

Emissions from Photovoltaic Life Cycles

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Photovoltaic (PV) technologies have shown remarkable progress recently in terms of annual production capacity and life cycle environmental performances, which necessitate timely updates of environmental indicators. Based on PV production data of 2004–2006, this study presents the life-cycle greenhouse gas emissions, criteria pollutant emissions, and heavy metal emissions from four types of major commercial PV systems: multicrystalline silicon, monocrystalline silicon, ribbon silicon, and thin-film cadmium telluride. Life-cycle emissions were determined by employing average electricity mixtures in Europe and the United States during the materials and module production for each PV system. Among the current vintage of PV technologies, thin-film cadmium telluride (CdTe) PV emits the least amount of harmful air emissions as it requires the least amount of energy during the module production. However, the differences in the emissions between different PV technologies are very small in comparison to the emissions from conventional energy technologies that PV could displace. As a part of prospective analysis, the effect of PV breeder was investigated. Overall, all PV technologies generate far less life-cycle air emissions per GWh than conventional fossil-fuel-based electricity generation technologies. At least 89% of air emissions associated with electricity generation could be prevented if electricity from photovoltaics displaces electricity from the grid.

1. Introduction

The production of energy by burning fossil fuels releases many pollutants and carbon dioxide to the environment. Indeed, all anthropogenic means of generating energy, including solar electric, create pollutants when their entire life cycle is taken into account. Life-cycle emissions result from using fossil-fuel-based energy to produce the materials for solar cells, modules, and systems, as well as directly from smelting, production, and manufacturing facilities. These emissions differ in different countries, depending on that country's mixture in the electricity grid, and the various methods of material/fuel processing.

Previous life-cycle studies reported a wide range of primary energy consumption for PV modules. Alsema

reviewed studies of crystalline silicon photovoltaics from the 1990s and found considerable variance among investigators in their estimates of primary energy consumption. In those days, manufacturing of solar cells was for the most part using off-spec products of electronic-grade silicon and various allocation rules were applied to the energy and material inputs for each grade of silicon; also solar cells were much thicker than the current ones (1). Meijer et al. evaluated 270- μm -thick Si PV with 14.5% cell efficiency fabricated from electronic-grade high-purity silicon (2). They estimated energy payback time (EPBT), the time it takes for a photovoltaic (PV) system to generate an amount of energy equal to that used in its production) for the module only of 3.5 years for the low level of insolation in The Netherlands (1000 kWh/m²/yr). Jungbluth reported the life-cycle metrics of various PV systems (2000 vintage) under average insolation in Switzerland (1100 kWh/m²/yr) (3). He estimated greenhouse gas (GHG) emissions in the range of 39–110 g CO₂-equiv/kWh and EPBT of 3–6 years.

There are a few life-cycle studies of thin-film PV technologies; these include those of CdTe PV by Palz and Zibetta, Hynes et al., and Kato et al., and the amorphous silicon studies by Keoleian and Lewis (4–7). The CdTe studies were based on R&D data and hypothetical production lines since commercial production of such modules started in 2004 (4–6). The study of Keoleian and Lewis was based on data from the early operations of UniSolar, Alburn Hills, MI (7). Their study presented that the EPBT of the frameless module of double-junction amorphous silicon with 5% efficiency is 4.6 years in Detroit, MI and 2.2 years in Phoenix, AZ. This study is not applicable to the current production from the same company which comprises triple-junction modules of 8% efficiencies. Fthenakis and Alsema (8) reported the 2004–early 2005 status of the EPBTs and of greenhouse gas (GHG) emissions in four different photovoltaic rooftop installations, namely ribbon-Si, multicrystalline Si (multi- or mc-Si), monocrystalline Si, and thin-film CdTe systems. Their corresponding EPBTs, under the average Southern European insolation of 1700 kWh/m²/yr, were 1.7, 2.2, 2.7, and 1.1 years. The EPBT of CdTe PV was much lower than that of the other systems although its electrical-conversion efficiency was the lowest in the group (i.e., 9% for CdTe vs 11.5% for ribbon, 13.2% for multicrystalline Si, and 14% for monocrystalline Si).

Reporting and comparing life-cycle emissions from energy technologies that draw public health concern is an important facet in assuring the acceptability of any particular one. In this paper, we update the greenhouse gas emissions, and present the first comprehensive assessment of emissions of criteria pollutants and heavy metals, from cradle to gate, of four commercial PV systems based on the most recent data (i.e., 2004–2006): ribbon-silicon, multicrystalline silicon, monocrystalline silicon, and thin-film cadmium telluride. The heavy metal, toxic gas, and GHG emissions are the main emissions from the considered commercial PV technologies. These are, for the most part, indirect emissions associated with the use of fossil fuels in the generation of energy required in the life cycle of photovoltaics. Direct emissions of heavy metals from mining and smelting including particulate matter are also included, whereas liquid and solid waste are for the most part being recycled, and were not considered in this study. The choice of electricity and fuel sources plays an important role in determining the total emissions. In this context, we investigated a scenario of PV breeding where PV supplies a fraction of the electricity required in manufacturing.

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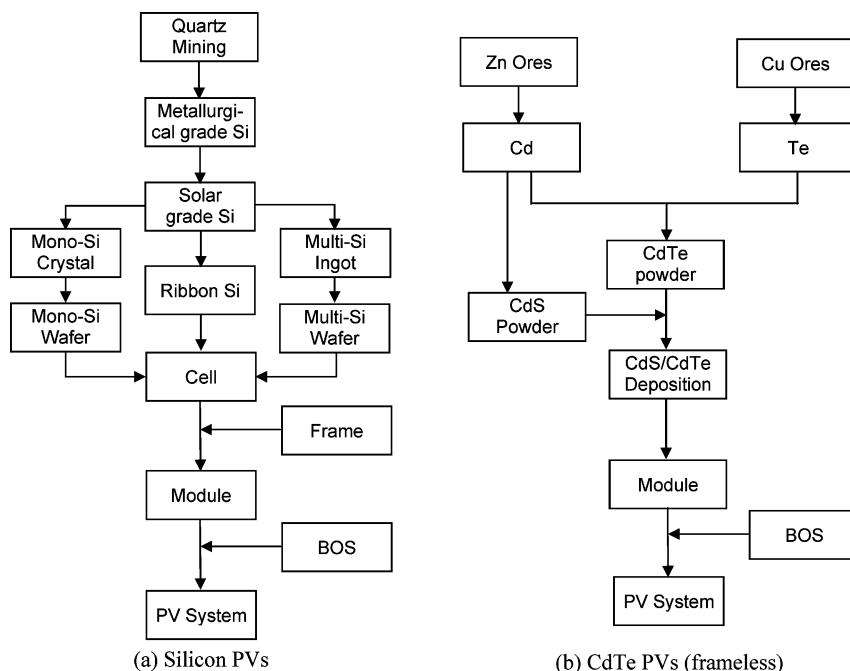


FIGURE 1. Simplified process-flow diagrams from mining to system manufacturing stages, namely cradle-to-gate for (a) mono-, ribbon-, and multi-Si PVs, and (b) thinfilm CdTe PVs. Detailed descriptions of the life cycles are available elsewhere (10, 12, 13).

2. Life Cycle of Silicon and Thin-Film CdTe Photovoltaics

The life cycle of PV systems starts with the mining of quartz sand (silicon PV) or metal ore (CdTe PV). The silica in the quartz sand is reduced in an arc furnace to obtain metallurgical grade silicon, which has to be purified further into “electronic grade” or “solar grade” silicon (Figure 1). The silicon purification step involves either the “Siemens” process in which a reactor chamber with trichlorosilane (SiHCl_3) and hydrogen (H_2) gases is heated to 1100–1200 °C for growing silicon rods, or the “modified Siemens” process in which silane (SiH_4) and hydrogen (H_2) gases are heated to ~800 °C for the same, resulting in lower energy consumption (9).

A detailed life-cycle inventory (LCI) of crystalline silicon modules for polycrystalline silicon feedstock purification, crystallization, wafering, cell processing, and module assembly with the current status of technology (2004–early 2005) was recently completed within the “CrystalClear” European Commission project (10). The sources of LCI data for this project include 11 commercial European and U.S. photovoltaic module manufacturing companies supplemented by numbers from the literature. Depending on the type of cell material, crystallizing or growing the silicon wafer follows, along with tailoring the wafers. Cell manufacturing and subsequent module assembly, which is virtually equal for each module, concludes their life cycle (Figure 1). Each module assembly typically consists of seventy-two $0.125 \text{ m} \times 0.125 \text{ m}$ solar cells with silver contacts in front and back sides. Ethylene-vinyl acetate and glass sheets encapsulate the PV module to provide protection from the physical elements during operation. Crystalline silicon modules typically have aluminum frames for additional strength and easy mounting.

Ethenakis (11) described the material flows of cadmium (Cd) and emissions from the entire life-cycle stages of cadmium telluride (CdTe) PV. The life cycle starts with the production of Cd and Te which are byproducts of Zn and Cu smelting. Cd is obtained from a waste stream of Zn smelting, namely particulates collected in electrostatic precipitation and bag house and slimes collected from Zn electrolyte purification stages. Te is recovered from the slimes produced

during electrolytic copper refining, which also contain Cu, Se, and other metals. The slimes are treated with dilute sulfuric acid to extract Te. After cementation with copper, CuTe is leached with caustic soda to produce a sodium-telluride solution that is used as the feed for Te and TeO_2 . Cadmium is further processed and purified either through leaching and vacuum-distillation, or through electrolytic purification followed by melting and atomization or vacuum-distillation, to produce the 99.999% purity required for the synthesis of CdTe. Tellurium is also further purified by the above-mentioned methods. CdTe is produced from Cd and Te via proprietary processes.

We analyzed in detail the life-cycle inventory of CdTe PV modules in commercial scale production (12). The data were obtained at a CdTe PV manufacturing plant in Perrysburg, OH with a 25-MW production capacity (www.firstsolar.com). The dimensions of this plant’s typical frameless CdTe module are $1.2 \text{ m} \times 0.6 \text{ m}$ with an electricity conversion efficiency of 9% (The efficiency of the modules produced by this plant has increased to 10% as of September 2007; this improvement is not reflected in the current article). The cadmium telluride (CdTe) absorber layer and cadmium sulfide (CdS) window layer in First Solar’s production scheme are laid down by vapor transport deposition (VTD), based on subliming the powders and condensing the vapors on glass substrates. A stream of inert carrier gas guides the sublimed dense vapor cloud to deposit the films on glass substrates at 500–600 °C with a growth rate over $1 \mu\text{m/s}$ (13). Depositing layers of common metals followed by series of scribing and heat treatment forms interconnections and back contacts. No rare metals/elements are used in the back contact layers.

Table S1 in the Supporting Information of this paper presents the material compositions of silicon- and CdTe-modules. Glass is the heaviest part of PV module components, particularly of the frameless CdTe module where two panes of glass ensure structural toughness. The double-glass design eliminates the need for an aluminum frame which accounts for a significant fraction of emissions for the silicon modules. The use of CdTe powder per m^2 of thin film CdTe module is minimal compared with silicon modules since the thickness of cell materials of the former is $\sim 3 \mu\text{m}$ compared with

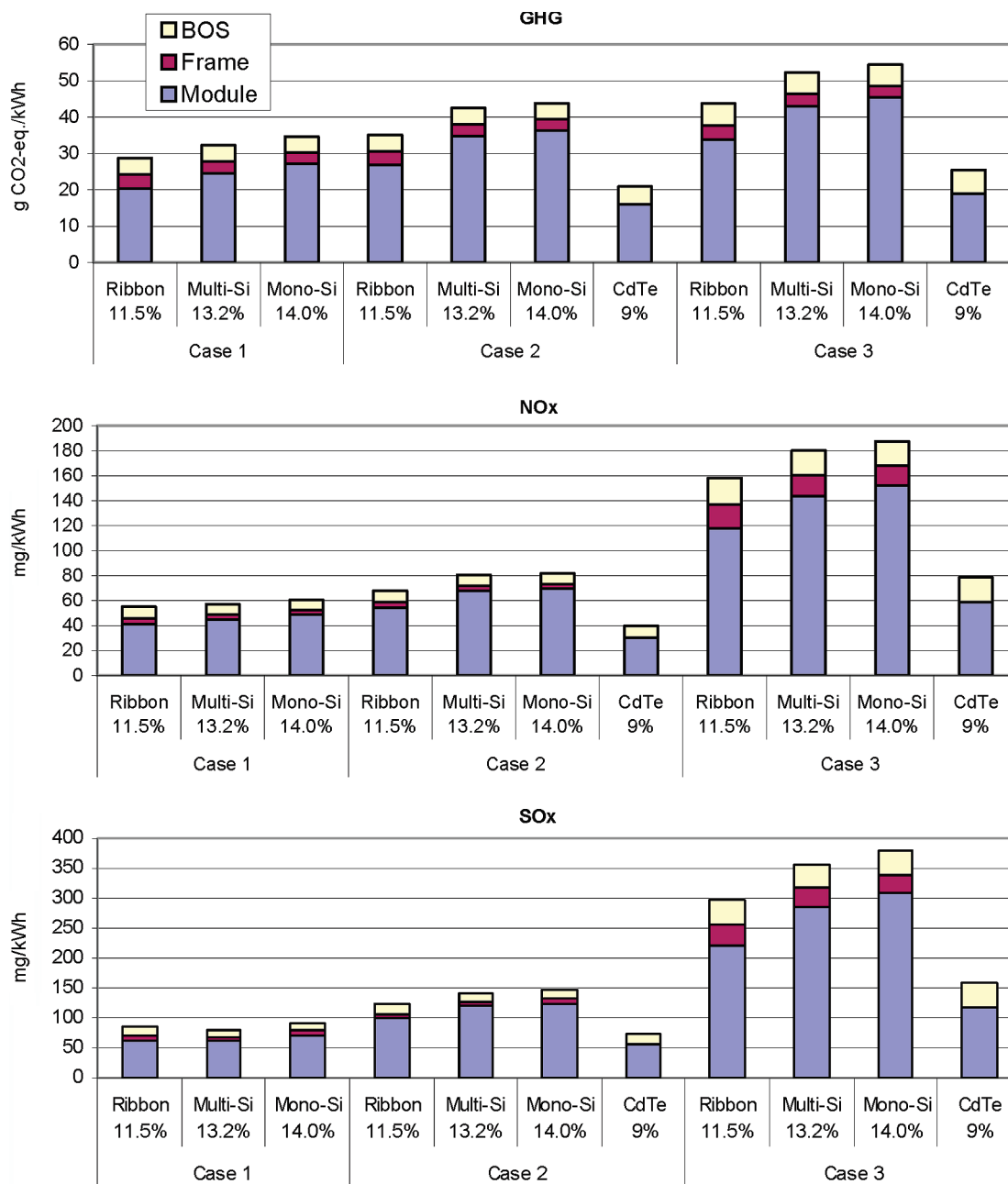


FIGURE 2. Life-cycle emissions from silicon and CdTe PV modules. BOS is the Balance of System (i.e., module supports, cabling, and power conditioning). Conditions: ground-mounted systems, Southern European insolation, 1700 kWh/m²/yr, performance ratio of 0.8, and lifetime of 30 years. Case 1: current electricity mixture in Si production—CrystalClear project and Ecoinvent database. Case 2: Union of the Co-ordination of Transmission of Electricity (UCTE) grid mixture and Ecoinvent database. Case 3: U.S. grid mixture and Franklin database.

270–300 μm for silicon modules. The CdTe module also requires smaller amounts of gases, liquids, and other consumables than does a silicon module.

3. GHG and Criteria Pollutant Emissions

We estimate the emissions GHG, SO₂, and NO_x during the PV life cycles. Together with the heavy metal emissions assessed later in this paper, these emissions comprise the main hazards to the environment and human health from energy use and materials extraction during the PV life cycle. These emissions are normalized by the electricity generated during the life cycle of PV. The major parameters for the life cycle, i.e., lifetime electricity generation of a PV system, include conversion efficiency (*E*), solar insolation (*I*), performance ratio (PR), and lifetime (*L*). The total lifetime

electricity generation (*G*) per m² of PV module is calculated as follows: $G = E \times I \times PR \times L$. We consistently use, for our own analysis, the Southern European average insolation of 1700 kWh/m²/yr, a performance ratio of 0.8, and a lifetime of 30 years.

Alsema and de Wild report that the GHG emissions of Si modules for the year 2004 are within the 30–45 g CO₂-equiv/kWh range, with an EPBT of 1.7–2.7 years for a rooftop application under Southern European insolation of 1700 kWh/m²/yr and a performance ratio (PR) of 0.75 (8, 10). Their estimates are based on the electricity mixture for the current geographically specific production of Si (Figure 2, Case 1).

Fthenakis and Kim (12) recently investigated the GHG emissions and EPBT of CdTe PV modules, based on U.S. production and insolation conditions (insolation = 1800

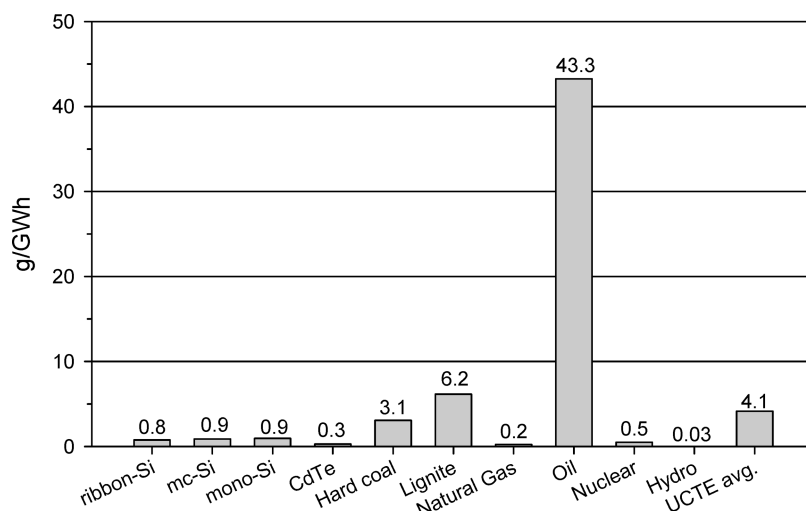


FIGURE 3. Life-cycle atmospheric Cd emissions for PV systems from electricity and fuel consumption, normalized for a Southern Europe average insolation of 1700 kWh/m²/yr, performance ratio of 0.8, and lifetime of 30 yrs. Ground-mounted BOS (18) is assumed for all PV systems; comparisons with other electricity generation options.

kWh/m²/yr; performance ratio 0.8; lifetime 30 years). Their estimates were 24 g CO₂-equiv/kWh of GHG emissions, and 1.1 yrs of EPBT for ground-mounted installations. In the following we updated the previous estimates and normalized them for constant solar irradiation, performance ratio, and electricity mixture. Figure 2, Case 2 shows emissions corresponding to upstream electricity for the average grid mixture for continental Europe (Union of the Co-ordination of Transmission of Electricity, UCTE), and Figure 2, Case 3 shows the same for the average U.S. grid mixture. The most commonly used LCA databases, Ecoinvent for the European grid and Franklin for the U.S. grid mix, are employed for the energy and emission factors (14, 15).

The production of polycrystalline silicon is the most energy-consuming stage of the silicon module's life cycle; it accounts for 45% of the total primary energy usage in the multi-Si module life cycle (10). Electricity demand during CdTe film deposition accounts for the greatest use (i.e., 54%) of primary energy in the CdTe module life (12). The estimated emissions from Case 1 which is based on the electricity mix of CrystalClear project, are lower than those from Cases 2 and 3, mainly because of the higher portion of hydropower and natural-gas-fired combined-cycle power plants currently used by the producers of polycrystalline solar grade silicon (Table S2 in the Supporting Information). For the same reason, the emission estimates based on the UCTE grid mixture (Case 2) typically are lower than those based on the U.S. grid (Case 3) (i.e., the former is a cleaner fuel mix). The life-cycle emissions from mono-Si PV are greater than those from other Si PVs mainly because the mono-Si requires substantial energy during the ingot growing process (by Czochralski crystal pulling).

4. Heavy Metal Emissions

We followed the direct and indirect (due to energy use) emissions of heavy metals (arsenic, cadmium, chromium, lead, mercury, and nickel) during the life cycles of the four PV technologies we studied. The CdTe PV can emit Cd both directly and indirectly whereas the crystalline Si PV stages would emit such only indirectly.

4.1. Direct Cd Emissions. Fthenakis (11) compiled the direct, atmospheric Cd emissions from the life cycle of CdTe PV modules based on 30 years of module lifetime, 9% efficiency, and the average U.S. insolation of 1800 kWh/m²/yr. The total direct emissions of cadmium during the mining, smelting, and purification of the element and the synthesis

of CdTe are 0.015 g/GWh. The total direct emissions of cadmium during module manufacturing are 0.004 g/GWh (11). Emissions during accidental releases (e.g., fires) are extremely small, if any. Such emissions could add to the total of 0.02 g/GWh. The latter have been investigated experimentally with the aid of high-energy synchrotron X-ray microprobes (16). Cd emissions from the life cycle of CdTe modules (Table S3 in the Supporting Information) are estimated to be 90–300 times lower than those from coal power plants, which are 2–7 g Cd/GWh (17).

4.2. Indirect Cd Emissions due to Electricity and Fuel Use. We hereby accounted for Cd emissions in the generation of electricity used in producing a PV system. Electricity generation by fossil fuels creates heavy metal emissions as those are contained in coal and oil and a fraction is released in the atmosphere during combustion. The electricity demand for PV modules and BOS were investigated based on the life-cycle inventory of each module and the electricity input data for production of BOS materials. Then, Cd emissions from the electricity demand for each module were assigned, assuming that the life-cycle electricity for the silicon- and CdTe-PV modules are supplied by the UCTE grid.

Indirect Cd emissions include those from using fossil fuel, such as natural gas, heavy oil, and coal for providing heat and mechanical energy during materials processing, for climate control of the manufacturing plant, and for the transportation of materials and products throughout the life cycle of PV modules. The dominant sources of such indirect Cd emissions were found to be the use of coal during steel-making processes and the use of natural gas during glass-making processes. The cadmium emissions from natural gas use are indirect, from the boiler materials and from the electricity supply needed in the boiler, not from the burning of gas itself.

The complete life-cycle atmospheric Cd emissions were estimated by adding the Cd emissions from electricity and fuel demand associated with manufacturing and materials production for PV module and Balance of System (BOS). These are shown in Figure 3. The results show that CdTe PV displacing other electricity technologies actually prevents a significant amount of Cd from being released to the air. Every GWh electricity generated by CdTe PV module can prevent around 4 g of Cd air emissions if used instead of or as a supplement to the UCTE electricity grid. The direct emissions of Cd during the life cycle of CdTe PV are 10 times lower than the indirect emissions due to the electricity and fuel use in

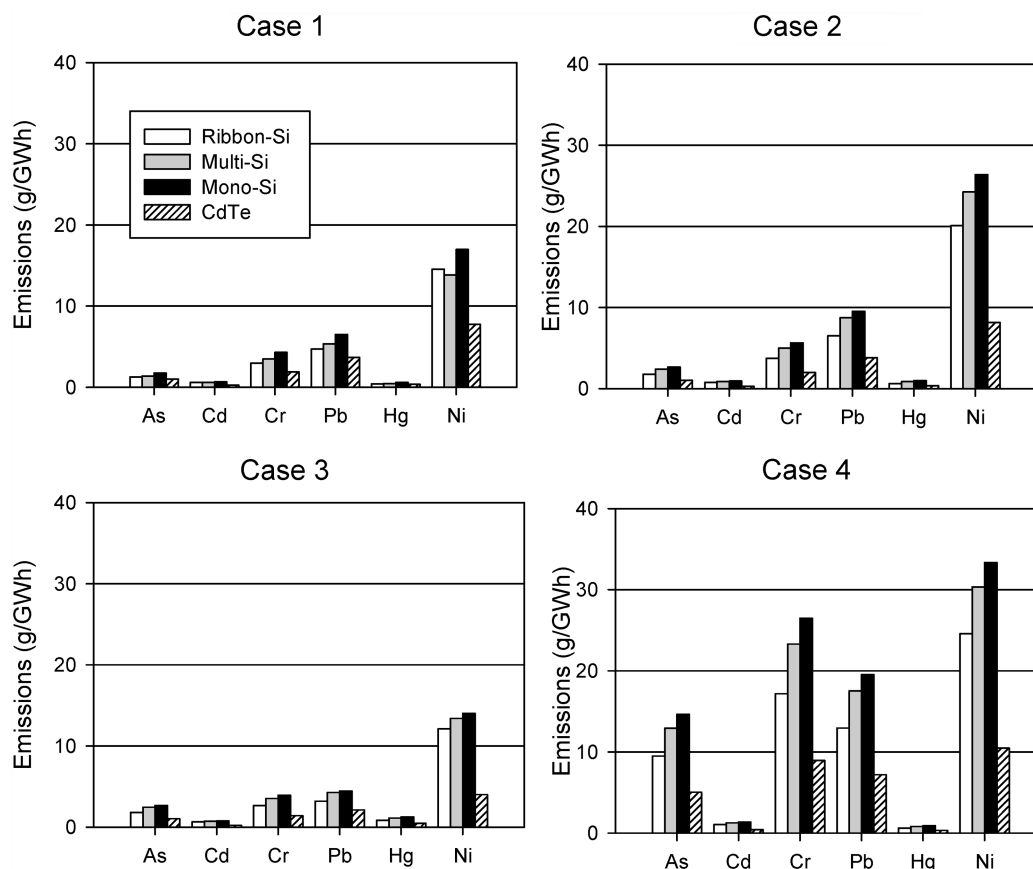


FIGURE 4. Life-cycle atmospheric heavy-metal emissions for PV systems (normalized for Southern European average insolation of 1700 kWh/m²/yr, performance ratio of 0.8, and lifetime of 30 yrs). Each PV system is assumed to include a ground-mounted BOS as described by Mason et al. (18). The four types of PV modules and corresponding efficiencies are ribbon-Si 11.5%, multi-crystalline Si 13.2%, monocrystalline 14%, and CdTe 9%.

the same life cycle, and about 30 times lower than those indirect emissions in the life cycle of crystalline photovoltaics.

Other heavy-metal emissions from the life-cycle electricity and fuel usage of PV systems are shown in Figure 4. The calculated emission factors are the products of electricity and fuel usage during the life cycle of PV modules and the emissions factors taken from the LCA databases. The heavy-metal emission factors in Cases 1–4 are based, respectively, on the following grid mixtures and databases: Case 1, Ecoinvent database and the grid mixture of the CrystalClear project in which electricity mix of gas-fired combined cycle and hydropower was used for production and purification of polycrystalline silicon (10, 14); Case 2, Ecoinvent database for medium-voltage electricity of the UCTE grid (14); Case 3, Franklin database for the U.S. average grid mixture (15); and Case 4, emission factors of a recent study by Kim and Dale for the U.S. grid mixture (19). The last one adopts the DEAM LCA database and the eGRID model from the U.S. Environmental Protection Agency. Emissions across different data sources vary greatly, with the factors quoted by Kim and Dale (19) being the highest. In particular, the Cr emissions for this source are 5 times higher than the Ecoinvent estimate. The CdTe PV module performs the best, and replacing the regular grid mix with it affords significant potential to reduce those atmospheric heavy-metal emissions.

4.3. Direct Emissions during Material Processing. Other than the Cd emissions depicted above, direct, heavy-metal emissions from materials processing have not been determined by the present study for several reasons. First, emissions during processing highly depend on the selection of the system's boundary, and therefore, the allocation method that an LCA study adopts. For example, a significant

amount of Cd emissions are allocated to recycled aluminum because unwanted copper scraps containing Cd as an alloy additive are mixed and melted with aluminum scrap during recycling. In this case, allocation can be avoided (according to ISO guideline) if the Cd emissions are assigned to the primary copper alloy production. Moreover, the amount of unabated emissions may significantly decrease with technological progress and stricter regulatory standards. For instance, Cr emissions from steel production using an electric arc furnace based on one database is 15 times higher than that cited from another database (1.5 mg/kg of steel from one database vs 0.1 mg/kg of steel from another). Finally, the composition of the metal, in other words, the amount of impurities mixed with matrix metal, often decides heavy-metal emission factors. According to the Ecoinvent database, low-alloyed converter steel generates six times more arsenic, and 150 times more chromium than unalloyed steel (14). Therefore, estimating heavy-metal emissions directly from materials processing, i.e., from mining, smelting, and purification, entails large inherent uncertainties.

For demonstration purposes, we first compared the heavy-metal emissions from electricity and fuel, with the direct emissions from material processing based on heavy-metal emission factors from the Ecoinvent database (Figure 5). Direct heavy-metal emissions from copper, lead, and steel alloying processes together with aluminum recycling that is unrelated to electricity or fuels have been estimated for the multi-Si PV module. It is shown that the electricity consumption is the most important source of heavy-metal emissions for As, Cd, Hg, and Ni emissions. The high fraction of direct Pb emission from material processing is related to solar glass manufacturing, which accounts for about 80% of

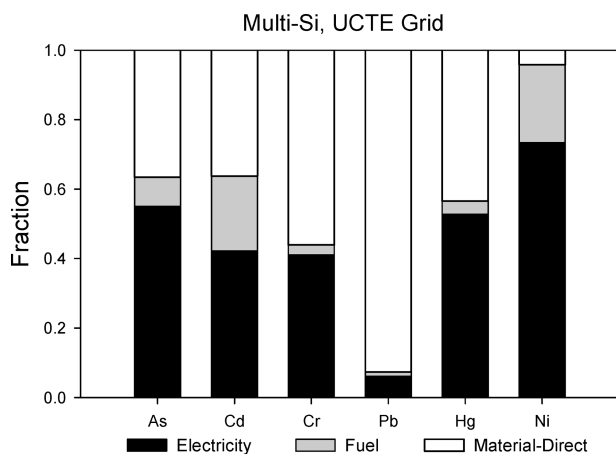


FIGURE 5. Breakdown of heavy-metal emissions for PV modules. UCTE grid mix and Ecoinvent database are used for heavy-metal emission factors of electricity, fuel, and materials.

such Pb emission. However, this result may be an overestimation since Ecoinvent database assumes a construction-grade glass for the solar glass, although the glass used in PV modules typically contains less Pb because lead is not added to solar glass as an additive (20). In fact, the lead emission factor of glass manufacturing in the ETH-ESU database (the predecessor of Ecoinvent) is lower than that in Ecoinvent by a factor of 250 (14, 21). For the above reasons estimates of direct heavy-metal emissions carry higher uncertainties than the energy-related emissions. Further work is required to improve reliability of estimating such emissions.

5. PV Breeder

As part of prospective analysis, one could evaluate the effect of increased PV penetration in the “quality” of the energy mixture used in PV production. At the limit, all electricity used in PV manufacturing can be generated by onsite or nearby PV. In this section, we explore potential benefits of returning electricity generated by PV to the PV fuel cycle. As the electric power generated by PV is variable to insolation, an electrical storage system will be needed to fully meet the electricity demand for the PV production; with the reality of today’s electricity grid (22), around 30% of the electricity required for PV production can be supplied without a storage system. In Figure 6, we illustrate the effect of incrementing electricity supply from a PV breeder scheme (i.e., PVs that supply electricity to the PV life cycles) of multicrystalline (mc)-Si and CdTe PVs. For mc-Si, around 250 kWh per m² of electricity is required throughout the consecutive process of polycrystalline silicon, wafer, cell, and module production, while producing the same area of CdTe requires 59 kWh of electricity (10, 12). If the considered PV breeder system supplies 30% of the electricity required in each Si PV production process, i.e., silicon, wafer, cell, and module, as well as in CdTe PV production process, 6 and 2 g/kWh of GHG emissions will be curbed from the case that uses UCTE grid mix (Figure 6). A recent study demonstrates that large-scale PV plants can utilize compressed air to store electricity (23), which could enable a 100% electricity supply for PV manufacturing. This would reduce around 50% of life-cycle GHG emissions for both Si and CdTe PVs (Figure 6). A similar exercise by Pacca et al. resulted in greater GHG reductions, i.e., 68% and 82% for multi-Si and amorphous-Si PV, respectively (24). The greater reductions are related to the higher CO₂ emissions from the background electricity being replaced in their study, i.e., the U.S. average grid mix, which is 45% more carbon-intensive than the UCTE grid (14, 15). A PV breeder system could directly supply a large part of the electric energy used in manufacturing. This scenario indicates

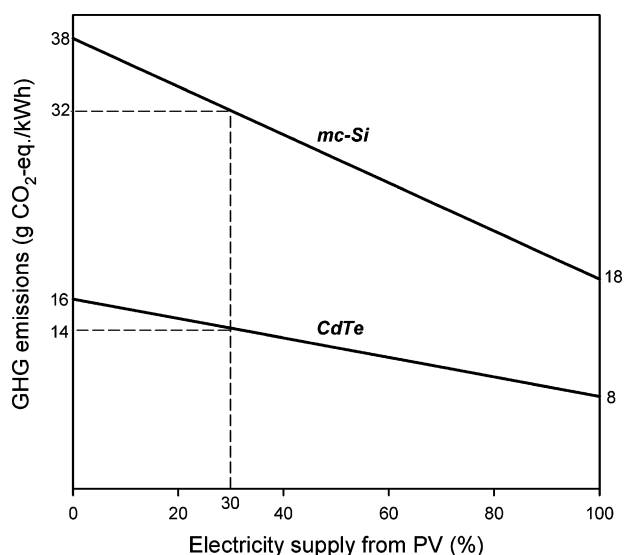


FIGURE 6. Greenhouse gas emissions profile for PV modules when using a PV breeder that supplies electricity for PV production. Insolation of 1700 kWh/m²/yr, performance ratio of 0.8, and lifetime of 30 yrs are assumed. BOS is not included. In 2005, the total (100%) electricity corresponded to 250 kWh/m² for mc-Si and 59 kWh/m² for CdTe PV.

the potential of further reducing GHG emissions in the future by employing more carbon-free electricity generation. Other electricity generation and production related-parameters, for instance, photon-to-electricity conversion efficiency and cell/film thickness are also advancing in parallel and would also result in reduced emissions.

6. Discussion

Using data compiled from the original records of twelve PV manufacturers, we quantified the emissions from the life cycle of four major commercial photovoltaic technologies and showed that they are insignificant in comparison to the emissions that they replace when introduced in average European and U.S. grids. According to our analysis, replacing grid electricity with central PV systems presents significant environmental benefits, which for CdTe PV amounts to 89–98% reductions of GHG emissions, criteria pollutants, heavy metals, and radioactive species. For roof-top dispersed installations, such pollution reductions are expected to be even greater as the loads on the transmission and distribution networks are reduced, and part of the emissions related to the life cycle of these networks are avoided. It is interesting that emissions of heavy metals are greatly reduced even for the types of PV technologies that make direct use of related compounds. For example the emissions of Cd from the life cycle of CdTe PV are 90–300 times lower than those from coal power plants with optimally functioning particulate control devices. In fact, life-cycle Cd emissions are even lower in CdTe PV than in crystalline Si PV, because the former use less energy in their life cycle than the later. In general, thin-film photovoltaics require less energy in their manufacturing than crystalline Si photovoltaics, and this translates to lower emissions of heavy metals, SO_x, NO_x, PM, and CO₂. In any case, emissions from any type of PV system are expected to be lower than those from conventional energy systems because PV does not require fuel to operate. PV technologies provide the benefits of significantly curbing air emissions harmful to human and ecological health. It is noted that the environmental profiles of photovoltaics are further improving as efficiencies and material utilization rates increase and this kind of analysis needs to be updated periodically. Also,

future very large penetrations of PV would alter the grid composition and this has to be accounted for in future analyses.

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Supporting Information Available

Material and energy inventories and emissions of individual contaminants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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