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Comparative evaluation of lead emissions and toxicity potential in the cradle-to-gate life cycle of lead halide perovskite photovoltaics

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Abstract

Lead halide perovskites (LHP) are an emerging class of photovoltaic (PV) materials that have drawn intense interest due to their power conversion efficiencies above 23% and their potential for low-cost fabrication. However, the toxicity of lead causes concern about its use in LHP-PV at large scales. Here, we quantified lead utilization and toxicity potential of LHP-PV in potential commercial production. Lead intensity in LHP-PV life cycles can be 4 times lower and potential toxic emissions can be 20 times lower than those in representative U.S. electricity mixes, assuming that PV operational lifetimes reach 20 years. We introduce the metric “toxicity potential payback time”, accounting for toxic emissions in the life cycle of energy cycles, and showed that it is <2 years for perovskite PVs produced by and displacing the same grid mix. The toxicity potential associated with the energy of manufacturing a PV system dominates that associated with release of embodied lead. Therefore, the use of lead should not preclude commercialization of LHP-PVs. Instead, effort should focus on development of low-energy manufacturing processes and long service lifetimes. Additional detailed investigations are

needed to quantify the full life cycle of commercial production of perovskites and to minimize potential emissions.

Keywords

Thin film solar cells; Lead halide perovskite; Photovoltaics; Life Cycle Assessment; Toxicity

Highlights

- Quantified lead intensity, toxicity potential of lead halide perovskite PV
- Toxicity potential from embodied energy much greater than from release of lead
- Perovskite PV has lower lead intensity and toxicity potential than grid electricity
- Toxicity potential payback time <2 years for perovskite PV

1. Introduction

The rapid growth of the global solar photovoltaic (PV) market provides electrical power while addressing important environmental challenges such as reducing the use of fossil fuels and their associated greenhouse gas emissions. The cumulative installed capacity of PV has increased approximately 50 times in just a decade, from merely 6.6 GW_p in 2006 to more than 300 GW_p at the end of 2016, and is projected to reach 900 GW_p in 2021 [1]. Monocrystalline and multicrystalline silicon wafer-based technologies currently capture ~94% of the market, while thin film cadmium telluride (CdTe) and copper indium gallium (di)selenide/(di)sulfide (CIGS) technologies contribute the remainder [2]. Thin film technologies offer potential benefits compared to wafer technology, including ~100x thinner absorber layers and opportunities for low-cost, continuous glass-in-module-out manufacturing.

In addition to these established technologies, lead halide perovskite photovoltaics (LHP-PV) have emerged over the last decade and show enormous promise for high efficiency and low production cost. The efficiency of LHP-PVs has increased at an unprecedented rate to 23.3% within 8 years of the first reports of LHP-PVs. This fast improvement in efficiency is extraordinary in comparison to the learning curve of established PV technologies, which needed more than three decades to achieve similar efficiency advances [3-5].

These new materials exhibit the perovskite crystal structure with formula ABX_3 , where A is a large cation such as organic methylammonium (MA, CH_3NH_3^+), B is typically lead, and X is

a halogen such as iodine. The intrinsic perovskite layer is interfaced with electron and hole transport layers in an n-i-p or p-i-n configuration [6-8]. The past few years have seen rapid improvement in the performance of LHP-PVs at multiple scales, including small-area cells ($\sim 0.1 \text{ cm}^2$), large-area cells ($\sim 1 \text{ cm}^2$), and modules ($>10 \text{ cm}^2$) [9,10]. These improvements have been largely based on enhanced understanding and control of composition [11], microstructure, [12-13] and complementary charge transport layers in the device structure, [7,8,14] as well as innovations in solution chemistry [15-16] and the fabrication process [9,10]. Also, there has been notable progress toward potential large-scale LHP-PV manufacturing by adopting scalable deposition strategies for all device layers, including the perovskite photoactive layer, electron-transport layer, hole-transport layer, and electrodes (top- and back-contact layers) [9-10]. Challenges in scaling up LHP-PVs include improving stability, developing procedures for fabricating perovskite modules, and understanding the impact of each device architecture on the performance of the module. Diverse technical directions are being pursued to commercialize perovskite solar technologies – at present some companies are working on the scale-up of LHP-PVs towards pilot-scale manufacturing (such as Oxford Photovoltaics Ltd), and other companies are developing light weight and flexible perovskite modules (such as Saule Technologies, Greatcell Solar, and Panasonic) [17].

Despite the excitement, lead has acute toxicity risks that must be mitigated at every stage of the life cycle if LHP-PVs are to be commercialized. These risks are primarily associated with occupational exposure as well as chronic exposure to lead in air or water, with potential effects on hematopoietic, renal, reproductive, and central nervous systems [18]. Some reports indicated that use of any amount of lead is unacceptable. EU Directive 2002/95/EC, “Restriction of Hazardous Substances”, sought to ensure, beginning in 2006, that “*new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium...*”, but made an exception in 2011 for photovoltaic modules [19]. Asif et al. stated that “*there are absolutely no prospects of manufacturing perovskite solar cells*”, partially because they would not meet environmental health and safety criteria [20].

Avoiding lead altogether may be the most desirable option. However, efforts to discover alternative lead-free perovskite materials have not yet yielded competitive PV efficiencies. Specifically, the reported efficiency of lead-free organic inorganic halide perovskite solar cells has reached only 9% at lab scale, using tin as alternative candidate because of its similar electronic configuration and similar effective ionic radius [21]. Other options are under investigation, such as germanium, bismuth, and antimony, but at present their power

conversion efficiency is very low (<3%) [22]. Additionally, Serrano Lujan et al. have reported that tin-based LHP-PV have larger environmental impacts than lead-based ones in the considered life cycle assessment categories, mainly due to their low efficiency [23]. Tin-based LHP-PVs had a resource depletion score 50 times higher than lead-based PVs due to the production of tin as well as the extraction of gold, which was used in tin-based LHP-PVs as the back electrode.

In contrast to such dire views of the use of lead and the future of LHP-PVs, Fabiani reported that the amount of lead potentially used would be extremely small compared to lead usage in other industries, such as in electronic solder and aviation fuel [24]. Additionally, Hailgenaw et al. stated that the areal density of lead in LHP-PVs is so small that even releases from large solar electric power plants would not likely cause severe damage to the environment [25]. However, both of these sets of calculations were based on the amount of lead in the product, and they neglect lead emissions during mining and manufacturing, both of which could be significant. According to Zhang et al. the lead used in the perovskites only contributes to about 1.1% of the life-cycle human toxicity potential, mainly due to its very small amount of usage per area of module (<2 g/m²) [5]. Other studies also report that the life cycle contribution from lead is insignificant in all impact categories (less than 0.2% of total impacts) [5, 23, 26-28]. However, with the exception of Celik et al. [26], the mentioned studies focused on small-scale production of perovskite solar cells that employ methods such as spin-coating and electrode materials such as gold that are not scalable. Concerns remain regarding the potential toxicity associated with large scale commercialization.

The current study examines the cost and benefits of using lead in perovskite PVs. Improved understanding of potential impacts of lead and pathways of environmentally sustainable manufacturing would aid in more effective distribution of R&D funds. If use of lead is truly a non-starter for commercialization, then R&D funds should be directed toward lead-free alternatives. In contrast, if the intensity and risk of lead are acceptable, then directing R&D funds toward improved stability, efficiency, manufacturability, and cost would be more beneficial, since low-carbon solar-generated electricity offsets electricity from fossil energy sources.

The apprehension regarding the heavy metals associated with large-scale penetration of LHP-PVs is reminiscent of the CdTe PV debate from the early 2000s, where the potential for relatively high efficiency and low manufacturing costs were enticing; however, concerns about cadmium toxicity required careful evaluation of all aspects of the technology [27-28]. Eventually, mitigation of toxicity risks, combined with increased efficiency, reduced

manufacturing costs, and module recycling programs, have enabled commercialization of CdTe PV modules [29].

Now is the ideal time to develop increasingly detailed environmental sustainability studies of LHP-PVs. CdTe and LHP-PVs present relevant differences in terms of their potential toxicity risk because the risks associated with exposure to different compounds depends on their stability and solubility. Specifically, CdTe is a thermally and chemically stable compound with a low solubility constant (K_{sp}) of 10^{-34} . In contrast, LHPs are unstable and can easily degrade to Pb compounds, while their K_{sp} is up to 29 orders of magnitude higher than CdTe [30]. When water interacts with methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), the $\text{CH}_3\text{NH}_3\text{I}$ is decomposed to hydroiodic acid (HI) and methylamine (CH_3NH_2). Lead iodide (PbI_2), which remains behind, has a solubility product on the order of 10^{-8} , which is much higher than those of other common heavy metal compounds in solar cells. Hence, detailed assessments of the toxicity potential of LHP-PVs are necessary to thoroughly investigate such risks.

In view of all these considerations, the main purpose of this work is two-fold: first, to assess the life cycle intensity and toxicity potential of lead associated with LHP-PVs; second, to compare these metrics with three representative U.S. electricity grids with a range of compositions and coal intensities. We also provide a comparison with the emissions associated to coal fired plants as a benchmark and to provide background data for the lead intensity of current electric power generation. Finally, from a methodological perspective, we introduce a new life cycle metric “toxicity potential payback time” (TPPBT) that provides a comparison between toxicity risk per unit of electricity supplied by LHP-PV versus the same risks in the grid electricity displaced by LHP-PV.

2. Methodology

Life Cycle Assessment (LCA) is an analytical method widely used in the scientific community for assessing environmental impacts of products and systems. LCA takes into account all stages of the life cycle, from the extraction of resources and the production of raw materials to manufacturing, distribution, use and re-use, maintenance, and finally recycling and disposal of the final product [31-33].

In this study, we applied an attributional LCA to assess lead emissions and human toxicity potential, comparing the life cycle impacts of producing electricity from LHP-PVs to those

from (i) three different regional U.S. electricity grid mixes and (ii) coal power generation, with particular emphasis on lead and other heavy metals. The three grids are the Reliability First Council (RFC), Northeast Power Coordination Council (NPCC), and Midwest Reliability Organization (MRO) [34]. Compositions and geographic locations of these grids are shown in the Supporting Information (SI). To test the robustness of our conclusions, we considered grids ranging from coal-intensive (70% coal, MRO) to low-coal (10.6% coal, NPCC). We assessed the midpoint metric human toxicity potential (TP), using ReCiPe v1.13 as the life cycle impact assessment method [35], with the Ecoinvent v3 Database (Ecoinvent, Zurich, Switzerland) for the inventory of background data [36]. We followed the hierarchic perspective to evaluate the potential impact of deploying 1 GWh of electricity, chosen as the functional unit in this analysis. The TP resulting from emissions of lead and other pollutants to air, water, and soil are quantified as equivalents of 1,4-dichlorobenzene (DB-eq). The relevant TP factors of lead are 16,218 kg_{DB-eq}/kg for airborne emissions, 220 kg_{DB-eq}/kg for emissions to surface water and 3 kg_{DB-eq}/kg for industrial discharges onto soil. The life cycle inventory for calculating lead emissions and toxicity impacts from US coal electricity production, and from the RFC, NPCC and MRO grids consists of the Ecoinvent v3 [36] database. The analysis was performed using the LCA software package SimaPro 8 (Pré Consultants, Amersfoort, The Netherlands). Additionally, as a guide to the most important direct emissions from coal power, we also included recent literature data [37-39], which we mainly discuss in SI. This way, crossing data sources, we report also (i) publicly available process data of modern plants, (ii) a clear and critical statement of the considered methods and assumptions, (iii) a critical discussion of data source uncertainty, and (iv) distinguished direct and indirect emission data (as discussed in Section SI.1). The various primary literature data presented are informative only, while the Ecoinvent data have been used for the further comparative analysis and calculation of TPPBT for the different grids. A discussion about data sources and data quality, as well as a tabular overview of parametric values for LHP-PV calculations (Table S1), are given in SI.

TPPBT is defined as the minimum service life of offsetting conventional energy required for LHP-PVs to overcome both their manufacturing burden (including both PV modules and the electrical and mechanical balance of systems) and the risk from release of embodied lead. TPPBT is calculated by

$$TPPBT = \frac{TP_{PV,area}}{E_{(PV,annual)} TP_{offset}}$$

$TP_{PV,area}$ is the toxicity potential of the PV system per area and includes cradle-to-gate manufacturing, lead release, and balance of systems. $E_{PV,annual}$ is the annual AC electricity

generated per area by the PV system, which depends on system performance and local irradiance. TP_{offset} is the TP offset per kWh of displaced electricity. TPPBT is similar in concept to energy payback time (EPBT), which is a life cycle metric that aims to measure how many years it takes for the PV system to return an amount of electricity that is considered to be equivalent to the primary energy invested [40-43]. However, we note that the toxicity potential does not directly characterize exposure pathways. Therefore this study is not to be interpreted as a risk analysis, but should be viewed from a systemic perspective. The evaluation presented includes uncertainties and assumptions that are related to different types of emissions, which are aggregated through the ReCiPe midpoint characterization factors and merely distinguish very generic emission location data. Hence, as an aggregated quantity, TPPBT does not reflect the local toxicity risk of lead exposure to individuals.

2.1 Analyzed system

In this analysis, we assumed a solar irradiance of $1700 \text{ kWh m}^{-2}\text{y}^{-1}$, module efficiency of 17%, and performance ratio of 0.75, resulting in electricity generation of $289 \text{ kWh}_{\text{DC}}\text{m}^{-2}\text{y}^{-1}$ or $217 \text{ kWh}_{\text{AC}}\text{m}^{-2}\text{y}^{-1}$. We chose this value of module efficiency as an expected potential target of commercial perovskite modules to compete with other commercial PV technologies such as c-Si (16-22%) and CdTe (16%) [44]. In light of the remarkable increase in efficiency of small perovskite PV cells to 23.3% [45] and mini-modules to 17.2%, [46] the availability of modules with efficiencies of 17% by the time of their commercialization is not unreasonable. The value is also in line with other efficiency numbers reported in LCA literature, such as 15% used by Celik et al. (2016) [26], and 15.4% by Espinosa et al. (2015) [47]. Nevertheless, we perform a sensitivity analysis, varying perovskite solar module efficiency between 14% and 20% to test its effect on model results.

Life cycle impacts were quantified as a function of system lifetime ranging up to 20 years because stability remains a major challenge for LHP-PVs. However, intense competition from crystalline silicon and other thin film photovoltaics will likely inhibit commercialization of LHP-PVs if their average production module efficiencies are lower than 17% or their expected lifetimes are below 20 years, so we chose those values as the base case for this study. High-efficiency LHP-Si tandem cells were recently reported to be stable for over 1000 h in damp heat, indicating a potential for long lifetimes [48].

The energy input requirement for the manufacturing of LHP-PVs was estimated based on the existing literature data of Celik et al. [26], who reported on multiple candidate device

stacks and manufacturing processes. We consider several options based on two of their scenarios: (1) a stack of glass/F:SnO₂/SnO₂/CH₃NH₃PbI₃/CuSCN/MoO_x/Al/C-paste deposited using vacuum deposition and carrying a cumulative electricity demand for manufacturing of 821 MJ/m², and (2) a similar stack without the CuSCN hole transport layer (HTL-free) and with the absorber deposited from solution, carrying a cumulative electricity demand of 504 MJ/m². Given the uncertainty in what a future commercial product and process will entail, we used an average of these values, 663 MJ/m² (184 kWh/m²), as the energy for manufacturing, which is assumed to be electricity from the grid. We included the direct and indirect lead emissions from mining and smelting processes for the lead incorporated in LHP-PVs, estimated from literature sources including the Ecoinvent database (SI) [49-50]. The balance-of-system (BoS, structures and supports) is not significantly different from traditional PV panels, and also induces lead emissions over its life cycle. We included those emissions using data from Ecoinvent v3 reported for fixed-tilt BoS. We assumed that lead incorporated in the BoS (in metal alloys) is not likely to be released in a relevant time frame.

We evaluated two end-of-life scenarios, one in which the PV panels remain intact and another in which lead is completely released to groundwater. Scenarios and benchmarks are summarized in **Table 1**. Release of lead to groundwater may be the result of improper waste management (open dumps, improper leachate management in landfills) that would occur at or after the end of the service life, which is presumably 15-20 years or longer for potential commercialization scenarios. Any release before that is considered incidental, and would result from a more catastrophic and local damaging event, which is very unlikely and is more the subject of a risk assessment rather than a systemic consideration. Nonetheless, for completeness we provide calculations for complete lead release and associated toxicity potential for very short service lives.

The scenarios investigated assume that each GWh of electricity produced from LHP-PVs offsets electric grid power from the average fuel mix of RFC, NPCC, or MRO grids, as shown schematically in **Figure 1**. Various pollutants (with focus on lead) that contribute to the overall

Table 1. Description of scenarios and benchmarks considered.

Scenario 1*	No lead release at end of service life
Scenario 2*	Complete release of lead to water at end of service life
Benchmarks	Electricity from grid mix (RFC, NPCC, MRO)
	Coal electricity

* Common features: average of vacuum deposition and HTL-free manufacturing energy from Celik et al. (2016) [26]; using electricity from grid; Fixed-tilt BoS

toxicity impact are emitted from lead supply (mining and smelting, from various electricity-generating sources supplying the grid, and (in one scenario) from release of lead from the panels. As a point of reference, we also compare the emissions and toxicity potentials to those from US coal electricity production, which was modeled including both use and production phases. Coal emissions arise from coal supply, coal residues, infrastructure, and the power plant stack.

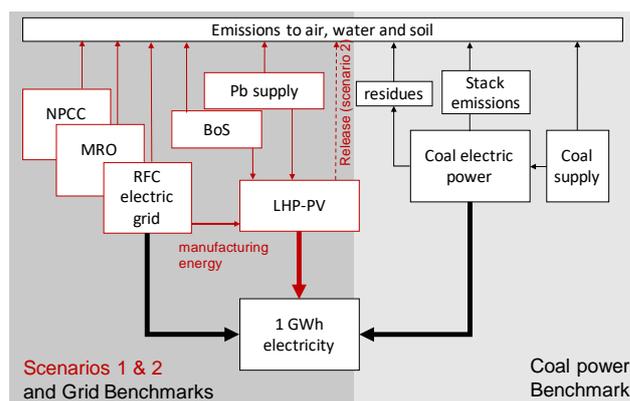


Figure 1. Schematic of emissions pathways for life cycle assessment of scenarios and benchmarks.

3. Results and discussion

3.1 Lead intensity and life cycle impact of LHP-PVs on human toxicity potential

Lead intensity

Because perovskites strongly absorb light, the active layer thickness can be less than one micrometer, with the result that less than 1.4 g m^{-2} of lead is required. Displacing the entire $4.1 \times 10^{12} \text{ kWh yr}^{-1}$ annual electricity generation in the U.S. would require 2400 GW_p of LHP-PV, corresponding to utilization of only 17,000 metric tons of lead embodied in the perovskite active layer itself (see SI Table S2). This amount is miniscule compared to the one million tons of lead utilized annually in lead-acid battery production alone in the U.S. [51]. With the 1-micron-thick absorber assumed here, the amount of lead required for LHP-PV is approximately double that required for the manufacturing of crystalline silicon PV panels, which have conventionally used lead-containing solder [52]. Efficient small-area LHP-PV cells can be made with absorber thicknesses of 250 nm or less, so the embodied lead could be even lower than for crystalline silicon PV.

Even though the amount of lead is small and the lead-containing perovskite layer in LHP-PVs would be encapsulated between glass layers, accidental cracking of the panels could result in solubilization in rainwater runoff, and potential contamination of surface or groundwater. $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) perovskite decomposes in water into HI and PbI_2 , releasing CH_3NH_2 [25]. Lead leaching is limited by the solubility of PbI_2 and also by the precipitation of $\text{Pb}(\text{OH})_2$ and PbCO_3 , depending on the final pH. The extractive leaching by slightly acidic rain would transfer the majority of lead from MAPbI_3 perovskite to runoff water [25], constituting a potential source for human uptake. However, if leached lead spread and did not concentrate in a limited volume of groundwater, the final concentration of lead added to the environment would be small compared to its natural occurrence [25]. It should be emphasized that this worst-case scenario is highly unlikely, as it assumes simultaneous cracking of the panels, complete leaching of lead from the normally shielded perovskite layer by subsequent rainwater, and human uptake of undiluted runoff water. The use of lead in solar cells is in that respect not comparable to lead plumbing or leaded gasoline, by which continued human uptake of small amounts of lead was certain.

Under the aforementioned assumptions about performance and irradiance, only 0.3 kg of lead is embodied in the LHP-PVs per GWh_{AC} produced, and the unlikely complete release of waterborne lead from the panels after 20 years would therefore cause a TP of 63 $\text{kg}_{\text{DB-eq}}$ per GWh of power produced. If that same lead release would occur earlier, say after 1 year, the amount of lead released per GWh produced would increase to 5.7 kg. The toxicities of the other constituents of the investigated perovskite, MA and iodide, are considered negligible, and they are not listed by ReCiPe 1.13 [35].

Life cycle lead emissions and toxicity potential

With respect to the intensity of lead embodied in the LHP-PVs, the lead emissions associated with mining and smelting of the metal supply itself were very small (data sourcing in SI). Values are shown in **Table 2**, which compiles lead emissions and toxicity potential for each contributing category in LHP-PV manufacturing and operation for the case of the RFC grid. Following Celik et al. [26], we assume that the life cycle contribution due to materials other than lead (“materials impact” in Table 2) is 10% of that due to manufacturing energy. Values are reported on a per-area basis and also on a per-GWh basis, assuming a 20-year operational lifetime. Analogous tables for NPCC and MRO grids are in the SI. Emissions on an area basis and TP on a GWh basis are compared between grids in **Figure 2**.

Table 2. Lead emissions and toxicity potential associated with different categories of LHP-PV manufacturing and operation, using RFC grid for manufacturing energy. Values per GWh assume 20-year lifetime. Note: Emission Fraction is the contribution of each stage to the total impacts.

	Emissions (kgPb/m ²)	Emission Fraction	Emissions (kgPb/GWh)	TP (kgDBeq/m ²)	TP Fraction	TP (kgDBeq/GWh)
Pb Mining	1.0 x10 ⁻⁸	0.00	2.3 x10 ⁻⁶	2.2 x10 ⁻⁶	0.00	5.2 x10 ⁻⁴
Pb Smelting	2.0 x10 ⁻⁷	0.00	4.7 x10 ⁻⁵	3.3 x10 ⁻³	0.00	7.6 x10 ⁻¹
Materials Impact	2.5 x10 ⁻⁵	0.01	5.8 x10 ⁻³	4.4	0.07	1.0 x10 ³
Manuf. Energy	2.5 x10 ⁻⁴	0.07	0.06	44	0.74	1.0 x10 ⁴
BoS	1.7 x10 ⁻³	0.50	0.39	11	0.18	2.5 x10 ³
Release	1.4 x10 ⁻³	0.41	0.32	0.31	0.01	7.0 x10 ¹
Total	3.4 x10 ⁻³		0.78	59		1.4 x10 ⁴

While emission of embodied lead from encapsulated modules is unlikely, the life cycle lead emissions associated with the production of energy used in manufacturing of the panels and BoS are unavoidable. The production of solar panels requires an input of energy, mainly in the form of electricity, the emissions and TP of which strongly depend on its sourcing within the relevant supply grid. Lead emissions associated with manufacturing energy for the panel vary from 0.2 - 0.3 g/m² for the three grids studied. BoS is the dominant contributor to lead emissions, assuming that lead is not released. Potential lead emissions due to accidental release would be proportionately reduced if the perovskite layer thickness could be reduced below 1 micron while still maintaining the large-area uniformity needed for an industrial process. With a 20-year operational lifetime and the RFC grid, total lead emissions are 0.46 kg_{Pb}/GWh_{AC} without release, or 0.78 kg_{Pb}/GWh_{AC} if lead is released.

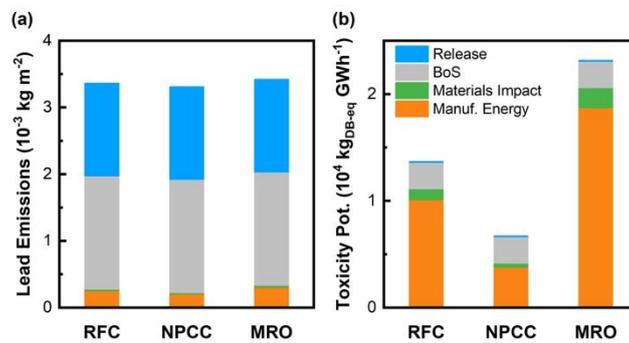


Figure 2. (a) Lead emissions on an area basis and (b) toxicity potential on an energy basis for the four most significant categories in the life cycle, compared across three representative US grid mixes.

When the whole toxicity potential is considered, the energy used in manufacturing is the dominant contributor (56%, 74%, and 81% of total for NPCC, RFC, and MRO, respectively, see **Tables 2, S7, and S8**). Manufacturing energy is of primary importance for TP because the grid includes air emissions of lead and other heavy metals, and emissions to air have much higher TP factor than emissions to water or soil [35]. The total TP of producing thin film solar panels amounts to 59 kg_{DB-eq}/m² for the RFC input, corresponding to 14,000 kg_{DB-eq}/GWh for a 20-year service life. For all grids investigated, the energy input for manufacturing entails far greater TP than mining, smelting, and even release of all the lead in the module to the environment. Therefore, the toxicity potential of LHP-PVs strongly depends on the amount and sourcing of energy used for manufacturing. The cleaner NPCC grid entails TP of 7,000 kg_{DB-eq}/GWh, while the more coal-intensive MRO entails 23,000 kg_{DB-eq}/GWh. Ultimately, manufacturing energy for LHP-PVs could be supplied by finished panels themselves, which would significantly reduce toxic emissions, including lead.

3.2 Toxic emissions from coal power generation

Despite the potential impact of deploying lead-containing PV technology, such modules will offset electric power and the associated emissions from grids that may have a large share of power generation by coal. Although PV technology may not offset coal power in the short run in an LCA approach, we use this benchmark to demonstrate the low amount of lead embodied in LHP-PV compared to contemporary power generation. In addition to offsetting greenhouse gas emissions from fossil fuels, as quantified in earlier studies [5, 23, 26, 47, 54], emissions of environmentally mobilized lead and other heavy metals from coal [54] may be displaced by PV. As demonstrated by data provided in SI, data on lead emissions from coal power plants are scarce and show a large distribution that depends on the age of the power plants, the geographical installation, and the type of flue gas cleaning system applied. Airborne emissions from US coal electricity production (use and production phases) are 0.22 kg/GWh, according to our calculation based on Ecoinvent v3 data. Also, lead emissions to water are 1.61 kg/GWh, and into soil are 0.05 kg/GWh. The total life cycle lead emissions to air, water and soil account for 1.89 kg/GWh. Combined, according to Ecoinvent v3 data, lead emissions from coal combustion are thus at least as high as the entire amount of lead embodied in LHP-PVs under our baseline scenario, which is unlikely to be released in any foreseeable scenario. Lead emissions alone from coal electricity production account for a TP of 3,930 kg_{DB-eq}/GWh, while the total airborne emissions, including also other toxic heavy metals, such as As, Hg and Se,

increase the life cycle TP to 735,000 kg_{DB-eq.}/GWh. Given the consensus on Ecoinvent data, we used these values for subsequent calculations.

In a more specialized study described in the SI, Meij and te Winkel [36] show airborne emissions for modern coal power plants as low as ~3.7 g/GWh of lead in the form of dust, based on coal-fired power plants in EU and Japan. These plants were equipped with state-of-the-art and well-maintained electrostatic precipitator and sometimes additional flue gas desulfurization pollution control equipment, with lead dust control efficiencies of 99.1% and 99.92%, respectively. In contrast, emissions can be much higher in countries where pollution control is lacking, during abnormal conditions, and with insufficient maintenance of coal-fired power plant pollution equipment. Coal mining causes additional lead emissions of 0.5 kg/GWh to water [37]. Lead emissions from ash leaching at disposal sites [55] over a subsequent 20-year period are small in comparison (see SI for calculations on lead emissions from coal).

3.3 Lead intensity and toxicity potential payback time

Figure 3 shows the potential lead emissions (lead intensity) and toxicity potential per GWh_{AC} of electricity supplied by LHP-PVs (power conversion efficiency 17%, performance ratio 0.75) as a function of service life, for manufacturing energy from each of the three grids and for cases with and without lead release. These calculations are benchmarked against the same metrics for electricity from the three US grids and from US coal (with data obtained in each analysis from Ecoinvent v3). For PV, the lead intensity and TP follow a reciprocal time (t^{-1}) function because they are associated with one-time events at the beginning of life (and end of life in the case of release) and are depreciated with the service life of the PVs. In contrast, in our considered scenario, emissions from grid aggregates and coal combustion are continuous with respect to electricity delivered.

The lead intensity of LHP-PV becomes lower than that of conventional electricity for service life of at least 8 years if there is no lead release, as shown in **Figure 3a**. The lead intensity of LHP-PVs with a 20-year lifetime is 2 – 4 times lower than that for the respective grids.

The metrics are even more favorable for LHP-PVs when TP is considered. The TP of LHP-PVs over a 20-year period is ~20x less than that of respective grid electricity and ~50-fold lower compared to that of coal power, with TPPBT of 1.0 – 1.5 years, as indicated by the intersection of curves of like color in **Figure 3b**. This means that the release of embodied lead to water bodies due to a dramatic event after only 2 years would still have a lesser overall toxicity potential burden compared to RFC grid generation of an equivalent amount of energy

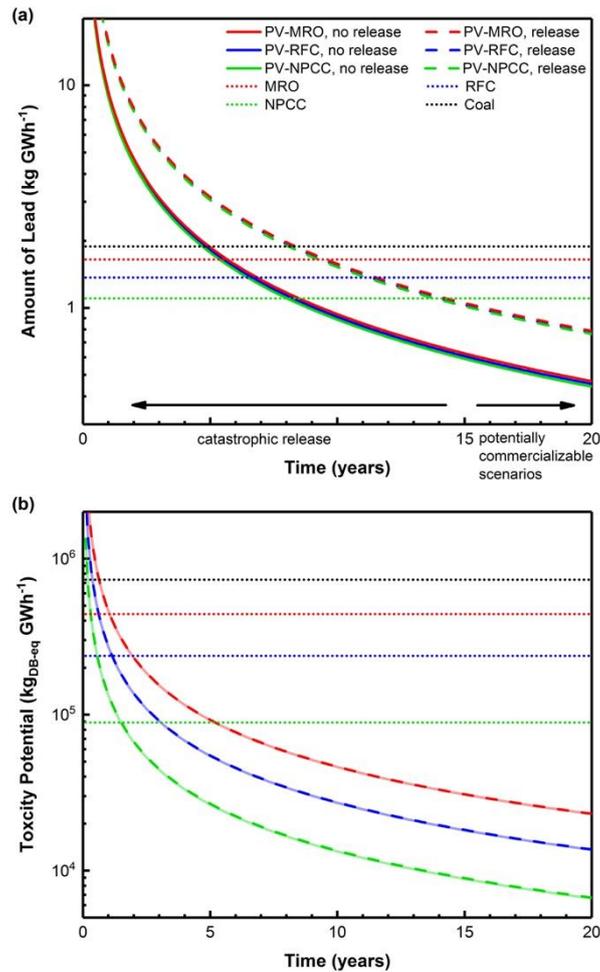


Figure 3. (a) Intensity of (potentially emitted) lead per GWh of electricity produced for LHP-PV with manufacturing energy supplied by the RFC, NPCC, or MRO grid, benchmarked against the grids and coal power emissions. (b) Toxicity Potential for life cycle potential emissions from LHP-PV, benchmarked against the TP of grid electricity and against all toxic heavy metal emissions from coal combustion. Both lead intensity and toxicity potential are shown as a function of the service life of the LHP-PV panels. Legend in (a) also applies to (b).

(although the local impact may be significant). TPPBT is sensitive to the energy required for PV production and the types of energy sourced and displaced, as shown in **Figure 3b**. Manufacturing panels using NPCC electricity and deploying them within the MRO grid would result in TPPBT of only 0.4 years, while the inverse would result in TPPBT of 5.2 years.

The major findings of our analysis – depreciated lead emissions from the manufacturing of LHP-PV and BoS resulting in a TPPBT of less than two years for manufacturing and deployment within the same grid, and insignificant contribution to the toxicity potential of release of embodied lead – are robust to changes in PV efficiency and manufacturing energy over a wide range of feasible conditions. **Figure 4** shows such a sensitivity study with RFC

electricity, and the conclusion is robust to grid mix as well. TPPBT of less than 0.5 years are attainable with 17% module efficiency if the manufacturing energy can be reduced to levels reported for CdTe of 59 kWh/m². Even with manufacturing energy double what was assumed for our baseline case and efficiencies of only 14%, TPPBT is still only 2.5 years with RFC. Given the robustness towards module efficiency in the sensitivity analysis, slow degradation of the efficiency over the lifetime of LHP-PVs would not alter the qualitative conclusion of this assessment.

The three US electric grids (RFC, MRO, NPPC) considered in our study are representative of different electricity grid mixes (see Section SI.1), with different associated emissions and toxicity potentials depending on the amount of fossil fuels. The aim is to provide three current scenarios as a benchmark for interpreting our results. We assumed a constant rate of emissions and TP over time, as indicated in **Figure 3**. Our analysis does not include future scenarios with potential “decarbonized” electricity grids because of the associated uncertainties. Decarbonization depends not only on technological aspects, but also on energy policy; and complex assumptions are required such as timeframe, displaced technologies, and decommissioning of conventional plants. While scenarios of potential decarbonization are beyond the scope of this study, the magnitude of the differences in emissions and TP indicate that our general conclusions are robust to a significant decarbonization of the grid.

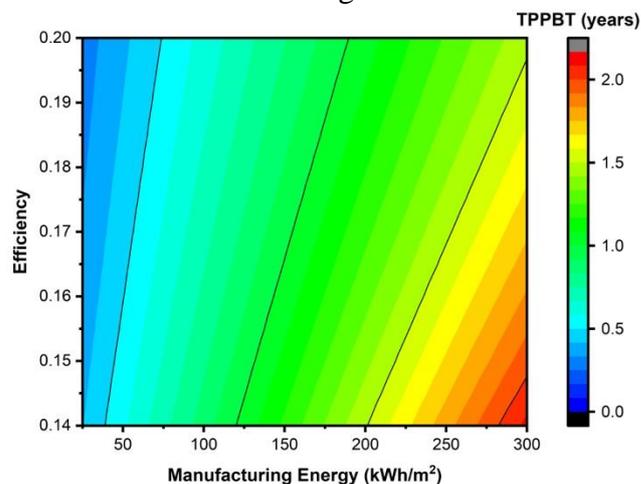


Figure 4. Sensitivity of TPPBT to PV efficiency (varied between 14% and 20%) and manufacturing energy, assuming that the RFC grid is used for the manufacturing energy and displaced by the PV electricity.

3.4 End-of-life treatment of lead-based perovskite photovoltaics

Commercialization of LHP-PVs will require improved long-term stability, improved scale-up to large area modules, development of safe, inexpensive, high-throughput

manufacturing processes, and an environmentally appropriate disposal method for lead-containing waste [56]. From a global systems perspective, the toxicity potential of disposal even with complete lead release is smaller than that of the offset grid electricity, as shown before (**Figure 3**). However, other impact categories and occupational and local public health risks were not addressed. Proper waste management can mitigate this local risk and improve life cycle environmental performance. Recycling protocols could follow those described for LHP-PVs [56-57] or those already developed for CdTe photovoltaics [55-58].

3.5 Risks related to production and use of lead-based perovskite solar panels

Despite their use of lead, LHP-PVs appear to be superior to conventional electricity sources in terms of global toxicity potential, assuming commercially relevant module efficiencies and lifetimes. However, we emphasize that occupational risks of lead exposure inherent to manufacturing and risks related to end-of-life fate of modules may be significant. In production facilities, workers may be routinely or accidentally exposed to lead compounds through inhalation, skin contact, and ingestion from hand-to-mouth contact [59], increasing their chances of lead poisoning. The combination of water-soluble lead compounds in commonly used solvents such as dimethyl sulfoxide (DMSO) that enhance skin penetration is a particular risk that may be avoided by using alternative solvents or by utilizing vapor deposition rather than solution deposition. In current CdTe manufacturing environments that rely on vapor deposition, good industrial hygiene has prevented any detectable uptake of cadmium by workers [58]. Similar practices, as well as those from other lead industries could be implemented for LHP-PV manufacturing.

In the field, glass-glass encapsulation strategies similar to those used for CdTe [58] should be used to minimize the risk of release of environmentally mobile lead that may result in human uptake and consequential toxic effects [30]. Although we have shown that the total potential release of lead from LHP-PVs is still much lower than emissions from the grid mix or from coal power (**Figure 3**), our results do not quantify the direct risk for consumers as a result of concentrated proximate release. Therefore, future research should include improved estimates on service life, damage probability, leaching and exposure pathways, and toxicity in the framework of a thorough risk assessment.

3.6 Data quality considerations, challenges and future research

The scope of this study is appropriate for the evaluation of the life cycle intensity and toxicity potential of lead associated with LHP-PVs and for the comparison with three representative US electricity grids. However, there are limitations and uncertainties as well as challenges that have to be considered. In this study we have considered a prospective design of a perovskite PV module that could potentially be produced on an industrial scale with industrially relevant deposition processes, based on the literature [26]. At present, several device architectures and material compositions have shown high performance for stability, lifetime, and efficiency at laboratory scale; however, the optimal perovskite device architecture for commercial production has not yet been identified. Transferring the lab-scale knowledge to production scale will require significant effort in process engineering. Also, we have considered the most reputable data sources, including Ecoinvent database, but changes in electricity mix composition as well as country of production may affect the results. Moreover, emissions from coal power plants are subject to large variation depending on the pollution abatement technology used. To bolster the robustness of our conclusions, we have included in our analysis a range of grid compositions and a sensitivity analysis that considers device efficiency and operational lifetime. Additional discussion of data sources and quality is available in SI.

4. Conclusions

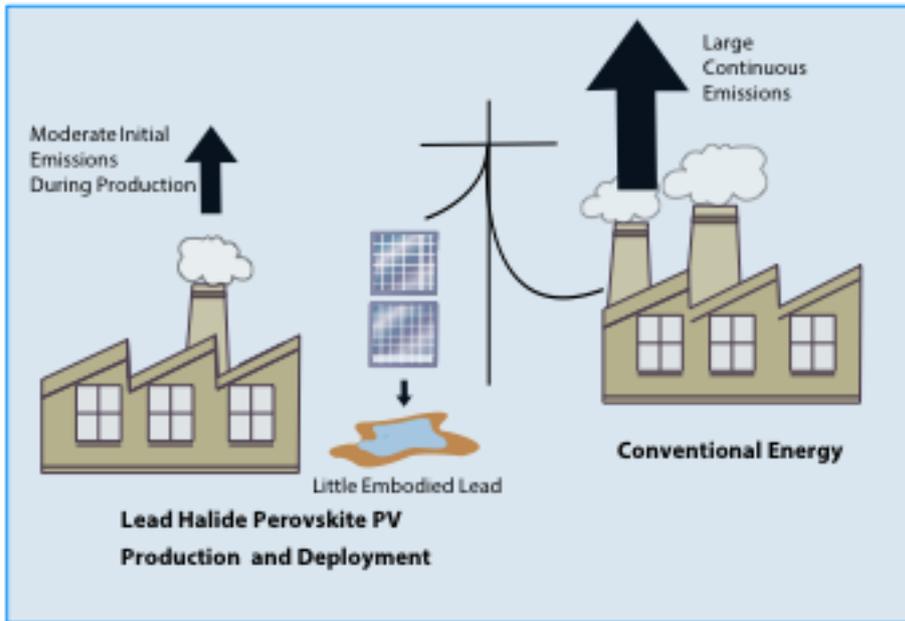
This study has shown that in a scenario of 2,400 GW_p of LHP-PV, only 17,000 metric tons of lead are embodied in the perovskite active layer, representing only 1.1% of the 1.6 million metric tons of lead consumed in the U.S. domestic market, *annually* [52]. Perovskites could, by displacing typical U.S. grid electricity, reduce total lead emissions by a factor of 2-4. Additionally, from a systems perspective, the effect of an unforeseen release of embodied lead on the life cycle toxicity potential is only marginal with respect to that of the manufacturing energy. These conclusions are based on assuming lead halide perovskite PVs with a module efficiency of 17% and a lifetime of 20 years, but hold over a broad range of conditions. Moreover, a new life cycle metric, the toxicity potential payback time (TPPBT), demonstrates that potential emissions of toxic compounds during manufacturing lead halide perovskite photovoltaics together with an unlikely total release of lead at their end-of-life would be offset within just two years by the avoided toxic emissions from current U.S. grids. Toxicity potential of electricity from perovskite PVs over a 20-year operational lifetime would be approximately 20 times lower than that of grid electricity.

As long as the toxicity burden of primary electricity supply to the U.S. grids is high, the toxicity potential of photovoltaics, regardless of their lead content, will primarily depend on the energy and energy mix used in manufacturing. Hence, research efforts should be directed toward developing energy-efficient manufacturing processes for perovskite photovoltaics and improving the stability of LHP-PV to enable a service life of decades. Nevertheless, the current study does not include local health effects from potential catastrophic breakdown of the panels with subsequent air- and water-borne emission of lead. Consequently, development of new photovoltaics incorporating toxic heavy metals should be accompanied with in-depth occupational and local population risk assessments and proper end-of-life management of manufactured systems.

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TOC Graphic:



References

- [1] Solar Power Europe (2017). Global Market Outlook for Solar Power 2017-2021; Solar Power Europe, European Photovoltaic Industry Association, available at: <http://www.solarpowereurope.org/reports/global-market-outlook-2017/>; 2017.
- [2] Solar Power Europe (2015). Global Market Outlook for Solar Power 2015-2019; Solar Power Europe, European Photovoltaic Industry Association: Brussels, Belgium; 2015.
- [3] McGehee M. D., Perovskite solar cells: continuing to soar. *Nature Materials* 2014; 13: 845–846.
- [4] Snaith H. J., Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *The Journal of Physical Chemistry Letters* 2013; 4: 3623–3630.
- [5] Zhang J., Gao X., Deng Y., Li B., Yuan C. Life cycle assessment of titania perovskite solar cell technology for sustainable design and manufacturing. *Chem. Sus. Chem.* 2015; 8: 3882–3891.
- [6] Etgar L., Gao P., Xue Z., Peng Q., Chandiran A. K., Liu B., Nazeeruddin M. K., Grätzel M. Mesoscopic CH₃NH₃PbI₃/TiO₂ Heterojunction Solar Cells. *J. Amer. Chem. Soc.* 2012; 134: 17396-17399.
- [7] Chen Q., De Marco N., Yang Y. M., Song T.-B., Chen C.-C., Zhao H., Hong Z., Zhou H., Yang Y. Under the spotlight: The organic–inorganic hybrid halide perovskite for optoelectronic applications. *Nano Today* 2015; 10: 355-396.
- [8] Meng L., You J., Guo T.-F., Yang Y. Recent Advances in the Inverted Planar Structure of Perovskite Solar Cells. *Acc. Chem. Res.* 2016; 49:155-165.
- [9] Yang M, Kim DH, Klein TR, Li Z, Reese MO, Tremolet de Villers BJ, et al. Highly Efficient Perovskite Solar Modules by Scalable Fabrication and Interconnection Optimization. *ACS Energy Lett* 2018; 3: 322–8.
- [10] Razza S, Di Giacomo F, Matteocci F, Cinà L, Palma AL, Casaluci S, et al. Perovskite solar cells and large area modules (100 cm²) based on an air flow-assisted PbI₂ blade coating deposition process. *Journal of Power Sources* 2015; 277: 286–91.
- [11] Bi D., Tress W., Dar M. I.; Gao P., Luo J., Renevier C., Schenk K., Abate A., Giordano F., Baena J.-P. C., Decoppet J. D., Zakeeruddin S. M., Nazeeruddin M. K., Grätzel M., Hagfeldt A. Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Science Adv.* 2016; 2: 1501170.
- [12] Zhang W., Saliba M., Moore D. T., Pathak S. K., Hörantner M. T., Stergiopoulos T., Stranks S. D., Eperon G. E., Alexander-Webber J. A., Abate A., Sadhanala A., Yao S., Chen Y., Friend R. H., Estroff L. A., Wiesner U., Snaith H. J. Ultrasoft organic–inorganic

perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells. *Nature Comm.* 2015; 6: 6142.

[13] Eperon G. E., Burlakov V. M., Docampo P., Goriely A., Snaith H. J. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. *Adv. Funct. Mater.* 2014; 24 (1): 151-157.

[14] Seo J., Noh J. H., Seok S. I. Rational Strategies for Efficient Perovskite Solar Cells. *Acc. Chem. Res.* 2016; 49: 562-572.

[15] Im J.-H., Jang I.-H., Pellet N., Grätzel M., Park N.-G. Growth of CH₃NH₃PbI₃ cuboids with controlled size for high-efficiency perovskite solar cells. *Nature Nanotechnology* 2014, 9(11): 927-932.

[16] Docampo P., Hanusch F. C., Stranks S. D., Döblinger M., Feckl J. M., Ehrensperger M., Minar N. K., Johnston M. B., Snaith H. J., Bein T. Solution Deposition-Conversion for Planar Heterojunction Mixed Halide Perovskite Solar Cells. *Adv. Energy Mater.* 2014; 4: 00355.

[17] Snaith, H.J. Present status and future prospects of perovskite photovoltaics. *Nature materials* 2018; 17(5) 372.

[18] Flora G., Gupta D. Tiwari A. Toxicity of lead: a review with recent updates. *Interdisciplinary toxicology* 2012; 5(2): 47-58.

[19] Werner, J.H., Zapf-Gottwick, R., Koch, M. and Fischer, K., 2011, November. Toxic substances in photovoltaic modules. In *Proceedings of the 21st International Photovoltaic Science and Engineering Conference, Fukuoka, Japan (Vol. 28)*.

[20] Asif A.A., Singh R., Alapatt G.F. Technical and economic assessment of perovskite solar cells for large scale manufacturing. *Journal of Renewable and Sustainable Energy* 2015; 7(4): 043120.

[21] Shao S, Liu J, Portale G, Fang H-H, Blake GR, Brink GH ten, et al. Highly Reproducible Sn-Based Hybrid Perovskite Solar Cells with 9% Efficiency. *Advanced Energy Materials* 2018;8:1702019.

[22] Sani, F., Shafie, S., Lim, H.N. and Musa, A.O., 2018. Advancement on Lead-Free Organic-Inorganic Halide Perovskite Solar Cells: A Review. *Materials* 2018; 11(6): 1008

[23] Serrano-Lujan L., Espinosa N., Larsen-Olsen T.T., Abad J., Urbina A., Krebs F.C. Tin- and Lead-Based Perovskite Solar Cells under Scrutiny: An Environmental Perspective. *Advanced Energy Materials* 2015; 5(20): 1501119.

- [24] Fabini D. Quantifying the Potential for Lead Pollution from Halide Perovskite Photovoltaics. *J. Phys. Chem. Lett.* 2015; 6 (18): 3546-8.
- [25] Hailegnaw B., Kirmayer S., Edri E., Hodes G., Cahen D. Rain on Methylammonium Lead Iodide Based Perovskites: Possible Environmental Effects of Perovskite Solar Cells. *J. Phys. Chem. Lett.* 2015, 6 (9), 1543-7.
- [26] Celik I., Song Z. N., Cimaroli A. J., Yan Y. F., Heben M. J., Apul D. Life Cycle Assessment (LCA) of perovskite PV cells projected from lab to fab. *Sol. En. Mater. Sol. Cells* 2016; 156: 157-169.
- [27] Fthenakis V. Life Cycle Impact Analysis of Cadmium in CdTe Photovoltaic Production. *Renewable and Sustainable Energy Reviews* 2004; 8: 303-334.
- [28] Fthenakis V. M., Kim H. C. CdTe photovoltaics: Life cycle environmental profile and comparisons. *Thin Solid Films* 2007; 515 (15): 5961-5963.
- [29] US DOE (2017) Energy, U. S. D. o. Cadmium Telluride. <https://energy.gov/eere/sunshot/cadmium-telluride> (accessed May 5, 2017).
- [30] Babayigit A., Ethirajan A., Muller M., Conings, B. Toxicity of organometal halide perovskite solar cells. *Nature materials*, 2016; 15(3): 247.
- [31] Consoli F., Allen D., Boustead I., Fava J., Franklin W., Jensen A., Oude N., Parrish R., Perriman R., Postlethwaite D., Quay B. SETAC-Society of Environmental Toxicology and Chemistry, 1993. Guidelines for Life-Cycle Assessment: A Code of Practice.
- [32] ISO 14040:2006, Environmental Management – Life Cycle Assessment – Principles and Framework; International Standardization Organization: Geneva, Switzerland, 2010.
- [33] ISO 14044:2006, Environmental Management – Life Cycle Assessment – Requirements and Guidelines; International Standardization Organization: Geneva, Switzerland, 2010.
- [34] Environmental Protection Agency (EPA). EGrid Summary Tables 2016. Available at: <https://www.epa.gov/energy/emissions-generation-resource-integrated-database-egrid>, (Accessed March 2018).
- [35] Goedkoop M., Heijungs R., Huijbregts M., De Schryver A., Struijs J., van Zelm R. A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level First edition (version 1.08) Report I: Characterisation, 2008.
- [36] Wernet, G.; Bauer, C.; Steubing, B.; Reinhard, J.; Moreno-Ruiz, E.; Weidema, B., The ecoinvent database version 3 (part I): overview and methodology. *Int J Life Cycle Ass* 2016, 21 (9), 1218-1230

- [37] Meij R., te Winkel H. The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations. *Atmospheric Environment* 2007; 41 (40): 9262-9272.
- [38] Babbitt C. W., Lindner A. S. A life cycle inventory of coal used for electricity production in Florida. *Journal of Cleaner Production* 2005; 13 (9): 903-912.
- [39] EPRI (2006), P. A., CA and U.S. Department of Energy, Pittsburg, PA, Characterization of Field Leachates at Coal Combustion Product Management Sites: Arsenic, Selenium, Chromium, and Mercury Speciation. 2006.
- [40] Fthenakis V., Alsema E. Photovoltaics energy payback times, greenhouse gas emissions and external costs: 2004–early 2005 status. *Progress in photovoltaics: research and applications* 2006; 14(3): 275-280.
- [41] Fthenakis V., Frischknecht R., Raugei M., Kim H.C., Alsema E., Held M., de Wild-Scholten M. Methodology guidelines on life cycle assessment of photovoltaic electricity. IEA PVPS Task, 12, 2011.
- [42] Raugei M. Energy pay-back time: methodological caveats and future scenarios. *Progress in Photovoltaics: Research and Applications* 2013; 21(4): 797-801.
- [43] Leccisi E., Raugei M., Fthenakis V. The Energy and environmental performance of ground-mounted photovoltaic systems—A timely update. *Energies* 2016; 9(8): 622.
- [44] Fraunhofer Institute for Solar Energy Systems (2016) Photovoltaics Report; Freiburg, Germany, 2016.
- [45] NREL, <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>, accessed October 21, 2018.
- [46] Green M.A., Hishikawa Y., Dunlop, E.D., Levi, D.H., Hohl-Ebinger, J., Ho-Baillie, A.W.Y. Solar cell efficiency tables (Version 52). *Progress in Photovoltaics: Research and Applications*, 2018, 26 (7), 427-436.
- [47] Espinosa N., Serrano-Luján L., Urbina A., Krebs F. C. Solution and vapour deposited lead perovskite solar cells: Ecotoxicity from a life cycle assessment perspective. *Sol. En. Mater. Sol. Cells* 2015; 137: 303-310.
- [48] Bush K. A., Palmstrom A. F., Yu Z. J., Boccard M., Cheacharoen R., Mailoa J. P., McMeekin D. P., Hoyer R. L. Z., Bailie C. D., Leijtens T., Peters I. M., Minichetti M. C., Rolston N., Prasanna R., Sofia S., Harwood D., Ma W., Moghadam F., Snaith H. J., Buonassisi

T., Holman Z. C., Bent S. F., McGehee M. D. 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nature Energy* 2017; 2.

[49] Gallon C., Tessier A., Gobeil C., Carignan R., Historical perspective of industrial lead emissions to the atmosphere from a Canadian smelter. *Environ Sci Technol* 2006; 40 (3): 741-747.

[50] Dudka S., Adriano D. C. Environmental impacts of metal ore mining and processing: A review. *Journal of Environmental Quality* 1997; 26 (3): 590-602.

[51] USGS (2016) United States Geological Survey Minerals Information: Mineral Commodity Summaries. <http://minerals.usgs.gov/minerals/pubs/mcs/> (accessed 2016).

[52] Frischknecht R., Itten R., Sinha P., deWild-Scholten M., Zhang J., Fthenakis V., Kim H.C., Raugei M., Stucki M. Life Cycle Inventories and Life Cycle Assessment of Photovoltaic Systems; Report IEA-PVPS T12-04:2015; International Energy Agency (IEA): Paris, France, 2015.

[53] Gong J., Darling S. B., You F. Perovskite photovoltaics: life-cycle assessment of energy and environmental impacts. *Energy Environ. Sci.* 2015; 8 (7): 1953-1968.

[54] Block C., Dams, R. Lead contents of coal, coal ash and fly ash. *Water, Air and Soil Pollution* 1975; 5: 207-211.

[55] EPRI (2003). Potential Health and Environmental Impacts Associated with the Manufacture and Use of Photovoltaic Cells; 1000095; EPRI, Palo Alto, CA, and California Energy Commission, Sacramento, CA: 2003.

[56] Kim B. J., Kim D. H., Kwon S. L., Park S. Y., Li Z., Zhu K., Jung H. S. Selective dissolution of halide perovskites as a step towards recycling solar cells. *Nature Comm.* 2016, 7.

[57] Kadro J.M., Hagfeldt A. The end-of-life of perovskite PV. *Joule.* 2017, 1(1), 29-46.

[58] Rix, A., Steyl, J.D.T., Rudman, J., Terblanche, U., van Niekerk, J.L. *First Solar's CdTe module technology – Performance, life cycle, health and safety impact assessment*; CRSES 2015/06; Stellenbosch University: South Africa, 2015; p 32

[59] Fthenakis V. M., Moskowitz P. D. Photovoltaics: Environmental, health and safety issues and perspectives. *Prog. Photovoltaics* 2000; 8 (1): 27-38.