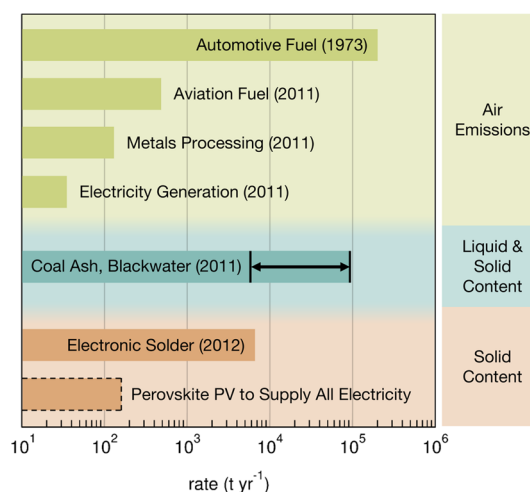


# Quantifying the Potential for Lead Pollution from Halide Perovskite Photovoltaics

Hybrid organic–inorganic lead halide perovskites with the general formula  $\text{APbX}_3$  (where  $A = [\text{CH}_3\text{NH}_3]^+$  or  $[\text{HC}(\text{NH}_2)_2]^+$  and  $X = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ) have attracted substantial research attention of late because of the great promise they display in solution-processed photovoltaic (PV) devices. PV devices employing these materials as the active component currently display efficiencies in excess of 20%.<sup>1</sup> The pace at which these high efficiencies have come about is remarkable given that the first report of these materials in this application appeared only in 2009.<sup>2</sup> However, significant technological challenges remain in the realm of stability and potential lead toxicity. The presence of lead in these materials raises substantial concerns regarding widespread application. Life cycle analyses considering a broad range of material and energy inputs and environmental impacts are beginning to appear for these materials.<sup>3,4</sup> A recent report by Hailegnaw et al. in this journal investigates the mechanism and magnitude of lead loss from  $\text{CH}_3\text{NH}_3\text{PbI}_3$  PV cells via exposure to water, as may happen if a PV module degrades, and considers the implications for lead pollution.<sup>5</sup>

In this Viewpoint, I attempt to quantify the total lead content of halide perovskite PV devices that would be required to supply current electricity needs in the United States as an indicator of the upper bound on possible lead pollution during the service life of this technology. This figure is compared with select historical and current sources of lead pollution in the U.S. On the basis of the crystal structure of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , typical device geometries, and forward-looking assumptions about PV performance, I find a lead intensity (total lead content per unit electricity produced) of  $38 \mu\text{g}/\text{kWh}$ , as detailed below. This corresponds to a total lead content of 160 t/year for all U.S. electricity generation. Consequently, if 1% of PV modules were to break while deployed, 1.6 t/year of lead could leech into the surrounding environment. Though it is beyond the scope of the current work, lead pollution generated during PV module manufacture and disposal or recycling must also be considered. Furthermore, lead pollution is but one of many environmental and resource factors in evaluating the suitability of a new PV technology, including other toxic pollutants, impacts on land use and water resources, greenhouse gas emissions, energy payback times, and abundance of material inputs.<sup>3,6,7</sup>

A comparison with select lead pollution sources and lead-containing products is summarized in Figure 1. In 1973, before the phase-out of leaded automotive gasoline, direct air emissions of lead from automobiles were estimated to be 200 000 t/year.<sup>8</sup> In 2011, air emissions from leaded aviation fuel, processing of metals, and electricity generation from fossil fuels were reported to be 440, 120, and 35 t/year, respectively.<sup>9</sup> Additionally, although figures are not directly reported, I calculate that between 5900 t/year and 93 000 t/year of lead are generated by the electric power sector during coal processing and combustion in the form of coal ash and blackwater. Lastly, in 2012, the lead content of electronic solder produced in the U.S. was reported to be 6200 t/year,<sup>13</sup> though



**Figure 1.** Select U.S. lead emissions sources,<sup>8,9</sup> lead content of coal wastes<sup>10–12</sup> and electronic solder produced in the U.S.,<sup>13</sup> and hypothetical lead content of perovskite photovoltaics (PV) to supply the entire U.S. electricity sector.<sup>12,14,15</sup> All quantities are in metric tons per year.

the lead content of solder present in all electronic products in the U.S. is likely somewhat higher due to imports.

The chemical and physical forms of lead are of course markedly different in these contexts. Direct emission to the air provides a facile route for lead to end up in soil, on surfaces, and in food and water supplies. Coal ash and blackwater are not emitted directly to the air, but slurry impoundment ponds at coal processing plants and power stations have been the site of recent large-scale environmental disasters.<sup>16,17</sup> In contrast, lead in halide perovskite PV is in the solid state, encapsulated, and specifically must remain there for the technology to be viable. The case of electronic solder is perhaps most analogous, though the quantity of lead appears to be substantially larger and the primary risk is associated with leaching from equipment improperly disposed of in landfills.

All technologies and processes present risks that must be weighed objectively against those associated with alternatives. In the case of leaded automotive gasoline, leaded solder for potable plumbing systems, and leaded paint, the lead pollution and toxicity burden is unacceptably high, and bans on these products have been in place for decades. In contrast, lead-acid batteries continue to be the standard for starting–lighting–ignition batteries in trucks and automobiles and are the primary source of recycled lead that makes up 91% of refined lead production in the U.S.<sup>13</sup> Effective regulation and management of manufacture, deployment, and disposal or reprocessing of technologies containing lead can significantly reduce the risks associated with these materials. In the case of halide perovskite PV, further study is required to determine whether or not these

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risks can be mitigated to an acceptably low level. These are indeed challenging materials, but the picture that emerges from this analysis is that the potential for lead exposure from large-scale adoption of this technology is relatively modest when compared with other, existing technologies and practices.

*Details of the Calculations.* The area density of lead in halide perovskite PV devices is calculated as

$$\sigma_{\text{Pb}} = \frac{N_{\text{Pb}}}{V_{\text{c}}} \times \frac{M_{\text{Pb}}}{N_{\text{A}}} \times l = 420 \text{ mg/m}^2$$

where  $N_{\text{Pb}}$  and  $V_{\text{c}}$  are the number of lead atoms per unit cell and the unit cell volume, respectively, for the room temperature polymorph of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ,<sup>14</sup>  $M_{\text{Pb}}$  is the molar mass of lead,  $N_{\text{A}}$  is Avogadro's number, and  $l$  is the absorber thickness (assumed to be 300 nm).

The lead intensity of energy produced from halide perovskite PV is calculated as

$$I_{\text{Pb}} = \frac{\sigma_{\text{Pb}}}{GT\eta C} = 38 \text{ } \mu\text{g/kWh}$$

where  $G = 1 \text{ kW/m}^2$  is the nominal solar irradiation at the Earth's surface,  $T$  is the PV plant lifetime,  $\eta$  is the PV conversion efficiency, and  $C$  is the PV plant capacity factor. Here, the lifetime is assumed to be 25 years and the efficiency 25% (perovskite/c-Si tandem, or similar), reflecting the stringent reliability and performance requirements for widespread implementation of this new technology. The capacity factor encapsulates the geographic and temporal variation in solar irradiation, and is here assumed to be 20%, which is typical of fixed axis solar PV performance in the United States to date.<sup>15</sup>

The total lead content of enough halide perovskite PV to supply all U.S. electricity is calculated as

$$m_{\text{Pb}} = I_{\text{Pb}} \times E = 160 \text{ t/year}$$

where  $E = 14.01$  quadrillion BTU is the net generation of electricity in 2011 (enough to supply all consumption plus transmission and distribution losses).<sup>12</sup> Possible additional lead pollution from sources upstream in the supply chain, as in air emissions from additional lead smelting, are not captured here. These sources are assumed to be secondary in quantity to the lead present in PV cells themselves and are likely more easily mitigated or contained than the potential pollution from geographically disperse lead-containing PV panels.

The lead content of U.S. coal wastes from electric power generation is calculated as

$$m_{\text{Pb,coal}} = c_{\text{Pb,coal}} \times C_{\text{coal}} = 5900 \text{ t/year} - 93\,000 \text{ t/year}$$

where  $c_{\text{Pb,coal}} = 7\text{--}110 \text{ } \mu\text{g/g}$  is the concentration of lead in coal<sup>10,11</sup> and  $C_{\text{coal}} = 928.6$  million short tons is the coal consumption of the electricity sector in 2011.<sup>12</sup> This calculation assumes that all lead in the coal ends up in blackwater, bottom ash, and captured fly ash. In practice, a very small proportion escapes precipitators and filters and enters the atmosphere (compare the magnitude of air emissions from the power sector, 35 t/year, with the original lead content of the corresponding coal, as calculated here). Additionally, some proportion of fly ash is repurposed as a partial substitute for Portland cement in concrete production or is used in embankments or other fill. This diversion of ash wastes is not captured here for lack of data, though the effect is likely to be significantly less than 1 order of magnitude.

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The authors declare no competing financial interest.

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