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## Assessment of the environmental and human health impact in the synthesis and processing of metal halide perovskite active layers using GVL

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Metal halide perovskites (MHPs) offer a potential alternative to crystalline silicon solar cells in terms of efficiency. Despite the impressive reported efficiencies exceeding 26%, the widespread uptake of perovskite solar cells still faces significant challenges, such as the use of lead precursors and hazardous reaction and processing media for their production. In fact, commonly used solvents such as *N,N*-dimethylformamide (DMF) or  $\gamma$ -butyrolactone (GBL) are particularly concerning due to their inherent hazards and toxicity, posing substantial risks to both environmental and human health. Safer alternatives, such as the biomass-derived  $\gamma$ -valerolactone (GVL) solvent, could alleviate such concerns. To evaluate the impact of various perovskite components, particularly the environmental and human health footprint associated with the use of specific solvents, we report a life cycle assessment (LCA) analysis on the synthesis and further processing of prototypical perovskite active layers. The characterization confirmed that GVL can mitigate the footprint of 17.8% and 15.9% compared to GBL and DMF respectively in the synthesis of MAPbI<sub>3</sub>, and 23.4% and 18.4% in comparison with GBL and DMF when producing FAPbI<sub>3</sub>. Moreover, the study highlights that designing greener, less impactful organic and metal cations is essential for significantly reducing the environmental footprint of MHP layers manufacturing.

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1. The LCA analysis conducted on MAPbI<sub>3</sub> and FAPbI<sub>3</sub> shows that using GVL reduces the overall environmental impact compared to using GBL (−17.8% for MAPbI<sub>3</sub> and −23.4% for FAPbI<sub>3</sub>) or DMF (−15.9% for MAPbI<sub>3</sub> and −18.4% for FAPbI<sub>3</sub>). Both midpoint and endpoint indicators reveal that MAI has a higher negative impact than PbI<sub>2</sub>, and replacing MAI with FAI decreases the environmental burden. Conversely, substituting PbI<sub>2</sub> with SnI<sub>2</sub> to produce FASnI<sub>3</sub> does not improve the situation because the synthesis of SnI<sub>2</sub> involves more steps, increasing the total environmental impact.
2. Endpoint analysis indicates that using GVL results in significantly lower single score values (1185  $\mu$ Pts for MAPbI<sub>3</sub> and 611  $\mu$ Pts for FAPbI<sub>3</sub>) compared to GBL (1441  $\mu$ Pts for MAPbI<sub>3</sub> and 798  $\mu$ Pts for FAPbI<sub>3</sub>) and DMF (1409  $\mu$ Pts for MAPbI<sub>3</sub> and 749  $\mu$ Pts for FAPbI<sub>3</sub>) as solvents and processing media. This demonstrates the environmental advantage of GVL in the synthesis and processing stages.
3. A comprehensive LCA evaluating the entire production process of a hypothetical device based on MAPbI<sub>3</sub> or FAPbI<sub>3</sub> would be essential to confirm the findings observed in the synthesis of the active layer. This holistic approach would provide deeper insight into the overall environmental impacts beyond just the material synthesis.

## 1. Introduction

Prompted by the overwhelming impact of climate change and geopolitical scenarios affecting Europe, the European

Commission released the “REPowerEU” program in 2022, aiming to save and diversify energy supplies while reducing dependence on fossil fuels, such as natural gas, and promoting the production of clean and renewable energy. Over the last few years, significant achievements have been made throughout the European region, resulting in a notable increase in the proportion of electricity generated from renewable sources, which now accounts for around 46% of the overall electricity market.<sup>1</sup>

As anticipated, the transition to cleaner energy supplies has also been adopted by several other countries, including China<sup>2</sup> and the USA,<sup>3</sup> which aim to significantly reduce greenhouse gas emissions through various action plans.

One of the most promising ways to minimize our dependence on fossil fuels is undoubtedly the harnessing of the

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photovoltaic effect through solar energy conversion. In recent decades, since the advent of first-generation solar cells made from crystalline silicon, which have achieved a maximum power conversion efficiency of 26.1%,<sup>4</sup> numerous advancements have been made in this field.

Perovskite solar cells (PSCs) are those which have been mostly investigated, reaching remarkable efficiency within a very short time.

From a chemical point of view, a perovskite is a molecular structure (chemical formula  $ABX_3$ ) composed of two different cations (A and B) and an anion (X). In metal-halide perovskites, A is usually an organic or inorganic cation such as  $CH_3NH_3^+$ ,  $CH_2(NH_2)^+$ ,  $Cs^+$ ,  $Rb^+$ , and B is a metal cation such as  $Pb^{2+}$ ,  $Sn^{2+}$ , and X is a halide anion such as  $Cl^-$ ,  $Br^-$  or  $I^-$ .<sup>5</sup>

Since the groundbreaking work of Kojima and colleagues,<sup>6</sup> several efforts have been devoted to increasing their efficiency,<sup>7</sup> with recent results exceeding 34.6%, as achieved in a perovskite/Si tandem.<sup>8</sup>

Despite these impressive achievements, PSCs are still far from their massive commercialization. The primary challenge hindering their widespread adoption is undoubtedly scaling them up to larger modules, along with their low durability. Multiple degradation factors have been identified, including exposure to oxygen and moisture, UV and visible light, as well as thermal and structural instability.<sup>5</sup>

Besides these technical concerns, the synthetic protocols used for the synthesis and further processing of the active layers, as well as the starting materials employed, including but not limited to the use of lead, pose a significant sustainability issue. The PSCs manufacturing process, like organic photovoltaics, typically employs solution-based fabrication techniques,<sup>9</sup> requiring the precursor salts dissolution in a suitable reaction/processing medium. When these are mixed, deposited, and annealed, they lead to the formation of a polycrystalline perovskite active film.<sup>10</sup>

Considering the chemical complexity of the precursors, the most commonly used solvents are usually dipolar aprotics, such as  $\gamma$ -butyrolactone (GBL), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylacetamide (DMAc).<sup>11</sup> While the first is usually labelled as "dangerous" by the European Chemical Agency (ECHA),<sup>12</sup> the others have been on the contrary included by the European Commissions through the REACH regulation 1907/2006 in the "substances of very high concern" (SVHC) list, because of their plausible toxicity to the human reproductive system.<sup>13,14</sup>

The solvent issue is a well-known and widely debated topic. As pointed out by Sheldon, solvents pose a significant environmental challenge, accounting for approximately 80% of the waste generated by chemical processes.<sup>15</sup> Research on safer and renewable raw materials, as well as greener solvents, is a crucial step toward developing sustainable products and processes.<sup>16</sup> Given the primary goal of decarbonizing our energy system through cleaner energy production, the manufacturing of perovskite solar cells is not exempt from the pursuit of alternative solvents.<sup>17,18</sup> Among these,  $\gamma$ -valerolactone (GVL) has emerged as a promising alternative for various chemical transformations.

This bio-based cyclic five-membered ester (lactone) is typically synthesized from lignocellulosic biomass through catalytic transformations. In this process, cellulose and hemicellulose are first converted into 5-hydroxymethylfurfural (5-HMF) and furfural, respectively. These platform molecules are then converted into levulinic acid and its esters (levulinates), a class of promising additives and bio-solvents,<sup>19</sup> which can subsequently undergo hydrogenation processes to produce  $\gamma$ -valerolactone (GVL).<sup>20–23</sup> In addition to its applications in cross-coupling and C–H activation processes,<sup>24</sup> as well as in the chemical pretreatment of lignocellulosic biomass,<sup>25,26</sup> GVL proved effective for synthesizing different perovskite solar cells active layers, including the prototypical  $MAPbI_3$ <sup>27</sup> and  $FAPbI_3$  perovskites.<sup>28,29</sup>

In this context, the primary objective of this study is to evaluate the environmental and human health impact associated with the use of hazardous and toxic reaction and processing solvents in the preparation of metal halide perovskites (MHPs), in comparison with the biomass-derived solvent  $\gamma$ -valerolactone (GVL) (Scheme 1).

Beyond identifying the most sustainable solvent system for enabling a greener synthetic route, the investigation also aspires to point out those critical factors, such as lead toxicity and the environmental burden of the organic components,<sup>30–32</sup> that contribute significantly to the overall impact of the different fabrication pathways under consideration.

While several LCA studies have focused on the overall impact of perovskite-based devices,<sup>33–36</sup> to the best of our knowledge, none have specifically concentrated on the chemical preparation of the active layers, particularly exploring the contribution of solvents.

## 2. Methods

This study adhered to the four phases outlined in the LCA methodology.<sup>37,38</sup> First, the goal and scope were defined, as well as the typology of the study. Next, the procedures for compiling material and energy flow inventories were detailed for each synthesis process, along with the methods and assumptions applied. Finally, the impact assessment approach was described.

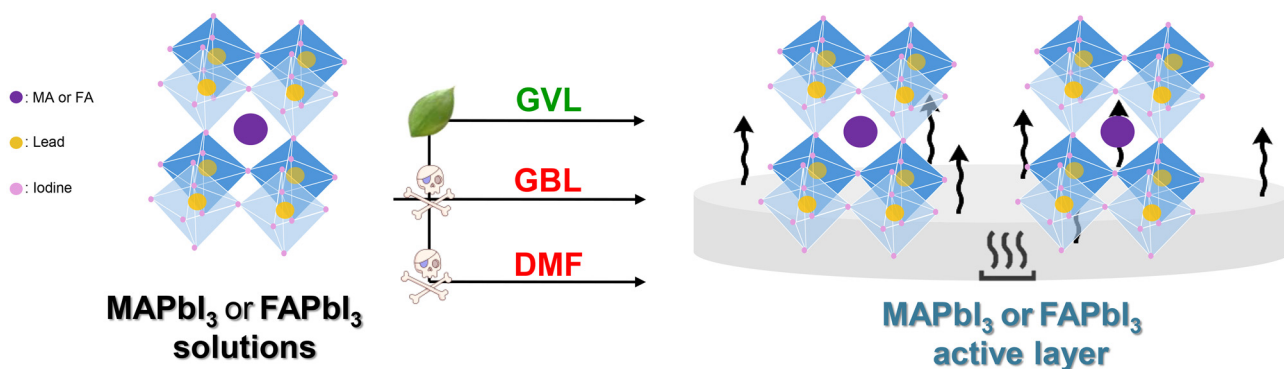
### 2.1 Goal and scope definition

The primary objective of the LCA study presented is to evaluate the environmental sustainability of manufacturing a metal-halide perovskite (MHP) active layer ( $MAPbI_3$  and  $FAPbI_3$ ) using GVL as a green reaction and processing solvent, and to compare its impact with that of GBL and DMF.

The experimental procedures referenced in this study for the impact evaluation of  $MAPbI_3$  and  $FAPbI_3$  production using GVL, GBL, and DMF as solvents (or solvent mixture in the case of  $FAPbI_3$ , where they are the predominant portion) were sourced from existing literature (secondary data).<sup>27–29,39</sup>

The functional unit was defined as 1 g of the desired target product. At the same time, the system boundary was deter-





**Scheme 1** Reference synthesis and processing of MAPbI<sub>3</sub> and FAPbI<sub>3</sub> active layer in different solvents.

mined based on a cradle-to-gate approach, considering the emissions and resource exploitation for both the extraction and manufacturing of all materials and energy, as well as the respective processes' emissions to water, air, and soil. Moreover, it was assumed that all the processes analyzed were performed at one location and that the synthesis proposals were set only to produce the active layer without by-products. The environmental effects of transporting raw materials have been assumed and included (100 km by lorry > 16 t and 600 km by train), as well as the impact of chemical factories, *i.e.* the infrastructures and facilities considered for the manufacturing processes ( $4.00 \times 10^{-13}$  unit).

## 2.2 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.

General assumptions were made regarding process energy (0.0002 MJ per gram of the compound) and electricity consumption (0.000333 kWh per gram of the compound) for all unavailable compounds that required specific modeling.

Given the European Union's statements that the production and use of energy account for over 75% of greenhouse gas emissions across Europe,<sup>40</sup> the contribution of electricity in the final synthetic steps for producing the perovskite active layers (*i.e.*, active layers synthesis and processing) has been excluded from the analysis, as it is nearly identical across all the procedures studied. Instead, the focus has been placed on the impact of the chemicals used, specifically the environmental and human health effects associated with the choice of one solvent over another.

The emissions to air during the synthetic processes (0.20% volatile input materials) and air (CO<sub>2</sub>), as well as water (river) and sludge emissions after wastewater treatment, were calculated. No emissions to the soil were determined, as no agricultural destination for 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 released into the air as CO<sub>2</sub>, and the remaining 9.70% were discharged into the river.<sup>41</sup> Assumptions regarding data gaps (*e.g.*, amount of solvents) were

made based on our expertise and are clearly outlined in the corresponding inventory tables (see SI).

For those inventories already available in the literature, material flows were adopted and adjustments were made to reflect our approach to electricity and steam consumption.

## 2.3 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, Water consumption*).<sup>42</sup>

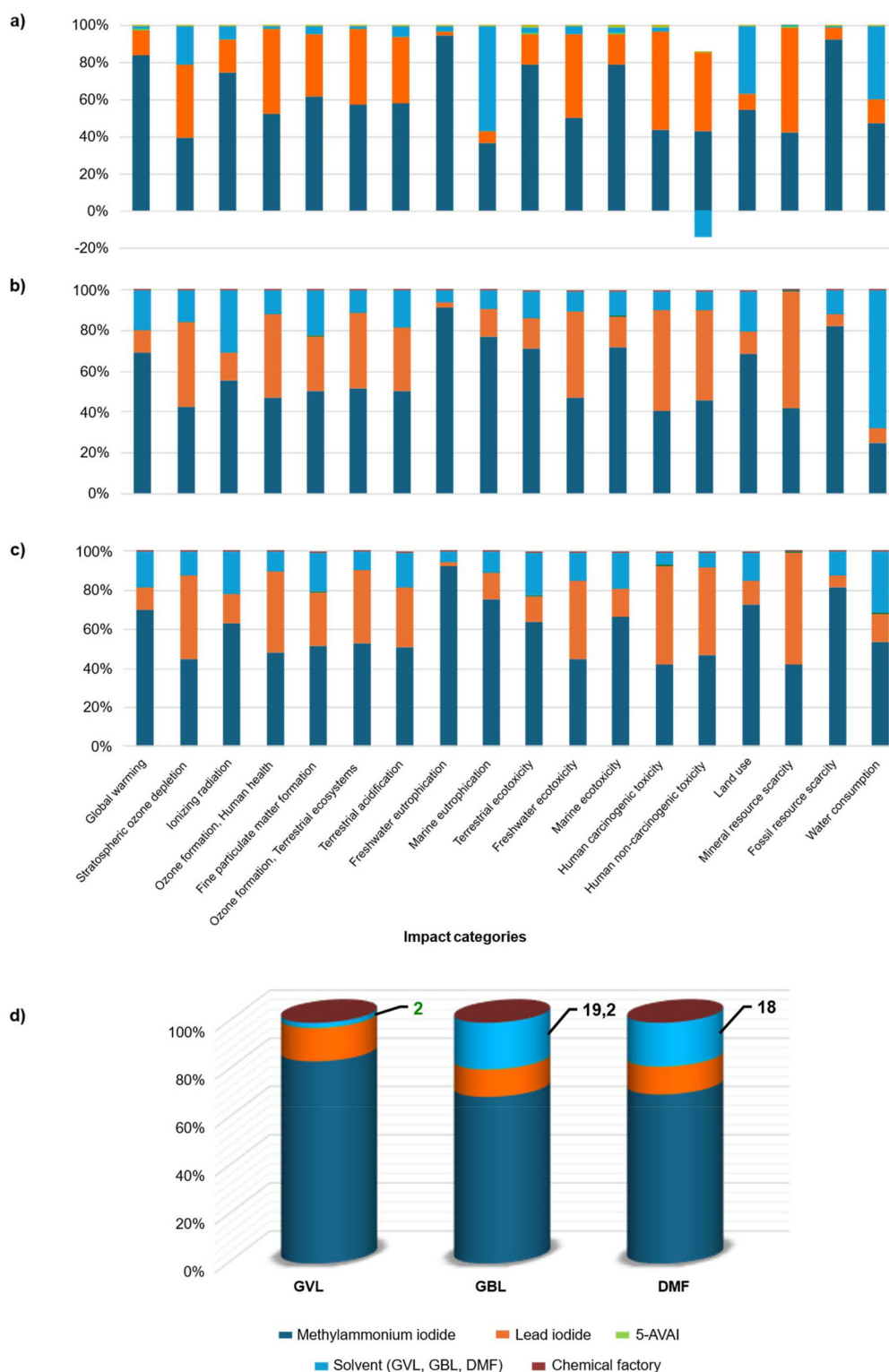
Midpoint impact categories and endpoint damage areas (*Human health, Ecosystems, and Resources*) were analyzed from a hierarchical perspective over a 100-year period. Long-term emissions, which affect scenarios beyond 100 years, were excluded due to their high uncertainties and their relationship to 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. This enables a comparison of our approach with 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 micropoints ( $\mu$ Pts), reflecting their severity within a global context.

# 3. Results and discussion

## 3.1 Solvents impact in the preparation of MAPbI<sub>3</sub>

Our investigation started with a midpoint characterization of MAPbI<sub>3</sub> synthesis using three different solvents (GVL, GBL, and DMF). As can be observed in Fig. 1a, the scenario when





**Fig. 1** Midpoint characterization deriving from the manufacturing of MAPbI<sub>3</sub> in GVL (a), GBL (b), and DMF (c); focus of the three processes in the “Global warming” impact category (d).

manufacturing MAPbI<sub>3</sub> in GVL is dominated by methylammonium iodide and lead iodide, whose production and use have a profound influence on both environmental and health

categories. GVL itself, due to its lignocellulosic biomass origin, plays a non-negligible role in various categories, including “Marine eutrophication”, “Land use”, and “Water consumption”.





The data for “*Human non-carcinogenic toxicity*” is also particularly interesting, as it shows a negative contribution (positive credits) assigned to GVL. This output is not uncommon when biomass is exploited for the production of goods and services because of its well-known ability to absorb heavy metals from the soil during its growth (Fig. 1a).<sup>43</sup> This behavior is furthermore reflected in the “*Fine particulate matter formation*” where GVL, shows a minimal contribution, compared both to the other components and solvents further investigated.

In fact, the scenario shifts significantly when examining the midpoint profiles for GBL and DMF (Fig. 1b and c), whose impact is generally higher compared to GVL. Apart from “*Water consumption*”, which, in the case of GBL, is due to the high volumes required for the 1,4-butanediol (industrial precursor of GBL) production,<sup>44</sup> the effects on “*Human carcinogenic toxicity*” and “*Human non-carcinogenic toxicity*” categories are those where the differences are most noticeable. Although DMF is widely acknowledged as a highly toxic compound with potential carcinogenic and mutagenic properties (H360), the findings suggest that GBL poses an even greater hazard. This conclusion arises from the significant psychoactive effects linked to its conversion into  $\gamma$ -hydroxybutyric acid (often referred to as a date rape drug), which have prompted several countries to regulate and restrict its commercialization and use.<sup>45</sup>

Interestingly, the midpoint characterization suggests that, without considering the solvent used to produce MAPbI<sub>3</sub>, the most influential component in nearly all 18 categories is not lead iodide, but rather methylammonium iodide. Analyzing the experimental procedure and the relative inventory data set (Tables SI-8 and SI-9) needed for their production, it is evident as its major footprint associated to the latter lies in the use of

large amount of solvents (constituting the 93% of the total mass required for the synthetic procedure), such as ethanol and, above all, diethyl ether, whose toxic and dangerous profile is well known.

Additionally, when examining the most assessed and intriguing category, “*Global warming*”, the results obtained after the calculations underline that the use of GVL is nearly trivial, accounting for only 2% of the total carbon dioxide emissions, while methylammonium iodide and lead iodide account for approximately 83% and 14%, respectively (see Fig. 1d).

The beneficial role provided by GVL to the environmental health compared to the other solvents is further confirmed if looking at the kg per CO<sub>2</sub> eq. emitted. In fact, when synthesizing the MAPbI<sub>3</sub> based active layer, GVL produce 0.000744 kg per CO<sub>2</sub> eq., which are 11.6 times less than those produced by GBL (0.0086 kg per CO<sub>2</sub> eq.) and 10.7 those emitted by DMF (0.00798 kg per CO<sub>2</sub> eq.).

This severe impact increment when transitioning from GVL to GBL or DMF, stems from their non-renewable origin.<sup>46,47</sup>

Although a detailed overview of the factors defining the methodologies considered has been provided, conducting an endpoint single-score analysis across all investigated routes is the most effective way to identify the most comprehensively sustainable option.

This evaluation categorizes all the impact categories within the macro damage area, providing a final score, expressed in  $\mu$ Pts (*vide supra*), that defines the greener method based on its impact on “*Human health*”, “*Ecosystems*”, and “*Resources*”.

As shown in Fig. 2, the “*Human health*” damage area significantly dominates the three endpoints for all the analyzed processes, representing approximately 90.7% of the total damage. In contrast, the average contributions from the “*Ecosystems*”

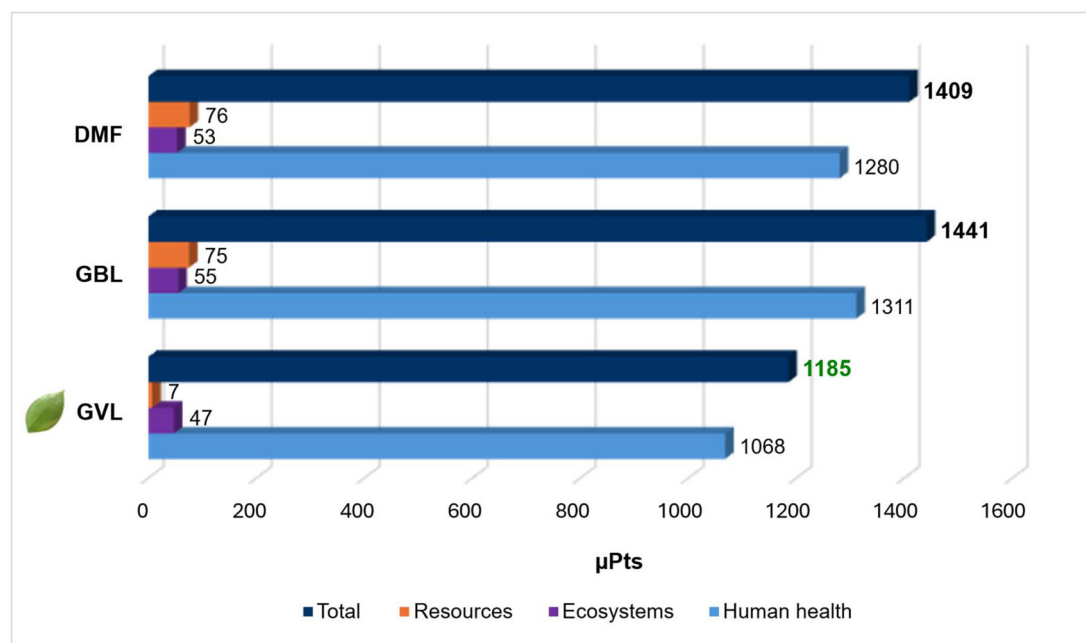


Fig. 2 Endpoint single-score analysis of the MAPbI<sub>3</sub> synthetic procedures considered using GVL, GBL, and DMF.



and “Resources” damage area account for 3.8% and 5.5% of the total, respectively. The endpoint calculations further confirm that the use of toxic and oil-derived solvents has a greater impact on both the environment and human health compared to renewable media, suggesting that choosing waste- or biomass-derived chemicals results in the most appropriate choice aiming at a green transition.

Specifically, GVL accounts for 2.3% of the total score (1185  $\mu$ Pts), while GBL (1441  $\mu$ Pts) and DMF (1409  $\mu$ Pts) contribute more significantly to the final value with a percentage impact of 19.7% and 17.7%, respectively (Table 1). This data confirm and corroborate what has been previously stated through the midpoint characterization, where GVL turns out to be, in absolute terms, less impactful than both GBL and DMF and that methylammonium iodide and lead iodide are the most significant factors affecting all the damaged areas. Interestingly, in contrast to the prevailing view within the scientific community, methylammonium iodide emerges as the primary factor limiting the environmental sustainability of perovskite active layers. It accounts for 73.2% (781  $\mu$ Pts), 74.9% (35.1  $\mu$ Pts), and 86.1% (60.3  $\mu$ Pts) of the environmental impact in the “Human Health”, “Ecosystems”, and “Resources” areas, respectively. Conversely, lead iodide, often regarded as the main threat to human and environmental health in the perovskite sector, contributes only 23.5% (251  $\mu$ Pts), 18.7% (8.8  $\mu$ Pts), and 12.9% (9.1  $\mu$ Pts) to these same areas (Fig. SI-1).

On the other hand, GVL, due to its biomass origin, as pointed out above, represents a key factor in enhancing overall sustainability when used as a reaction and processing medium.

In fact, as highlighted by the endpoint single score values (see Table 1), its use sensitively reduces the overall impact in the production of MAPbI<sub>3</sub> of 17.8% and 15.9% compared to GBL and DMF, respectively.

Despite the encouraging results that corroborate the benefits of the use of renewable reaction media, it should be noted that although GVL's impact is appreciably lower than that of the other solvents, its single score is only slightly lower than those of GBL or DMF. This observation stems from the fact that the study accounts for all the chemical transformations needed to produce GVL. As a value-added product derived from biomass, it is well known that, although significant advancements in technological innovation and manufac-

turing processes have been made, the manipulation of biomass remains costly and energy-intensive.

Furthermore, as highlighted throughout the study and further illustrated in Fig. SI-1, the contribution of additives, such as 5-ammonium valeric acid iodide (5-AVAI), to the overall assessment is minimal. Considering the minimal amounts of additives used, it is reasonable to conclude that the observed solvent-related trends would persist even without incorporating 5-AVAI in active layer production or when employing alternative additives.

### 3.2 Environmental and human health characterization of FAPbI<sub>3</sub> active layer

To provide a clear and comprehensive perspective on the impact of solvents, we also examined the use of GVL in the fabrication of another type of metal halide perovskite (MHP), specifically formamidinium lead iodide (FAPbI<sub>3</sub>).

As applied for MAPbI<sub>3</sub>, to focus attention on the impact induced by the most relevant chemical components, we did not consider the electricity adopted for FAPbI<sub>3</sub> manufacturing. On the contrary, we included eventual additives in the calculation because they are sometimes used in relevant quantities.

Following the same approach used for MAPbI<sub>3</sub>-type perovskite, we first analyzed the midpoint scenario when using the three different solvents (GVL, GBL, and DMF). For the sake of accuracy, this type of perovskite is usually employed in conjunction with dimethylsulfoxide (DMSO) when using GBL or DMF. This is because, as noted by Liu and colleagues, introducing high-boiling-point coordinating solvents into the perovskite precursor can delay both the nucleation and crystallization processes, inducing the formation of an intermediate phase that improves substrate coverage during the evaporation step.<sup>48</sup>

As denoted in Fig. 3, in the case of FAPbI<sub>3</sub> synthesized and processed using GVL,<sup>28</sup> the scenario is generally dominated by lead iodide, which represents the most impactful component in each category. Not negligible is the effect of methylamine hydrochloride, a phase stabilizer,<sup>49,50</sup> especially in the “Marine eutrophication”, since methylamine derivatives are well-known substrates for methanogenic and methylotrophic bacteria,<sup>51,52</sup> resulting in highly pollutant compounds. In contrast, the impact of formamidinium iodide (FAI) typically ranges from 20% to 40% across different categories, with its most significant effect observed in “Freshwater ecotoxicity” due to the use of hydrogen cyanide in the production of its precursor, formamidine acetate.

Regarding GVL, its impact aligns with previous findings observed for MAPbI<sub>3</sub>, showing a noticeable reduction in “Marine eutrophication” due to the presence of FAI. Additionally, we observed beneficial effects in the “Human non-carcinogenic toxicity” category when GVL is used, as illustrated in Fig. 1, and a irrelevant effect in the “Global warming” category, where, together with butyl acetate, they contribute 17.3%. In comparison, GVL contributes just 3.1% directly.

The previously mentioned butyl acetate, used as an antisolvent, has a generally limited impact, ranging from 0.8% to 16.1% among the different categories considered.

**Table 1** Endpoint single scores and impact of the solvents in the manufacturing routes studied for the preparation of MAPbI<sub>3</sub><sup>a</sup>

	(a)	(b)	(c)
Endpoint single score ( $\mu$ Pts)	1185	1441	1409
Impact (%) variation on the endpoint single score	—	−17.8 <sup>b</sup>	−15.9 <sup>c</sup>
Impact ( $\mu$ Pts) of the solvent in the final score	27	284	249
Impact (%) of the solvent in the final score	2.3	19.7	17.7

<sup>a</sup> Process in GVL (a), GBL (b) and DMF (c). <sup>b</sup> Footprint reduction driven by the use of GVL compared to GBL. <sup>c</sup> Footprint reduction driven by the use of GVL compared to DMF.



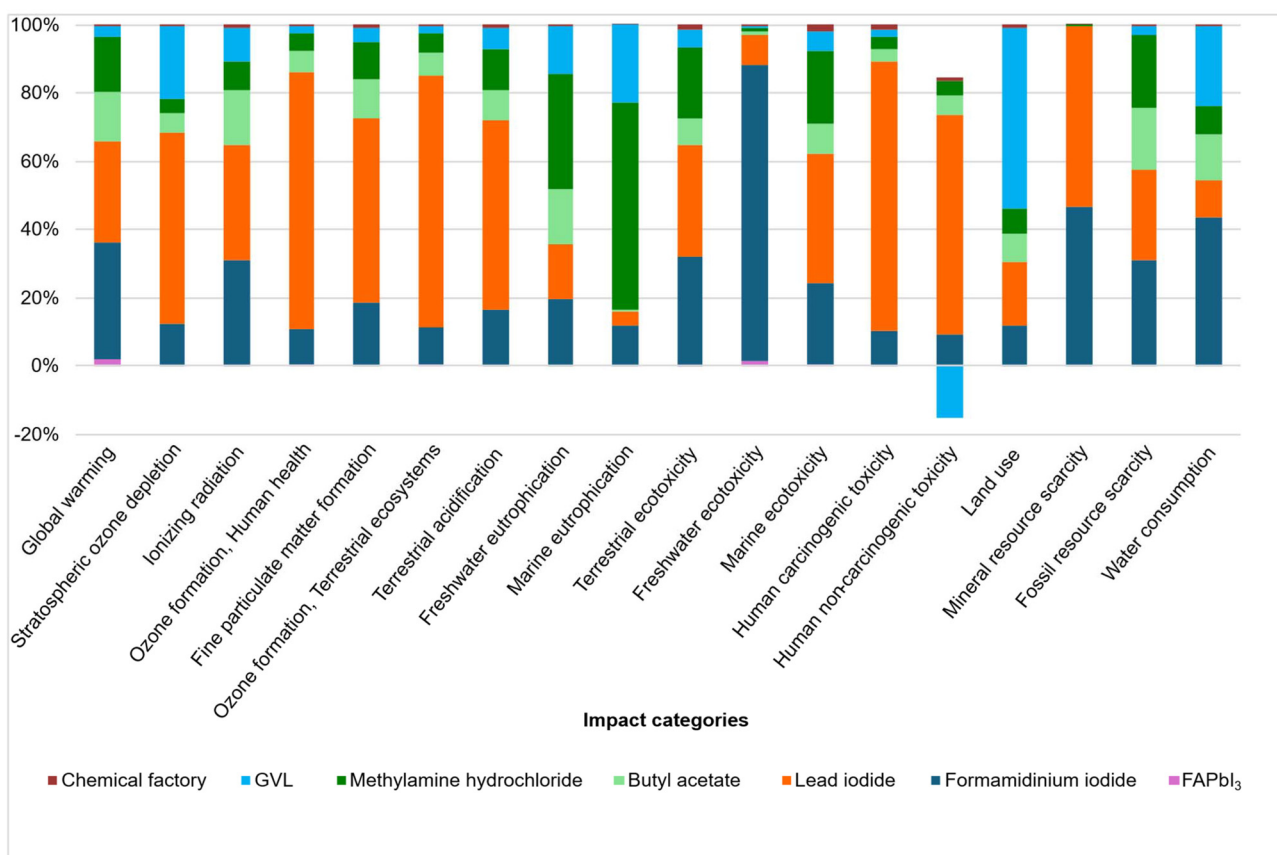


Fig. 3 Midpoint characterization deriving from the manufacturing of FAPbI<sub>3</sub> in GVL.

When GBL : DMSO (7 : 3) is adopted as solvent blend, the scenario changes dramatically as happened for the MAPbI<sub>3</sub>-type layer (Fig. SI-2).

In this case, the influence of lead iodide remains nearly unchanged, while the impact of the solvent increases significantly across the entire characterization. Specifically, whereas the average contribution of GVL and butyl acetate does not exceed 17.5%, GBL and DMSO under these circumstances account for an average of 33.3%.

Specifically, focusing on the “Global warming” category, the solvent mixture contributes 47.4% of the total impact, with 41.6% of this coming from GBL.

The role of chlorobenzene, used as an antisolvent during the spin coating, is generally minimal due to the small quantity employed and its ecotoxicological profile, which is confirmed to be not particularly harmful.

What has been denoted with GBL is endorsed when utilizing DMF : DMSO (9 : 1)<sup>28</sup> (Fig. SI-3). Lead iodide remains the most hazardous chemical, while methylamine hydrochloride also exerts a notably harmful impact on the aquatic ecosystem in this case.

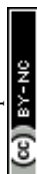
Considering the adopted solvent mixture DMF : DMSO with butyl acetate as the antisolvent, the combined impact averages 23%, rising to 34.6% in the “Global warming” category. To comprehensively evaluate the environmental and human

health impacts of FAPbI<sub>3</sub> manufacturing, an endpoint calculation, similar to the analysis carried out for MAPbI<sub>3</sub>, was conducted to determine the overall benign score expressed in  $\mu$ Pts.

As illustrated in Fig. 4, the process utilizing GVL proved to be the most environmentally favorable, achieving a final endpoint single score of 611  $\mu$ Pts, notably lower than the 798  $\mu$ Pts for GBL and 749  $\mu$ Pts for DMF. Specifically, GVL combined with butyl acetate contributed 14.4% (95  $\mu$ Pts) to the total score, GBL : DMSO (7 : 3) with chlorobenzene accounted for 44.7% (356.8  $\mu$ Pts), and DMF : DMSO (9 : 1) with butyl acetate contributed 31% (231.9  $\mu$ Pts). The trend observed for the total score aligns perfectly with the impact observed in the three damage areas when considered independently.

Moreover, when evaluating the solvents' contribution to the overall environmental impact, excluding co-solvents, anti-solvents, and additives, GVL represented 3.1% (19  $\mu$ Pts), GBL contributed 37.7% (301  $\mu$ Pts), and DMF accounted for 19.3% (144  $\mu$ Pts).

Generally, as detected previously in the production of MAPbI<sub>3</sub>, GVL plays in this case as well a beneficial role in the entire FAPbI<sub>3</sub> manufacturing process. In fact, considering the endpoint single score values, GVL reduces the overall impact of 23.4% and 18.42% compared to GBL and DMF respectively (Fig. 4).



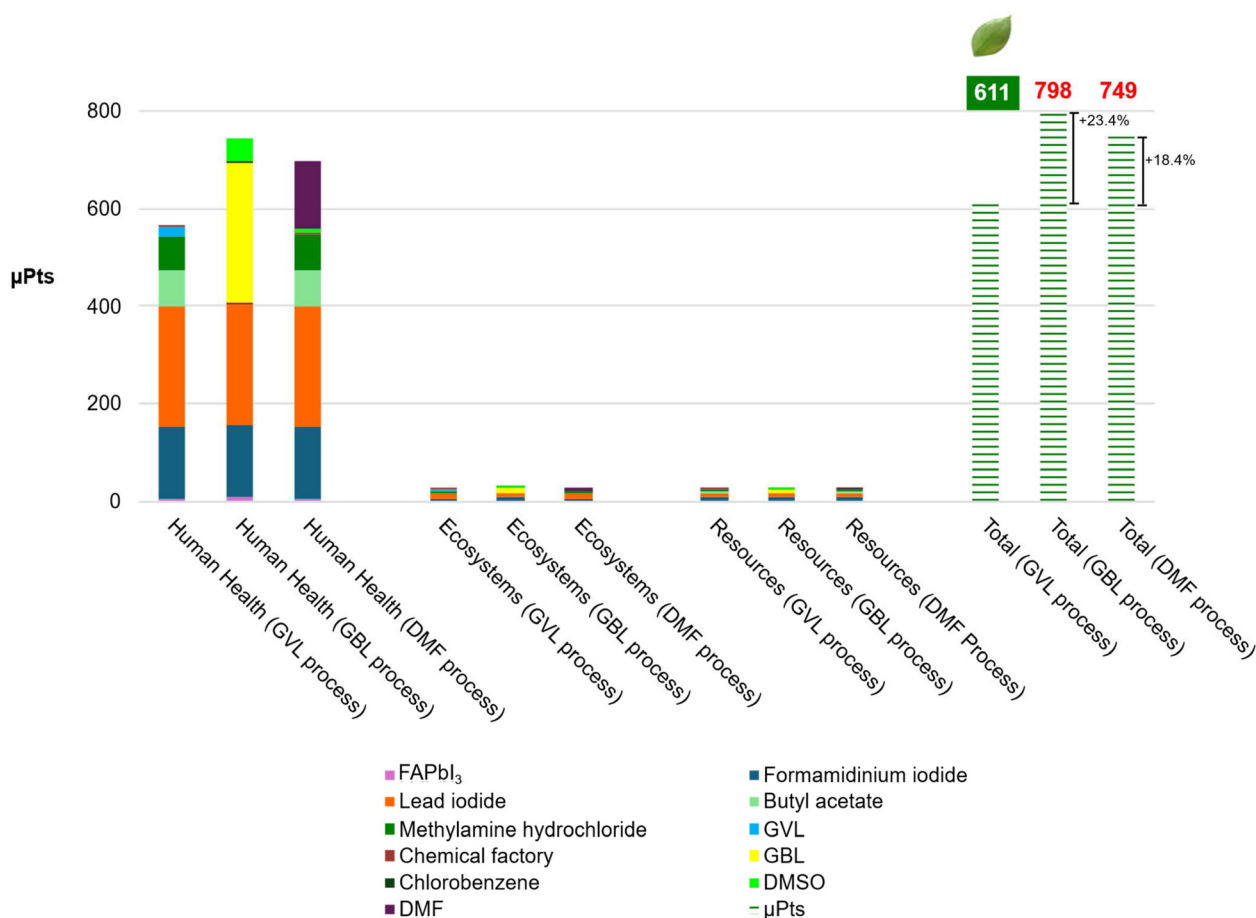


Fig. 4 Endpoint single score calculation for the manufacturing of FAPbI<sub>3</sub>-type active layer using different solvent mixtures.

The advantageous role of GVL in preparing this perovskite layer arises from several factors. First, as noted for MAPbI<sub>3</sub>, it benefits from its biomass-derived origin. Secondly, its high boiling point and coordinating ability allow it to be used without DMSO as a co-solvent, reducing the overall amount of chemicals employed while promoting a general shift towards greener practices.

Interestingly, upon reviewing the endpoint performed for MAPbI<sub>3</sub>, we observed that methylammonium iodide is the component that most significantly affected the global assessment, resulting in a more impactful outcome than lead iodide. When substituting methylammonium iodide with formamidinium iodide, the scenario is reversed, with lead iodide now emerging as one of the worst chemicals adopted in these syntheses, accounting for 43.6% in the GVL-based process, 33.5% when using GBL, and 35.6% in the case of DMF. As can be seen, its impact percentage increases proportionally to the solvent greenness.

At this stage, in addition to the primary considerations regarding the solvents used in the manufacturing and processing steps, we observed a general environmental improvement when substituting methylammonium iodide with formamidinium iodide.

To whet the researchers' appetite, we decided to assess separately the possible impact of lead with a plausible alternative,

tin iodide, in order to preliminarily evaluate the environmental benignity of FASnI<sub>3</sub> active layer-based perovskite.

Surprisingly, contrary to current trends, the endpoint calculation comparing lead iodide to tin iodide indicates that the latter is approximately twice as impactful (718 μPts) as the former (366 μPts). This higher impact is likely due to the additional synthetic steps required for tin iodide production.

It is worth mentioning that lead iodide should not be considered a green salt in general, especially for perovskites production, as confirmed by the midpoint comparison made (Fig. SI-4).

In fact, as lead results dangerous for a series of categories such as "Stratospheric ozone depletion", "Ozone formation", "Terrestrial acidification", "Marine eutrophication", "Freshwater ecotoxicity", "Marine ecotoxicity", "Human carcinogenic toxicity", "Human non-carcinogenic toxicity", tin iodide resulted the worse in the other nine categories. This observation is fundamental to understand better the meaning of the results obtained when performing a LCA assessment and generally from the calculation of green metrics, that indicate as all the impact categories are strictly connected each other, and as all of them influences the three macro damage areas (*Human health, Ecosystems and Resources*), offering solely in this way a comprehensive evaluation.





Furthermore, because the primary scope of this analysis was to evaluate the influence of the synthetic routes adopted for perovskite layers production, it is worthy of note that a more exhaustive evaluation of the whole device based on FAPbI<sub>3</sub> and FASnI<sub>3</sub>, considering and balancing its power conversion efficiency with the electricity consumed during the total manufacturing process, would be beneficial to actually assess the pros and cons of using one salt over another.

## 4. Future outlooks and challenges

The transition toward sustainable reaction and processing solvents useful for perovskite active layers manufacturing presents promising opportunities but also significant challenges. The adoption of  $\gamma$ -valerolactone (GVL) as a biobased-derived solvent offers a clear pathway to limit the environmental footprint associated with active layer synthesis. However, its widespread usage necessitates overcoming limitations, especially those related to the cost and energy requirements of biomass conversion, which currently limit process scalability. Furthermore, while GVL substantially reduces toxicity concerns compared to conventional solvents like GBL and DMF, thereby lowering the overall impact, the stumbling block lies with precursor salts, such as the herein considered methylammonium iodide and lead iodide.

In this context, even if the implementation with alternative and less harmful solvents can represent a valuable way to greening MHPs, most of the efforts in the future must focus on research for greener organic cation sources and identifying viable and less toxic alternatives to lead. Additionally, integrating solvent sustainability with improved recycling strategies and device-level life cycle optimization will be essential to achieving truly eco-friendly perovskite-based devices. Generally, progress in renewable solvent systems have to be coupled with innovations in precursor chemistry and scalable manufacturing to enable a holistic green transition.

## 5. Conclusions

In this work, we demonstrate that using  $\gamma$ -valerolactone (GVL), a safer, renewable, and non-toxic solvent, as a reaction and processing medium for producing MAPbI<sub>3</sub> and FAPbI<sub>3</sub>-type perovskite active layers represents the most sustainable option, offering a markedly lower environmental impact compared to traditional solvents such as GBL and DMF. In fact, considering the endpoint single score values obtained, GVL reduces the global footprint of 17.8% and 15.9% with respect to GBL and DMF when working with MAPbI<sub>3</sub>, and 23.4% and 18.4% in relation to the same solvents while manufacturing FAPbI<sub>3</sub>.

The primary environmental benefits of GVL arise from its minimal contributions to the “Global warming” and “Human non-carcinogenic toxicity” impact categories. Additionally, the analysis reveals that for MAPbI<sub>3</sub>, methylammonium iodide contributes more significantly to the overall environmental

impact than lead iodide, whereas for FAPbI<sub>3</sub>, the reverse is observed. To inspire future research, we also assessed the potential impact of substituting lead iodide with tin iodide. Preliminary findings suggest that replacing lead with tin to synthesize FASnI<sub>3</sub> may not be the most sustainable choice. This is primarily due to the higher environmental concerns associated with tin iodide, stemming from the greater number of synthetic steps required for its production.

Besides these latter findings, which confirm the need to proceed with caution before implementing radical changes, it is essential to thoroughly examine all plausible options.

In conclusion, this study highlights the importance of utilizing and exploiting residual biomass for valorization and upcycling as key tools in achieving an effective green transition.

## Author contributions

F. C.: investigation, methodology, inventories construction, data analysis, writing, review, editing; D. L.: investigation, inventories 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.

## Data availability

Supplementary information: methods, inventories and LCA impact assessment dataset. See DOI: <https://doi.org/10.1039/d5gc03582a>.

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