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# Lead in Perovskite Solar Cells

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## 1. Introduction

This report presents some context and discusses ongoing challenges related to the presence of lead in perovskite-based photovoltaic solar cells (PSC). PSC have been facing significant questioning and public skepticism due to the toxicity of lead and its potential to cause severe environmental and human health hazards.

Not only PSC, but current standard photovoltaic (PV) module manufacturing demands lead. Lead is currently widely used in standard crystalline silicon module manufacturing for the interconnection of solar cells. A typical 60-cell crystalline silicon solar module contains 12 grams of lead, a far too large amount that is viewed as a stigma for the industry. The use of lead is capped by the EC through the Restriction of Hazardous Substances Directive 2002/95/EC (RoHS), which establishes a maximum level of substance that can be used for manufacturing purposes. PV panels are currently exempted from the directive, this exemption is however expected to be reviewed soon, which would then require that the industry adapts to significant lead-use restrictions and to date, lead-free PV manufacturing methods are still scarce and under development.

After this brief introduction, Section 2 of this report describes main potential issues related to lead in the environment and human health, offering an overview of the reasons why the use of lead has been highly contested in perovskite solar cells. Section 3 presents data and discussions on challenges and risks related to lead in the different phases of the lifetime of perovskite solar cells, including the production, the use and the end-of-life. While Section 4 introduces research on lead-free perovskite modules and highlights the main challenges involved in lead-free PSC. Section 5 presents current legislations related to the use of lead in photovoltaics modules as well as discusses trends in the related regulations. Finally, Section 6 mentions a few of the latest research aiming at mitigating and avoiding the potential negative impacts from the use of lead in perovskite solar cells.

## 2. Environmental and health issues of lead-based perovskites

Lead is a cumulative toxic substance that can contaminate air, water and soil, while causing lead poisoning. Lead accumulates in the brain, liver, kidney and bones being estimated to account for 1.06 million deaths and 24.4 million years of health life lost due to long-term effects on health [1]. Many factors account for the risk of toxicity of lead, it is worth highlighting, however, that the high solubility in water could be indicated as one of the most hazardous factors for perovskite solar cells, i.e., its long-term instability namely in the presence of air, humidity and light [2].

Being a toxic heavy metal, lead has the potential to accumulate once it enters the food chain, or the so-called trophic magnification or biomagnification, which means that even considerably small concentrations of the element released to the environment represent a high risk. Figure 1 exemplifies how the biomagnification happens in the food chain.



Figure 1: Trophic magnification of lead. 1. Industrial activities release metals in the environment; 2. Water transports metals into plants, which small fishes consume; 3. Larger fishes consume small, contaminated fish; 4. Humans consume contaminated fish. Heavy metals accumulate up the food chain; thus, more in humans than in any species lower down in the chain [3].

As illustrated in Figure 1, when moving further into the food chain, the toxic material concentration increases, which means that humans or the top consumers will be receiving the highest concentrations.

A comprehensive environmental and toxicological analysis would require data on leaching tests, ecotoxicity analysis, Life Cycle Assessment (LCA), waste recycling analysis etc. Although this data is still scarce for perovskite solar cells, the fact that the concentration of lead in the currently working perovskite solar cells is over 10% in weight [3] sheds light on the related potential environmental and toxicological issues. Moreover, as this concentration does not meet the limits adopted by countries that regulate the use of heavy metals in electronics, a deeper analysis on the topic is highly recommended.

Figure 2 summarizes the potential effects of exposure to lead on human life such as high blood pressure, kidney failure, reduced fertility etc., as well as the main factors related to poor stability that can be responsible for PSC degradation, which might lead to the human exposure [4].

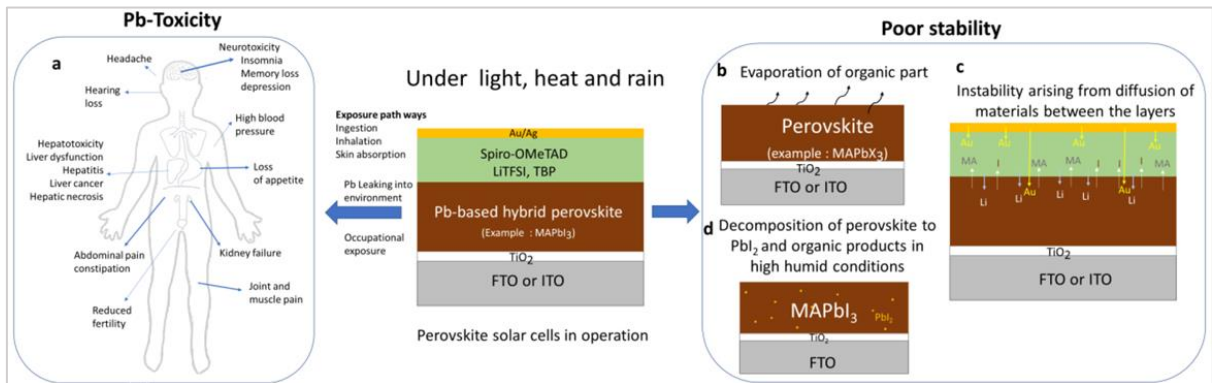


Figure 2: Illustration of (a) possible effects on human life if exposed to lead and (b, c, d) some possible causes of perovskite degradation [4].

Therefore, although thorough toxicological studies are still insufficient, it becomes clear that the elimination of lead could represent the most reasonable solution. For this reason, the present report brings a fully dedicated section on the topic - Section 4 that provides information on ongoing research on lead-free modules.

### 3. Use and consumption of lead in solar PV modules

#### a. Qualitative analysis of the different phases of the lifetime of a PSC

This section describes the risks related to the presence and use of lead in each phase of the lifetime of a perovskite PV Module. For this purpose, two different LCA studies were taken into consideration. The goal of an LCA is to evaluate environmental impacts and energy balance in every stage/phase of a product's life. Typically, the following phases are considered: raw material extraction, synthesis of starting products, fabrication/manufacturing, use and decommissioning/end-of-life [15].

A summary of the results of the first LCA study analyzed is illustrated in Figure 3. The authors considered that as the chemicals used as starting products for perovskite solar cells are already being used on an industrial scale for other applications, it was assumed that the corresponding material extraction and synthesis would have been already optimized in terms of health and safety [15]. Therefore, more focus was given to the manufacturing or fabrication, the use and the decommissioning. In Figure 3 the main hazards of each of these three phases is presented in red, while potential control strategies for the fabrication, use and decommissioning are written in green.

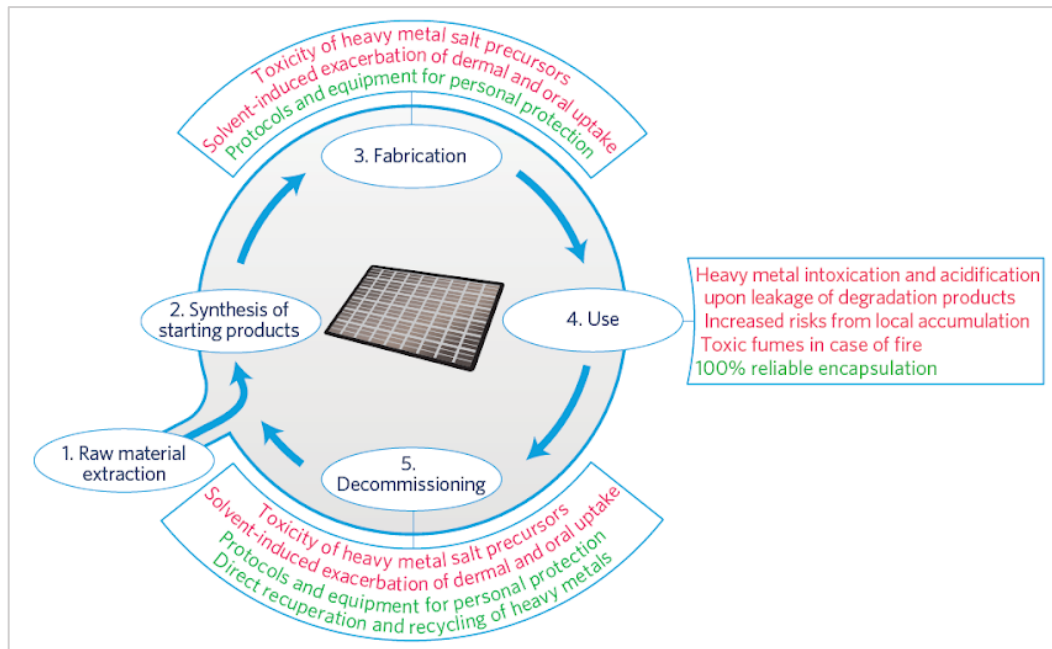


Figure 3: Concise schematic of the life cycle of perovskite solar cells, indicating the most important phases and corresponding hazards (in red) and possible control strategies (in green) [15].

It is worth noting that while the control strategies suggested for the fabrication and decommissioning phases include the use of protocols and equipment for personal protection, for the use phase, the indicated strategy to control lead-related issues in the use phase is related to encapsulation, which is further discussed in Section 3.

Differently, the second research analyzed focused on the comparison of the manufacturing phase and the end-of-life or decommissioning phase [5]. Two alternatives for the route followed in the end-of-life phase were considered i.e., landfill and incineration, hence considerable differences on the potential impact magnitudes can be seen. Figure 4 shows comparative results after the application of an LCA methodology with a system functional unit of 1 kWh focused on manufacturing and decommissioning. The graphic compares normalized environmental impacts between the manufacture of the cell and two disposal scenarios: cells being landfilled versus cells being incinerated. It is relevant to mention that it was considered that the latter could enable lead recovery and recycling and energy recovery from the combustion process. Therefore, environmental benefits or credits have also been accounted for. In terms of environmental impact, human toxicity, cancer and non-cancer effects are clearly the most relevant issues both in the manufacturing and in the end-of-life of PSC, regardless of if the end-of-life route is incineration or landfill [5].

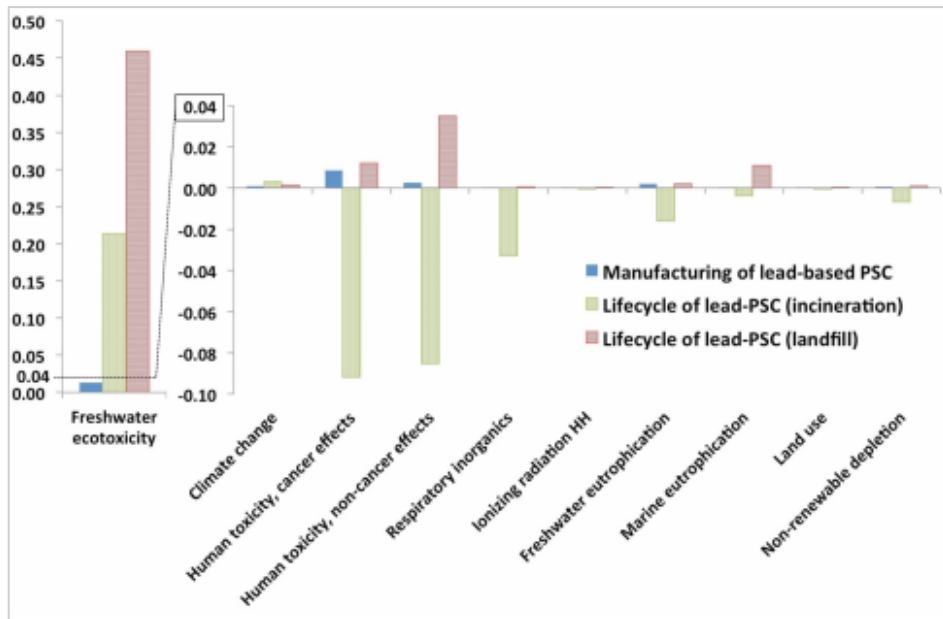


Figure 4: Normalized impact magnitudes following an LCA methodology for the comparison between solar cells manufacturing phase and two disposal scenarios: when the cell is landfilled and when the cell is incinerated, and lead is recovered [5].

It is worth emphasizing that within the analyzed studies, specific toxicity aspects related to the heavy metals used in hybrid perovskites have not been exhaustively discussed. Rather the goal of this section is to provide a concise qualitative assessment of the toxicity of the perovskite in solar cells, through the evaluation of examples and previous research.

### b. Quantitative analysis and projections

Current perovskite solar cells contain lead in the Perovskite layer in the form of Pbl (lead haloid) with an estimated quantity of  $1\text{g}/\text{m}^2$ . Moreover, although the architecture of perovskite modules is still under development, at present it can be considered similar to the one of a silicon cell module, which uses approximately  $12\text{ grams}/\text{m}^2$ . From the total  $12\text{ g}$  present in a typical silicon cell module, 85% of it is in the solder on the ribbons and 15% in the silver paste and the commonly used solder contains 60% tin and 40% lead.

The total yearly consumption of lead is about 12 million metric tons. Part of it is addressed to be used in photovoltaic modules. Considering that the amount of lead in a standard photovoltaic module (c-Si) is of about  $12\text{ grams}/\text{m}^2$ , as the number of modules being installed has reached considerably high values and is still expected to increase even at higher rates, the issue of toxic materials content, such as lead becomes increasingly relevant overall in the solar PV industry.

This section presents an estimate of the amount of lead used in the production of photovoltaic modules through the most common production methods and assumes the use of  $12$

grams of lead/m<sup>2</sup> of module providing insights on the urgency of the lead issue not only related to perovskite solar cells.

In 2019 the cumulated installed module area was of about 4Gm<sup>2</sup> (4\*10<sup>9</sup>m<sup>2</sup>). Considering that the use of solar modules will constantly be increased and in 2030 the installed module area may reach 31Gm<sup>2</sup>. Table 1 presents accumulated installed solar module power at year 2025, 2030 and 2040, estimated for different growth rates and based on the following assumption: lead content is 12 grams per m<sup>2</sup> and the power output from one m<sup>2</sup> of module was taken to be 150 watts.

The calculation covers present consumption and future consumption at some estimated growth rates of module production. By the year 2019, 633 GW of modules have been installed. The growth rate is expected to be 20%, and by 2020 further 127 GW is expected to be installed giving an accumulated installation of 750 GW.

Table 1: Projections of lead consumption for PV modules.

<b>Growth rate</b>	<b>Installed 2019</b>	<b>Installed 2025</b>	<b>Installed 2030</b>	<b>Installed 2040</b>	<b>Tot. lead 2019</b>	<b>Tot. lead 2025</b>	<b>Tot. lead 2030</b>	<b>Tot. lead 2040</b>	<b>Del lead 2029</b>	<b>Del lead 2040</b>
<b>%</b>	<b>GW</b>	<b>GW</b>	<b>GW</b>	<b>GW</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>		
10	633	1121	1806	4684	5,06E+06	8,97E+06	1,44E+07	3,75E+07	3,24E+07	
15	633	1464	2945	11914	5,06E+06	1,17E+07	2,36E+07	9,53E+07	9,02E+07	
20	633	1890	4703	29121	5,06E+06	1,51E+07	3,76E+07	2,33E+08	2,28E+08	
25	633	2415	7369	68630	5,06E+06	1,93E+07	5,90E+07	5,49E+08	5,44E+08	

From Table 1, the accumulated lead in modules from today's 5 million kilograms in the year 2040 increased to 37 to 590 million kilograms depending on the assumed growth rate. Here it can be argued that the maximum installed power can only reach a certain value. Certainly not higher than the need for power. If solar cells were to contribute to the future with 50% of the need for power, one has to discuss the following question - what will the need for power be in the future? A rough estimate can be obtained taking into consideration that today's solar power capacity (633 GW) contributes with 1 to 10% of the needed power in different countries. The reasoning above leads to the estimate that the expected maximum installed power could be in the order 10 to 20 times the power installed today.

Using the 633 GW installed today multiplied by 20, it would result in a total installed power of about 13,000 GW. With a life length of 30 years, 430 GW of solar modules would need to be replaced yearly. Which results in 34 million kg of lead used yearly if still the modules contain 12 grams of lead per m<sup>2</sup>.

A summary of the estimates above gives that the worldwide accumulated installed solar power can be of the order 13,000 GW. And the total lead content in the installed modules is 1,040 million kilograms of lead. And with a life length of about 30 years, solar modules containing 34



million kilograms of lead should be scraped yearly. Therefore, finding a cost-effective and efficient alternative for lead replacement overall in the solar PV industry is crucial.

### **3.1 Phase 1. Production of the PSC**

After an overview of the overall lead-related issues, this section brings additional information focusing on the manufacturing phase, i.e., the production of the PSC. It describes and aims to characterize dry and wet processing of PSC in terms of environmental and human health safety in order to explore their different lead-related risks and discuss their specific control strategies and procedures requirements.

It is however worth highlighting that the ongoing research on dry and wet processes seems to be more focused on ensuring and improving the PSC stability over time, the efficiency and the capital costs associated with the production methods, rather than running experimental comparison in terms of environmental and human health safety.

Although research focused on comparing both alternatives according to their last developments (structures and materials) still lacks in the literature, it is clear that both processes represent risks. While the wet processes based on solution-processed routes require special management of the solvents used and of the unused/waste materials, the dry processes, for instance, PVD and vacuum-based deposition processes might have its main risks related to the cleaning the tools or loading the materials.

In terms of health, the main sources of intoxication hazard are related to the starting compounds and/or solvents (if required in the adopted synthesis procedure) used [15]. The chemical nature of a compound, whether it is organic, or inorganic plays a significant role and influences the bioavailability and rate of uptake. Or in other words, the higher the correlation of the chemical solubility in fat and water, the higher the risks. Consequently, the overall risk of organic compounds is considered much higher compared to their inorganic counterparts as they can more easily pass biological barriers to reach vital areas [15].

#### **a. Wet processes related risks**

Intoxication risks by the chemicals being used can be significantly increased by the presence of frequently used solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) [15]. These solvents are toxic and also miscible with water, thus increasing the bioavailability and the risk of absorption by oral ingestion and via dermal contact.

Although the risk to human health from solvents used to produce perovskites is considered significantly lower compared to other industrial processes, recent research was dedicated in

understanding the potential dangers and identifying the least impactful alternatives with the aim of starting a roadmap for the further development of less hazardous solvents [16].

The study investigated existing databases of toxicity data as well as the solvents production process and the after life of the solvents i.e., what is done with the solvents after processing the perovskite active layers. It concluded that dimethyl sulfoxide (DMSO) poses the lowest risk to the environment or to human health among the solvents analyzed. Eight most used solvents were analyzed in this research, including the dimethylformamide (DMF), which is recognized as toxic to the human reproductive system. Researchers claim that considering the total amount of solvent used at the industrial scale, a significant impact on human health due to solvent use is not likely [16].

#### **b. Dry processes related risks**

Regarding occupational exposure in the context of perovskite research or production environment, lead in the form of airborne powders is known to have long lasting human health implications when exposure surpasses certain limits. Hence, dedicated procedures and specific attention is necessary to ensure the safety of the personnel working at labs and production facilities, dealing directly with the substances in discussion. It is worth mentioning that the World Health Organization (WHO) has revoked the once enforced maximum safe blood lead levels and provisional tolerable weekly intake (PTWI). Thus, currently the WHO basically considers exposure unhealthy altogether [13].

Taking into consideration the hazards aforementioned, sufficient protection in the form of gloves, masks, glasses and other personal protective equipment, as well as procedures for safe storage of waste products among others, represent needed laboratory practice, which is critical to guarantee personnel and environmental safety [15].

#### **c. Protection and safety directives**

Although it could seem advisable, perovskite-dedicated measures and procedures are generally not imposed in research labs [15] and no organization has published specific or dedicated directives. Some institutions, however, such as the KAUST Solar Center (Saudi Arabia), whose main expertise is centered on photovoltaic applications based on organic, hybrid and perovskite materials, has developed and established a set of instructions within its standard operation procedures for lead safety in labs. The material is made available on their website together with relevant literature [14].

Considering the hazards both for wet and dry processes, it is undoubtful that well-established laboratory procedures are essential to ensure personnel and environmental safety. In

this sense it is worth mentioning that research centers, as well as production facilities are obliged to follow specific material safety sheets, which cover specificities of each material and defines the necessary precaution, mitigation and control measurements depending on the risks offered by each of the processed materials.

Moreover, in terms of large-scale production facilities where processes can be more easily automated and shielded, it should be noted that the risks might potentially be reduced as the workers' immediate proximity to the toxicants can be minimized [15].

### **3.2 Phase 2. Use of PSC modules and lead pollution**

During the use of the PSC, the main concerns arise from how the structural integrity of modules that will be exposed to uncontrolled conditions, such as rooftops for instance. Modules could be, thus, modified over time due to degradation or due to more extreme events. The degradation of the modules might cause the leakage of toxic substances into the surroundings and the hazard related to toxicant accumulation cannot be disregarded [15] (see Section 2). Whereas in a more extreme event such as fire, heavy metal containing fumes would be emitted and these airborne toxicants represent a significant risk as they can be easily absorbed via inhalation [15]. Although a consolidated conclusion on the fire safety of perovskite-based photovoltaic technology still lacks numerical and experimental data, it has been observed that the encapsulation might play a significant role on the vulnerability of the modules [13].

As aforementioned, the use of the solar modules together with the end-of-life could be indicated as the phases that present the highest risks of environmental pollution related to lead. It is relevant to mention that in the usage phase, the encapsulation of the PSC plays an important role as lead leakage can be minimized if appropriate encapsulation is employed.

In general, encapsulation prevents environmentally related degradation (water and moisture) and enhances the mechanical resistivity against external impact, which means that in case of damage on the solar modules, the opposite direction of protection, i.e., lead leakage could be also significantly reduced. Figure 5 illustrates an experiment comparing 4 different methods with the main goal of assessing lead leakage from damaged perovskite solar modules. Method A represents solar cells without encapsulation and from B to D the encapsulation method is improved, i.e., Method D represents the solar cell with the best encapsulation method [6].

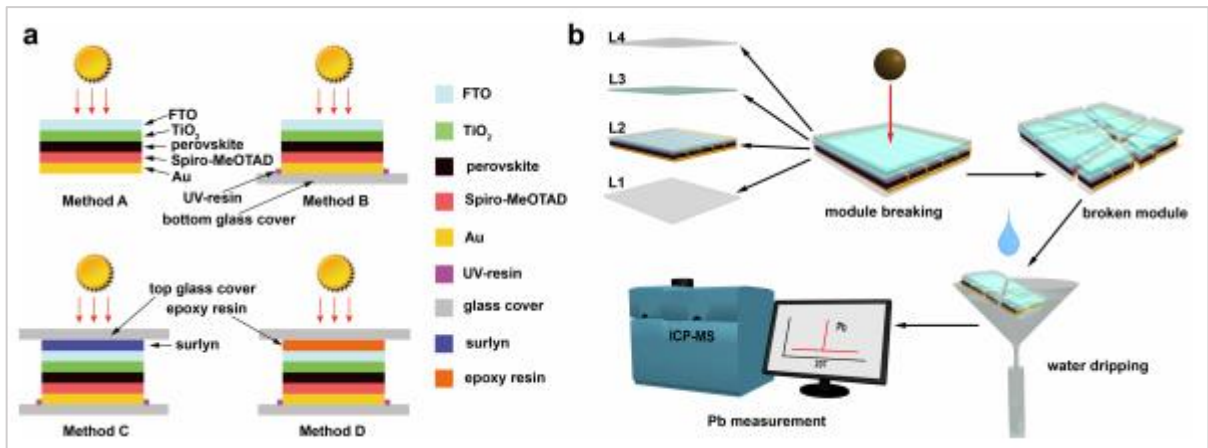


Figure 5: (a) Schematic of the encapsulation methods A, B, C and D; (b) Schematic of the experimental procedure to assess the quantity of the toxic lead leaked after a damage, caused by an external impact (for example, hail) [6].

Figure 6 shows the results confirming that the lead leakage is closely related to the encapsulation method, better encapsulation methods result in less lead leaks to the environment. It is worth noting, however, that even for Method D some leakage was observed, which might indicate that the elimination of lead in solar cells could be ultimately the best alternative, since avoiding that the lead ends up polluting the environment presents itself as significantly hard task that involves varied efforts throughout the lifetime of the solar cells.

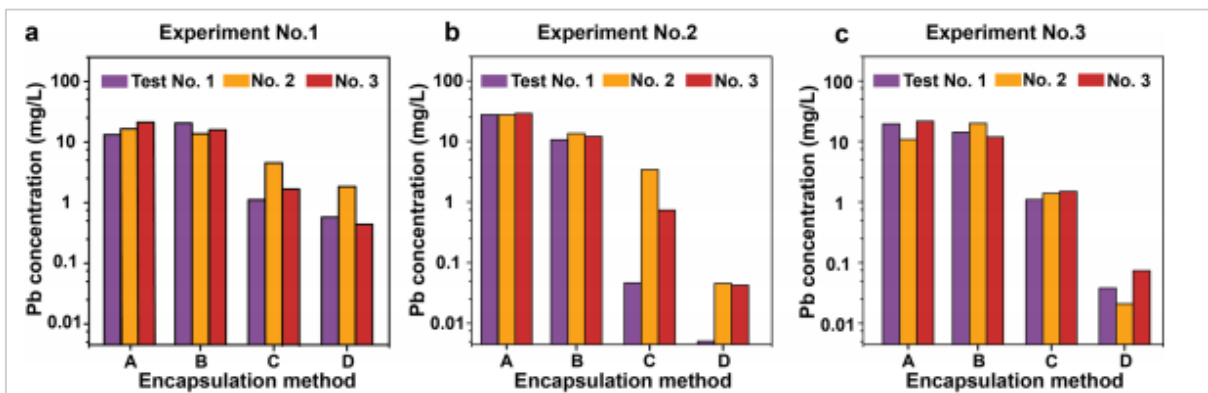


Figure 6: Lead leakage in different experiments simulating varied weather conditions, different temperature levels and rain intensities. Three samples for each encapsulation method were tested under each condition [6].

Alternative and more advanced encapsulation methods are also under analysis, however their efficacy still lacks verification through experimentation and they would demand further development to increase cost-effectiveness. These can include encapsulation with self-healing materials, materials with incorporated heavy metal capturing molecules, sulfides that react with the degradation products to form insoluble and inert compounds, among others [15].

Latest seemingly promising research related to the topic released at the time of the writing (February 2021) reveals a way to minimize and even eliminate the lead release from broken cells by using a device made of bioinspired mineral called hydroxyapatite. Scientists have created an in-

device 'fail-safe' system that captures the lead ions, i.e., limits the concentration of lead released in water from broken PSC by ion sequestration. If the PSCs are damaged, toxins would be stored in an inert mineral, instead of being released to the environment.

As an additional benefit, it was also found out that through the addition of hydroxyapatite, the efficiency of PSC increased to around 21%, higher than the approximately 18% efficiency of the control cells with no added hydroxyapatite. Researchers hope these combined benefits will increase the viability of a wider deployment of PSC worldwide [17].

### **3.3 Phase 3. Recycling of PSC modules**

This section provides an overview of the recycling of PSC, since it represents the least harmful end-of-life alternative both in terms of negative impacts on the environment as well as on the human health. Nevertheless, some factors remain to be analyzed and taken into consideration to ensure that the advantages of recycling are achieved.

Lead is considered one of the most effectively recycled materials in the world [15]. Most of the demand for this heavy metal goes into batteries and their recycling procedures have already been well established. However, a different scenario is found in the recycling of solar cells. Europe is the only continent with dedicated c-Si PV recycling facilities operating commercially, however, most of the PV modules recycled in Europe today are still operated in batches through existing glass or metal recycling lines [7]. In the current method of recycling, modules are shredded and then the glass is separated from the EVA embedding film. The glass goes into the glass recycling process and the lead is essentially bound up in the film with the cells. However, since these components are all in fragments, lead probably also enters the glass fraction and is thus, most probably, also in the recycled glass. Lead also enters the copper-aluminum fraction, which is further treated in the copper smelter and lead can be filtered out at that stage.

The most problematic fraction is probably the one contained in embedding films and cells when they are added to the waste that is then incinerated. That is because lead might end up diluted in the filter residue or ash. Laws specify the concentration at which this waste must be treated and how. However, with the low volumes of modules being recycled, this issue is far from being at a critical stage. In a few years' time, when large volumes of solar modules begin to be recycled, the cell and encapsulant waste will probably also be partially recycled, even if only to recover the precious silver content and therefore further investigation becomes increasingly relevant.

It is worth exploring some of the recycling procedures that have been under analysis and research which are focusing on lead waste avoidance. Figure 7 shows each step of a recycling process designed to avoid lead waste [8].

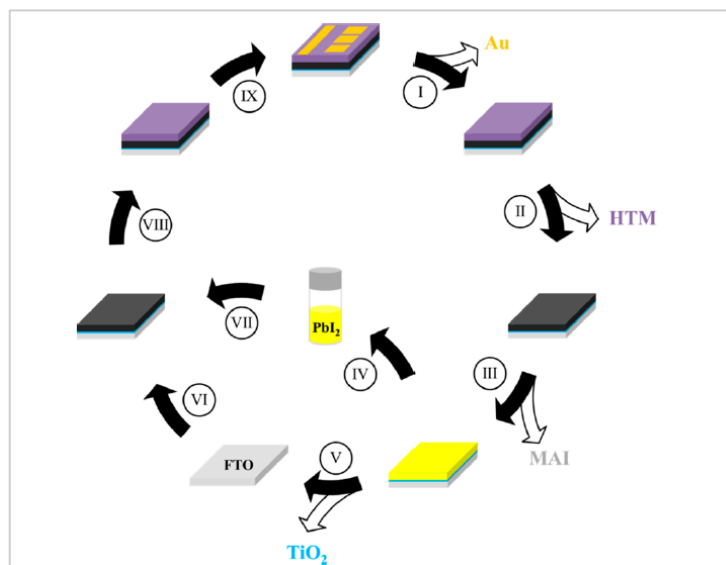


Figure 7: Scheme of a recycling process for perovskite solar cells focused on lead waste avoidance. (I) Removal of Au electrode with adhesive tape, (II) Removal of the Hole Transporting Material (HTM), (III) Transformation of the perovskite into methylammonium iodide (MAI) and  $\text{PbI}_2$  and extraction of MAI in water, (IV, V) Removal of  $\text{PbI}_2$  and  $\text{TiO}_2$ , (VI) Preparation of a new  $\text{TiO}_2$  film, (VII) Formation of the perovskite film on recycled conductive glass (FTO) from recycled  $\text{PbI}_2$ . (VIII) Preparation of the HTM layer. (IX) Evaporation of the Au top electrode [8].

The procedure described in Figure 7 not only is focused on lead waste avoidance, but it also aims to serve as an environmentally responsible and cost-efficient recycling method. The most relevant aspect of this application that should be highlighted is that it enables the recuperation and therefore reuse of the toxic  $\text{PbI}_2$  [8].

It is also worth noting that as perovskite solar cells technology is still under development, the most suitable recycling method remains to be defined. Standardized protocols for module recycling are to be established, however similar hazards from the PSC manufacturing apply to the recycling process and therefore similar precautions should be required [15]. It is relevant to anticipate such issues that will come to the fore once perovskite solar cells start being massively commercialized.

Recent research claims that the toxicity issue could be minimized by a sustainable lead management system, through which 99.7% of lead would be safely recycled using adsorbents. Scientists argue that the adsorption approach is a good candidate because as it has the potential to enhance the reactivity with lead, its retrieval from the solution is facilitated. The goal is to be able to return a lead iodide to the manufacturers, therefore a specially designed adsorption process was developed that works by clinging to the surface of the lead and separating it through magnetic fields [18]. This approach might have the potential to contribute to the definition of a future recycling methodology of PSCs.

## 4. Lead-free modules

Research efforts on lead-free perovskite solar cells have been increasing. Most of the current ongoing research focuses on the identification and investigation of absorber materials that could replace lead and improve power conversion efficiency. The elements that could replace lead include tin (Sn), cesium (Cs), germanium (Ge), copper (Cu), antimony (Sb) or bismuth (Bi) [3]. However, challenges related to lack of research on the relationship among component-structure-property, current lower efficiencies, reduced stability upon prolonged light/humidity/high temperature exposure and compatibility with large-scale manufacturing routes remain to be solved [9]. Therefore, Pb-free perovskites do not provide yet significant advantages in terms of cost, toxicity or environmental safety, nor present better stability and efficiency compared to Pb-based PSCs [19]. Table 2 shows performance comparison of examples of PSC with less lead or lead-free PSC while Figure 8 illustrates lower power conversion efficiency (PCE) of varied PSCs (Sn, Ge, Sb, and Bi) in comparison with lead-based PSCs.

Table 2: Comparison of the performance of PSCs with less-lead and lead-free absorption materials and HTM [10].

Absorption material	HTM	$J_{sc}/\text{mA}\cdot\text{cm}^{-2}$	$V_{oc}/\text{V}$	FF	PCE/%
$\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$	P3TH	20.04	0.42	0.50	4.18
$\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$	Spiro-OMeTAD+Li-TFSI	20.64	0.58	0.60	7.27
$\text{MASr}_{0.3}\text{Pb}_{0.7}\text{I}_3$	Spiro-OMeTAD+TBP	2.8	0.94	0.73	1.93
$\text{MASnI}_3$	Spiro-OMeTAD+(tBP,H-TFSI)	16.8	0.88	0.42	6.40
$\text{MASnI}_3\text{Br}_2$	Spiro-OMeTAD+Li-TFSI	12.3	0.82	0.57	5.73
$\text{FASnI}_3+20\%\text{SnF}_2$	Spiro-OMeTAD	12.4	0.26	0.44	2.10
$\text{CsSnI}_3+20\%\text{SnF}_2$	m-MTDATA	22.7	0.24	0.37	2.02

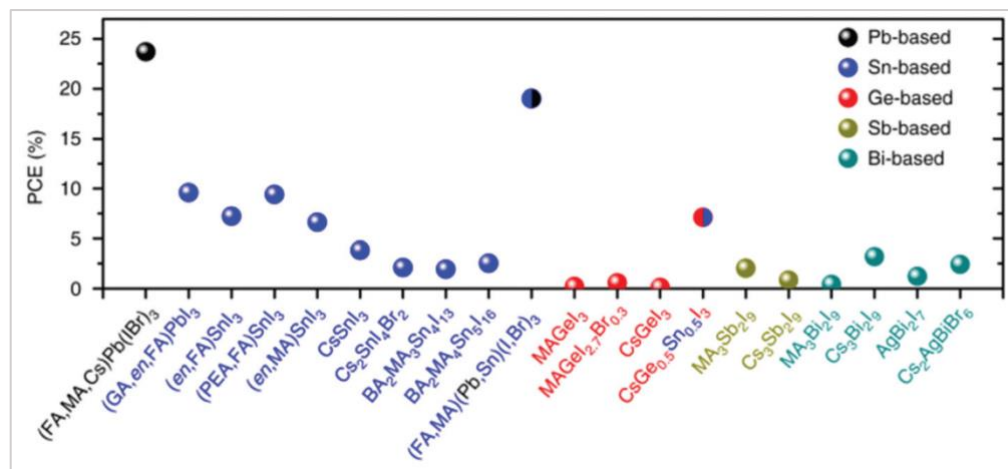


Figure 8: Power conversion efficiency (PCE) of different PSCs: Pb, Sn, Ge, Sb, and Bi. (Ke et al., 2019 apud [19]).

## 4.1 Sn-based perovskites

Based on available research as can be seen in Figure 8, of the possible elements to replace lead, Sn-based perovskite has been showing most promising PCE when appropriately prepared. Tin-based perovskites can have broader absorption spectra than lead-based perovskites. Nevertheless, still the efficiency and stability values reached for tin-based approaches are currently considerably inferior to those for lead-based PSC. Not to mention the fact that Sn is a harmful chemical which entails issues regarding environment and health [20]. Although less documented and debated, environmental and health potential impacts related to the use of Sn do not appear to be less detrimental than Pb in PSCs [19].

Moreover, an LCA-based article focused on a direct comparison of tin- and lead-based PSCs assessing both when they are produced and when they are emitted [5]. As a general output, tin-based PSC showed larger environmental impacts in all categories analyzed as summarized in Figure 9, which provides detailed information of each component's impact, i.e., back and front electrodes, hole transport layer (HTL), electron transport layer (ETL) and perovskite itself [5].

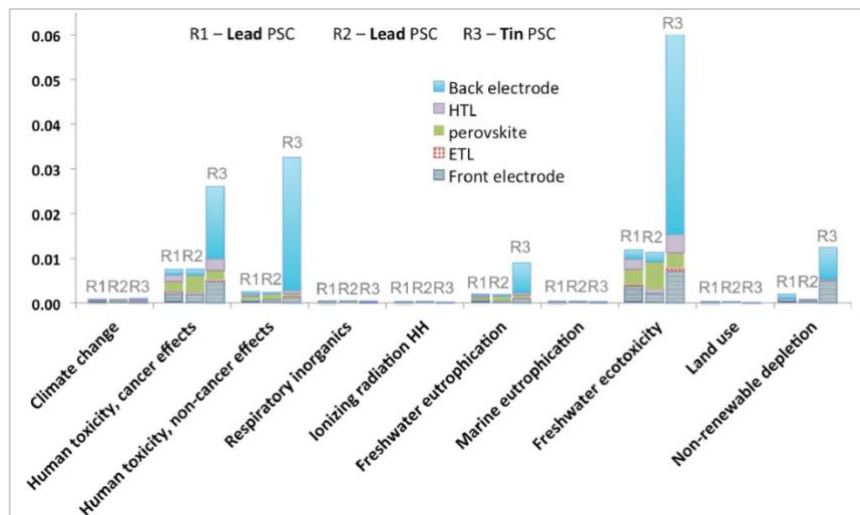


Figure 9: Illustration of results of environmental impact levels of PSC production. Lead based PSC (R1 and R2) and tin-based PSC (R3) [5].

## 4.2 Other issues related to lead-free devices

Not only the lead content in the solar cells is being targeted for reduction and elimination, but also lead contained in the solder can also be replaced and consequently avoided, by agents such as bismuth, for instance. However, lead-free soldering is still a more expensive method and requires further investigation and research in order to have its drawbacks mitigated. such as a more complicated process of recycling copper and a slight reduction of efficiency when lead in the silver paste is replaced.



Significant progress in this field is expected and in fact the International Technology Roadmap for Photovoltaic (ITRPV) 2020 projects that approximately 50% of the world market share will be composed of lead-free cell interconnection by 2030 as shown in Figure 10.

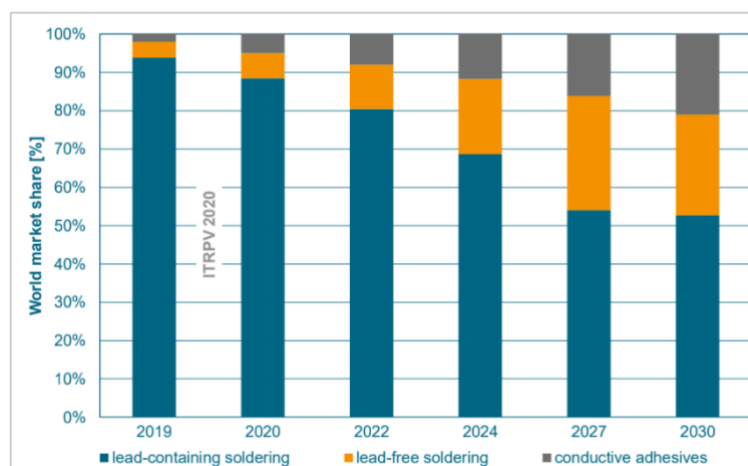


Figure 10: Expected market share for different cell interconnection technologies [11].

## 5. Regulation and legal aspects

The use of lead is currently severely restricted and banned for certain applications where it cannot practically be prevented from leaking into the environment. The European Union adheres to the international regulation called Restriction of Hazardous Substances Directive (RoHS) which also applies to lead. It goes so far as to impose an outright ban on the use of the element. However, the RoHS Directive provides exemptions according to certain criteria if there is no technical alternative. Solar PV modules still have RoHS exempt status since 2011 and the use of lead is therefore still permitted without restriction. Nevertheless, the RoHS directive shall be reviewed, and the exemption of solar cell modules might soon be reconsidered. This decision is critical to ensure that PV modules will be designed and prioritized to have a minimal environmental impact.

The current RoHS takes into account the understanding of long-term risks associated with continuous exposure to low levels of toxic heavy metals as described in Section 2 and defines the lead maximum concentration as 0.1% in weight or 1,000mg/Kg (Figure 10) in each homogeneous material contained in any electronic devices. In the specific case of PSC, it is worth highlighting that all the current effective halide perovskites contain more than 10% lead in weight [3] and would therefore demand significant efforts to comply with the regulation.

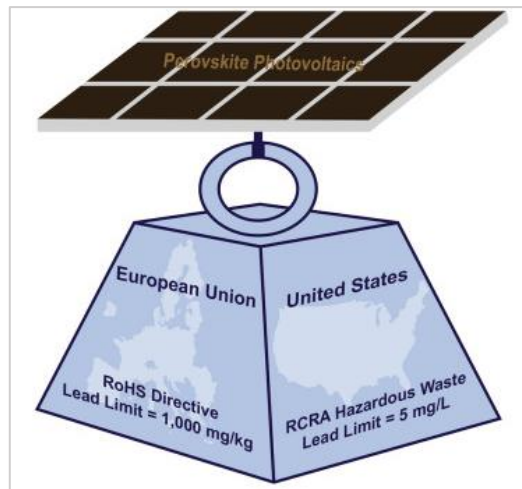


Figure 11: Per weight basis lead regulation [12].

Not only stricter regulation and legislation are expected, but also the demand for recycling of modules shall increase in a close future as discussed in Section 3. Therefore, with the significant increase of the PV market, concerns regarding the environmental impacts of solar modules come to the fore and solutions that involve lead-free waste and the production of lead-free modules might play a significant role.

## 6. Latest research on mitigation of lead-related issues

A potential solution for water soluble lead in Perovskite materials has been recently developed by scientists in the United States (December, 2021) [21]. It is a on device layer, a ‘scotch-tape like’ solution which could capture 99.9% of potential leaked lead from damaged perovskite solar cells, preventing the toxic material from entering the environment.

The lead absorbing film shall encapsulate PSC and can be integrated with existing encapsulation strategies, which means it causes minimal impact on existing production processes performance and operation [22]. Researchers claim that the technology mitigates the potential lead-leakage to a level safer than the standard for drinking water defined by U.S. Environmental Protection Agency (EPA). By considerable minimizing the potential lead leakage from PSC, this work might have the potential to facilitate future commercialization of perovskite-based PV technology.

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