tin-based device should reach a PCE of *ca.* 48%.

This major environmental footprint has been further confirmed by calculating the endpoint single score of both lead and tin iodide where, contrary to current trends, the latter was approximately twice as impactful (718 µPts) as the former (366 µPts). This higher impact as previously specified is likely due to the additional synthetic steps required for its preparation.

Setting aside the contribution of the metal to the overall impact, the most surprising finding is the significant influence of methylammonium, which is confirmed as the most impactful element.

Conclusions

A cradle-to-gate life cycle assessment was conducted to determine which of the two metal halides, lead or tin, has a greater environmental and human health impact in the preparation of metal halide perovskites (MHPs). To ensure an accurate comparison between the two salts, the reference procedures were standardized, using the same solvent (DMF or GBL) and the same precursor concentration (40 wt% relative to the solvent).

Although there is a great interest in the scientific community to develop new metal-based perovskites aiming at replacing lead, particularly focusing on tin, the results presented here reveal for the first time that tin, the only viable alternative to lead, has actually a greater environmental impact, when considering the active layer synthesis.

In the LCA details, this is specifically evident when looking at the "*Global Warming*" and "*Fine Particulate Matter Formation*" categories, which are the most influential factors in the overall assessment. The endpoint-level characterization further supports this finding, indicating that tin is 1.85 times more environmentally harmful than lead (1.61 if mmol are considered). Taking into account the current average power conversion efficiencies (PCEs) of approximately 26% for MAPbI$_3$ and 8% for MASnI$_3$, a tin-based device would need to achieve a PCE of *ca.* 42–48% to balance the environmental impact of its lead-based counterpart.

Additionally, the analysis highlights methylammonium iodide as a key contributor to the overall environmental burden of perovskite active layers. Therefore, while much of the research has focused on replacing lead with tin, these findings suggest that future efforts should be prioritized on developing a less impactful organic components to enhance the sustainability of perovskite solar cells.

In conclusion, the analysis confirms that global assessments are influenced not only by the toxicological or environmental

profiles of the substances studied, but also often by a combination of both. While earlier debates on lead *versus* tin mainly focused on toxicological effects on human health, this study demonstrates that a comprehensive evaluation must also include environmental impacts. In this context, life cycle assessment (LCA) emerges as a key tool.

It remains the most robust and internationally recognized method for assessing the sustainability of products and processes, especially in the chemical and energy sectors. By providing accurate, complete, and reliable data, LCA offers a solid foundation for informed decision-making by policymakers, researchers, and industry stakeholders. Further research should focus on analyzing the impacts of these metals across different environmental categories to identify critical points in the value chain and determine the most effective and sustainable alternatives to lead and tin for reducing the overall environmental footprint.

Experimental section

Goal and scope definition

The main aim of the LCA study presented is to assess the environmental sustainability of lead and tin in the manufacturing of a metal-halide perovskite (MHP) active layer ($MAPbI_3$ and $MAPbI_3$) disclosing which among them is less impactful.

The experimental procedures referenced in this study for the impact evaluation of $MAPbI_3$ and $MASnI_3$ production were sourced from existing literature (secondary data).[14,15]

The present work follows the four phases that define the LCA methodology: goal and scope definition, inventory analysis, impact assessment and, finally, the interpretation of the results.[23]

Moreover, according to the ISO 14040 family standards and the more completely elaborated ILCD Handbook Guidelines,[24,25] the system boundary was determined based on a cradle-to-gate approach. The functional unit was defined as 1 g of the desired target product, considering emissions and resources exploitation for both the extraction and manufacturing of all materials and energy and the respective process's emissions to water, air, and soil. Moreover, it was assumed that all the processes analysed were performed at one location and that the synthesis proposals were set only to produce the active layer without by-products. The environmental effects caused by transport to provide raw materials have been included, as well as the impact of chemical factories.

Because our aim was to focus just on the footprint derived from the chemical compounds adopted, the influence of the electricity consumption required for the active layers manufacturing steps was not considered.

Moreover, in order to make the analysis as accurate and truthful as possible, it was assumed the both the syntheses were performed with the same reaction solvent (DMF), as well as at the same active layer concentration (40 wt%).

Inventory analysis

While setting up the LCA analysis, new inventories for different materials have been created to be included in the model, adopting a retrosynthetic approach. If an existing inventory data set was available for a specific compound that needed to be modelled, it was considered and utilized in the study.

General assumptions were made regarding process energy (0.0002 MJ per g of the compound) and electricity consumption (0.000333 kWh per g of the compound) for all unavailable compounds that had to be specifically modelled.

The emissions to air during the synthetic processes (0.20% volatile input materials) and air (CO_2), water (river), and sludge emissions after wastewater treatment were calculated as well; no emissions to the soil were determined since no agricultural destination of the digested sludge was considered. In this wastewater treatment, 65.80% of the organic compounds were retained in the sludge, 24.50% were oxidized and emitted to air in the form of CO_2, and the remaining 9.70% were released into the river.[26]

The chemical factory values, as well as assumption adopted to calculate the impact of transport have been included in the study.[26]

Assumptions regarding data gaps (*e.g.*, solvent amount) were made based on our expertise and are clearly outlined in the corresponding inventory tables.

For those inventories already available in the literature, material flows were adopted without modification, while adjustments were made to reflect our approach to electricity and steam consumption.

Impact assessment

The impact assessment was performed using SimaPro 9.6 software and the ReCiPe 2016 method, considering 18 impact categories (global warming, stratospheric ozone depletion, ionizing radiation, ozone formation (human health), fine particulate matter formation, ozone formation (terrestrial ecosystems), terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, human non-carcinogenic toxicity, land use, mineral resource scarcity, fossil resource scarcity, and water consumption).[27]

Midpoint impact categories and endpoint damage areas (*Human health, Ecosystems, and Resources*) were analyzed from a hierarchical perspective over a 100-year period. Long-term emissions, which affect scenarios beyond 100 years, were excluded due to their high uncertainties and their relationship to heavy metal toxicity. Therefore, they are not particularly relevant in organic chemical processing. The results from the various protocols examined are presented and analyzed in midpoints, with outcomes weighted and normalized in endpoint damage areas (*Human health, Ecosystems, and Resources*). This allows for a comparison of our approach to others using a single indicator as a benchmark for global environmental impact. During this process, midpoint characterization results are transformed into intermediate units, which are then weighted and normalized to represent the relative impact in millipoints (mPts), reflecting their severity within a global context.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

F. C.: investigation, methodology, inventory construction, data analysis, writing, review, editing; D. L.: investigation, inventory construction, data analysis, writing, review, editing; F. D. A.: investigation, writing, review, editing; L. V.: conceptualization, project administration and manuscript review/editing.

Conflicts of interest

There are no conflicts to declare.

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