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Published in:
Energy & Environmental Science

Link to article, DOI:
10.1039/c6ee00578k

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Outdoor fate and environmental impact of polymer solar cells through leaching and emission to rainwater and soil†

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The emission of silver and zinc to the aqueous environment (rain, fog, dew) from polymer solar cells installed outdoors is presented. Studies included pristine solar cells and solar cells subjected to mechanical damage under natural weather conditions in Denmark. We find the emission of silver and zinc to the environment through precipitated water for damaged solar cells, and also observed failure and emission from an initially undamaged device in an experiment that endured for 6 months. In the case of the damaged cells, we found that the drinking water limits for Ag were only exceeded on a few single days. We also progressed our studies to include end-of-life management. To assess the implications of improper practices (uncontrolled disposal, landfilling) at the end-of-life, we buried different OPV types in intact and damaged forms in soil columns. In the case of high Ag emission (shredded cells), the potential for migration was confirmed, even though the soil was found to exhibit sequestration of silver. We conclude that recycling of Ag at the end-of-life is mandatory from an environmental point of view.

1. Introduction

The environmental emission of pollutants through novel energy technologies has important implications for their environmental sustainability, and we must ask the questions and find answers to:

how “green” are new energy technologies? Most often, the manufacturing stages are studied in great detail, with respect to both energy and material use (referred to as “cradle-to-gate”). Still, the use phase and the end-of-life management often impacts the overall sustainability significantly (referred to as “gate-to-grave”). Organic photovoltaics (OPV) have in the past few years progressed from the minimal manual laboratory scale preparation to serial production in a larger and marketable scale. They have been subject to a number of detailed life cycle assessment (LCA) studies focussed on the manufacturing stages. They have been heralded as the only energy technology that potentially presents energy payback times as short as one day and an ultra-low environmental impact (in a cradle-to-gate scenario).1–4 Since they have now progressed to operational trials, it is crucial to provide proof of their validity as a future large scale energy technology that is truly green (i.e. from cradle-to-grave). The first kilowatt-scale deployment was successfully installed in 2013.5 Significant efforts within the OPV scientific community are currently directed towards studying their Achilles heel: degradation/stability.
Despite having a shorter operational lifetime compared to other thin-film PV technologies (aSi, CIGS, CdTe), they present the advantage of avoiding highly toxic/bioaccumulative elements such as cadmium (Cd), selenium (Se) or tellurium (Te) through the use of organic polymers as light-absorbing layers. Numerous (benchtop) studies have shown that OPV perform considerably better in life cycle assessments (LCA) when compared to other thin-film photovoltaic technologies, and based on this, have been regarded as a truly green energy technology. First (direct) experimental evidence points to OPV releasing minor amounts of metals to the environment in comparison to other thin film technologies in laboratory studies. However, direct evidence of such release in actual outdoor installations is completely lacking today. In particular, impaired physical integrity may result in the increased release of cell materials. Thus, the potential environmental impact associated with OPV cell components being released to the environment can only be established in a systematic and quantitative manner by field data.

OPV are well packaged in a thin plastic barrier that is designed to be impervious to liquid water. When in operation (i.e. when producing electricity), no leaching or emission to the environment should thus take place, even when the solar cells are deployed outdoors. A complex interplay of recoccurring stress factors (UV radiation, thermal expansion, freeze–thaw, rain, snow, sea spray, etc.) or singular events (heavy winds, hail) constantly challenge the integrity of the operating solar cell. Eventually this may cause damage to the encapsulation, e.g. crack formation or delamination. Cracking or delamination at the edge are opening paths for air and water to enter. In this event, OPV cell compounds will be emitted to the environment, either to surface waters or soils. It should be noted that such degradation mechanisms include unintended induction of damage during manufacture or improper installation leaving the embedding layers scratched.

Next to the emissions during use, the emission of compounds at the end-of-life will, in particular, negatively impact the overall environmental burden. Whereas the recycling of metals is a proactive means of counteracting the latter, it is likely that some solar cell material is not recycled or decommissioned in the recommended manner.

Though generally LCA can account for impacts associated from the mining of raw materials to their disposal, compounds with an unknown fate and/or particular concern for ecotoxicity are not represented in standard databases. For instance, released silver (Ag) and zinc (Zn) might be in nanoparticulate form, raising nano-toxicity concerns (though this has been questioned). However, harmful effects from OPV components emitted into environmental compartments such as air, soil, water and biota have as yet not been quantified. Besides metals, it would be of particular interest to look at the environmental factors of the organic molecules contained in OPV. These organic molecules are highly degradable by light, oxygen and water (e.g. P3HT, PEDOT:PSS and PCBM), and do not yet exist in databases. The main challenge of using toxicology indicators in LCA is the lack of data in life cycle inventories. Although we cannot provide molecular data on the myriad of organic degradation components that form during the degradation of OPV, we can quantify the emission of metals to the environment when OPV devices are subject to simulated and controlled failure as a result of normal (intended) operation, and operation subject to deliberate damage. These data can serve to adjust the inputs for LCA models, allowing for realistic assessments of the sustainability of OPV.

For the purpose of measuring the enhanced release of OPV-borne metallic components into the environment in real outdoor OPV installations, two novel set-ups were designed:

1) a rain runoff scenario with OPV installed outdoors, simulating use-phase

2) a soil sequestration scenario with OPV buried in soil, simulating uncontrolled waste disposal

The rain runoff experiment was set up in Denmark at the DTU OPV solar park at Risø campus in a 1 kWp grid-connected solar park with OPV modules. Duplicate samples of all OPV types were mounted on the tilted structure, placing a gutter at the end of each sample to collect the rain water and water from condensation (dew and fog). The water was collected by a tube where it was stored in a canister, from where periodical sampling over half a year was performed (Fig. 1). Since the focus of our work was to correlate visible damage (and performance) with the release of metals during the use phase, and evaluate environmental concerns in case of failure and for the end-of-life of the devices, we chose to carry out the experiment in duplicate. For the soil sequestration experiment, different OPV samples (shredded and non-shredded, containing silver and silver-free) were buried in soil columns exposed to outdoor conditions (Fig. 2). The experiment ran for over a year, including all seasons and their distinct weather conditions. For both scenarios, samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for their metal content. Eventually, we included this quantitative data and assessed the environmental impact in a refined life cycle impact assessment.
2. Material and methods

2.1. OPV samples, chemicals and soil characterization

The “Ag-OPV” samples were manufactured as described previously employing ITO- and vacuum-free processing. The architecture of the devices was comprised of barrier/Ag-grid/PEDOT:PSS/ZnO/P3HT:PCBM/PEDOT:PSS/Ag-grid/barrier. Concerning the metal content, 4.9 g of Ag and 0.07 g of Zn were contained in 1 m² of Ag-OPV. The “C-OPV” samples were ITO-, vacuum- and Ag-free, the manufacturing of which was described earlier. Their architecture was comprised of barrier/PEDOT:PSS/ZnO/P3HT:PCBM/PEDOT:PSS/carbon/adhesive/barrier. Concerning the metal content, only 52.3 mg of Zn was contained in 1 m² of C-OPV. All chemicals were purchased from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland). The soil used in this study was taken from DTU, Riso campus, Roskilde, Denmark and homogenized prior to usage. Analyses of moisture content (method DS 204, gravimetric), pH (CaCl₂, PD. FAJ. III 8), organic carbon content [ISO 10694 Dumas (TCD)], CaCO₃ content (Ca content based on SM 3120, ICP-OES), electric conductivity (PD. FAJ. VI 1) and C/N ratio was performed by Eurofins Miljo A/S, Vejen, Denmark (Table S1, ESI†). Metal content was determined by digestion and ICP-MS analysis, as described below.

2.2. Scenarios description

2.2.1. Rain-runoff scenario. The rain runoff installation was set up in the solar park structure at DTU Riso campus, Roskilde, Denmark (Fig. 1). The following three OPV samples (each in duplicate; total area of 0.46 m²) were installed for rain collection. (i) Ag-OPV damaged by regular cutting (scissors) simulating severe mechanical stress (prolonged exposure to hail, wind, thermal stress etc.; see Fig. 1 for detail); (ii) pristine Ag-OPV without any damage; (iii) set of 32 laser cut postcard sized (0.1 × 0.14 m; total area 0.46 m²) pristine C-OPV without any damage. Two areas on the installation were left blank as a negative control. The area of sample collection was protected with a plastic foil in order to limit metal contamination from external sources (nails, screws from the wooden platform structure, dust). For the rain collection, plastic rain gutters (0.4 m long) were installed with funnels connected through plastic tubes to 10 L plastic canisters. The total area of collection per sample was 0.84 m². Water samples were taken when the canisters were full depending on the precipitation. The content of the canisters was homogenised (shaking) and samples of 250 mL were stored for analysis. The DTU wind research facility, at the same campus, provided an online information source for precipitation from the local weather station. The setup was completed and the experiments started on April 10th 2015 and finished on October 15th 2015. The total precipitation during that half a year period was 446.8 L m⁻².

2.2.2. Soil sequestration scenario. At DTU, Riso campus, Roskilde, Denmark, a novel setup to study the outdoor soil sequestration behaviour of OPV components was installed (Fig. 2). The following four OPV samples were selected to be buried: (i) 0.25 m² pristine Ag-OPV foil rolled-up; (ii) 0.158 m² Ag-OPV shredded to fragments measuring 4 × 20 mm; (iii) 0.25 m² pristine C-OPV rolled-up; (iv) 0.158 m² C-OPV shredded to fragments measuring 4 × 20 mm. The samples buried in soil were filled in glass columns (cross-sectional area of 122.72 cm²), mounted on a trolley and placed outdoors at DTU, Riso Campus, Denmark. Rolled-up OPV modules were buried in the centre of the column, in a total of 4.5 kg of soil, leaving soil up and down in the column, whereas shredded OPV modules were buried homogenously distributed in all columns in 2 kg of soil. In all columns, 10 cm of soil was added on top as a cover layer. Leachates were collected below the columns in glass flasks connected with glass funnels. Between the soil and funnel, a layer of sand and 120 mesh polyester filters was applied to avoid soil loss to the collection flasks. This trolley was exposed to outdoor conditions (Fig. 2) for almost one year, starting on November 5th 2014 and ending on October 29th 2015. Leachates were taken when the glass flasks were full. At the end of the experiment, all column contents were divided into five soil depth layers and three soil samples were taken from every depth layer, as well as from the sand layer.

2.3. Sampling and elemental analysis

Rain runoff was taken after every rain event and acidified to a final concentration of 1% HNO₃ prior to analysis. Semiconductor grade acids were used for ICP-MS sample preparation. The same was applied to the leachates of the soil column experiment. The soil and sand samples were digested as follows: 501 ± 4 mg of material was digested with 2 mL of aqua regia (65% HNO₃ and 32% HCl, 1 : 3 v/v) at room temperature overnight and diluted to a final concentration of 5% aqua regia prior to analysis. Ag and Zn were quantified using matrix matched calibration (1% HNO₃ or 5% aqua regia) with multi-element standards (Sigma-Aldrich). The isotopes Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb (as internal standard),
98Mo, 106Cd, 107Ag, 115In, 118Sn, 121Sb, and 208Pb were analysed on an Agilent 7500cx ICP-MS (Agilent Technologies AG, Basel, Switzerland) using a dwell time of 0.3 s per isotope. The argon plasma was operated at 1550 W, 15 mL min⁻¹ plasma gas, 0.79 mL min⁻¹ carrier gas and 0.35 mL min⁻¹ makeup gas. The octopole was pressurized with 5.0 mL min⁻¹ helium, except for 78Se, where 3.6 mL min⁻¹ hydrogen was used.

2.4. Life cycle assessment methods

LCA methodology was applied to evaluate the potential environmental impact on groundwater from metal leaching in the rain-runoff setting. ILCD, the recommended methodology for the evaluation of the impact potential, was used. The model of the process was a simple one, accounting for the long term effects that the emissions to groundwater would cause. More details can be found in the ESI.

3. Results and discussion

3.1. The need for monitoring: preventing constituents from reaching the environment

As outlined above, a thorough environmental assessment should consider the emission of pollutants of particular concern during the use-phase (which should include unintended use) of the life cycle. The outdoor-installed OPV modules were therefore studied in the context of their potential emission of inorganic pollutants to the environment during both their normal (intended) use phase operation and when inadequately disposed at the end of their life. In addition, the experiments assessed the kinetics of pollutant release. This allowed conclusions on the requirements for the immediacy of reaction: how critical it is to react fast in the case of a catastrophic failure that opens up the device, to minimize the emissions to the environment?

3.2. Emission of silver and zinc into rain runoff during use

The rain runoff setting concluded after a 6 month period with some modules damaged (Fig. 3), whereas only pristine Ag-OPV No. 2 did not show delamination with visible water ingress. The cumulative element leaching (Fig. 4) showed a virtually linear release of Ag to the environment from the damaged Ag-OPV modules, reaching 7.9 and 14.3 mg of Ag from 1 m² OPV over the six months (Fig. 4). This corresponded to about 0.16–0.29% of the total contained Ag. The two samples differed by a factor of almost two at the end of six months, since between days 129 and 182, a clog in the rain gutter of sample No. 2 was unnoticed and rain water was lost. Extrapolating the linear trend between day 35 and day 129 suggested that the module had emitted a similar amount of Ag compared to the duplicate module.
Concerning Zn, the same linear leaching behaviour was observed, reaching 65.7 and 79.0 mg of Zn from 1 m² OPV, corresponding to the complete release of the Zn contained (94–113% of the theoretical value). Again, some of the variation between the duplicates may be due to the relatively small scale of the field set up. The pristine Ag-OPV did not release any of its contained metals (Ag, Zn) until day 90. Then, one of the duplicates started to delaminate (Fig. 3, and marked with an asterisk in Fig. 4). Thereafter, Ag leaching reached 0.29% of the total contained Ag, which was very similar to the case for the deliberately damaged Ag-OPV, yet within a shorter time period (~165 vs. ~95 days). Simultaneously, Zn started to leach after the onset of delamination, reaching 54% of the overall contained Zn by the end of the experiment. The Ag and Zn emissions for the Ag-OPV intact (2) are in the range of the reference devices coming from rain, atmosphere and dust in the outside setup. As shown in Fig. 4, we observed similar levels of Zn in the reference samples and in Ag-OPV intact (2), while there was no sign of Ag in any of the references, C-OPV or Ag-OPV intact (2) samples. Only when failure took place (either induced or spontaneous) did the emission levels rise.

Obviously, the Ag-free devices (C-OPV) did not release any Ag, however, in contrast to the reference, C-OPV released Zn in the range of 25–31% of the overall contained Zn, with a similar rate to Ag-OPV (damaged and delaminated). It should be stressed that C-OPV only started to emit Zn after 4 months of outdoor exposure. C-OPV devices were not specifically sealed on the edges after being cut into their final shape, thus providing a path to water ingress.

3.3. Silver and zinc sequestration in soil at the end of life

The second scenario tested whether metals could be sequestered by soil throughout a whole year after unintended disposal (using shredded materials as the worst case, and intact rolls as the best case). We made two clear observations:

1. A higher overall amount of Ag reached the soil matrix and leachates in the case of the shredded Ag-OPV on the timescale we explored.

2. The deeper column layers showed an enrichment of Ag in the case of shredded Ag-OPV.

The homogeneous distribution of Ag and the absence of Ag in the leachate of the intact Ag-OPV soil columns (Fig. 5) indicated that the soil had a sufficient, inherent capacity of sequestering Ag (whereas the actual mechanism may be complex and depend on the prevailing redox conditions in the soil layers).\(^\text{22}\) The migration of Ag towards the bottom of the column in the worst case scenario, however, strongly points towards the fact that the natural sequestration capacity was exceeded, though break-through was not yet reached, even after a year of experiment. In comparison to the rain runoff scenario (maximal release of 0.29% of total Ag), the release of Ag was considerably enhanced by contact with the soil (maximal release of 15.7% of total Ag), which represents a strong increase in contrast to laboratory leaching studies using (other) shredded OPV.\(^\text{9}\) This suggests that soil related properties, such as redox-chemistry, microbial communities and their exudates, and/or perturbation by micro-/macrofauna, may favour Ag release. Due to the inherent risks associated with Ag, this certainly warrants further detailed studies.

In the case of Zn, we found a low natural content in the soil (~lowest 15% of European top soils).\(^\text{23}\) Despite this very low content, the release of all Zn contained in the Ag-OPV modules would only increase soil Zn concentration by a factor of ~3 to 4, to a concentration between 57–73 mg kg\(^{-1}\), depending on the scenario. Since EU top soils contain as much as 52 mg kg\(^{-1}\) (median), the impact of OPV derived Zn can be considered minor. Similarly, the impact of C-OPV modules regarding Zn addition to soils can be considered minor, since they contained even less Zn than Ag-OPV.

The results also give important indications towards an end-of-life management scheme that would involve land-filling.
Certainly, the physico-chemical conditions, matrix and hydrology of a modern landfill are substantially different in comparison to the soil columns. However, the fast (e.g. upon delamination in the rain runoff experiment) and extensive (soil column experiments) release of Ag upon failure of the embedding material integrity appears to be a common phenomenon (and potentially not limited to OPV, but also other thin film PV technologies). Mechanical damage during landfilling itself is very likely. The resulting rapid release of large amounts of Ag may thus represent a challenge for landfill management with regards to leachate treatment (peak loads). This holds particularly true if part of the treatment relies on biological processes, considering the antibiotic properties of Ag.24

3.4. Ecotoxicological implications

From the present study, we derive three major eco-toxicological implications:

(1) Though little Ag was leached during the use phase, peak concentrations occurred after only a few days upon delamination, thus stressing the need to act fast upon failure to limit the release to the environment.

(2) Zn concentrations did not exceed even the most stringent drinking water limits at any time, and Zn is concluded to be of less concern.

(3) A more complete release of Ag occurred when shredded Ag-OPV were incubated in soil (15.7% of the total contained Ag), resulting in critically elevated soil Ag contents, thus highlighting that landfilling is not a viable option and Ag must be recovered from waste.

The threshold value for Ag in drinking water enforced by the World Health Organization (WHO) is at 100 μg L⁻¹. In this study, the measured rain runoff Ag concentrations exceeded this limit twice: 127 μg Ag L⁻¹ for the damaged Ag-OPV No. 1 (day 158) and 181 μg Ag L⁻¹ for pristine Ag-OPV No. 1 delaminating over time (day 144). All the other Ag concentrations in the rain water remained below the WHO limit. Since the drinking water limits are set most conservatively, any acute/chronic effect by exposure to such a peak concentrations seems improbable. Still, depending on the covered area of an actual installation and the precipitation collected, higher concentrations certainly may occur. Similarly, the highest measured Zn environmental concentration was at 665 μg Zn L⁻¹ for the damaged Ag-OPV No. 2 (day 88), not exceeding the WHO limit of 3000 μg Zn L⁻¹. Overall, the results are in good agreement with our previous laboratory study, where we predicted the environmental emissions not to exceed WHO values.25 The fact that here we observe peak concentrations and direct effects of delamination, however, stresses that such field studies are a must for the verification of laboratory derived models.

When shredded cells were buried in the soil, we found that the release of Ag resulted in considerably increased concentrations (15.7% of the total contained Ag; Fig. 5), i.e. a maximum of 852.5 mg Ag per kg of soil in the central layer of the 5 depth layers (exceeding the soil Ag sequestration capacity). Whereas the resulting concentrations certainly depend on the actual amount of OPV that is dumped per volume of soil, a scenario using ~1/20 m² of OPV modules per kg soil does not seem to be an unrealistic loading. The detrimental effect of Ag will certainly depend on the complex interplay of chemical/biological redox-reactions influencing Ag speciation in soils. However, the fact that for a number of soil enzymatic activities, the “median effective concentration” causing 50% inhibition was found in the sub μg kg⁻¹ range of the total soil Ag (e.g. in Peyrot et al.),25 the overall Ag content resulting from Ag-OPV release raises a considerable eco-toxicological concern.

3.5. Life cycle impact assessment

Life cycle impact assessment was performed on the metal emissions in the rain runoff setup. The model of emissions to water and the table with the scores for the impact categories are shown in Table S2 and Fig. S1 (ESI†). All ILCD categories were evaluated, but only 2 of them showed an impact (the rest of the scores were equal to zero): i.e. human toxicity (non-cancer effects) and freshwater ecotoxicity. By taking the total impact during manufacture of the solar cells as a baseline (i.e. 100%), the share of the Ag leaching from the damaged modules is (in comparison) 15% and 30% for human toxicity non-cancer and freshwater ecotoxicity, respectively. It is only 1% for both categories when the Ag leaching is from the intact modules, since much less emissions were observed. As can be seen from the above, the actual eco-toxicological implications are aligned with LCA results. Ag concentrations in the rain runoff were mostly below even drinking water limits, suggesting no direct adverse impact on either freshwater environments or humans as the small fraction of 1% with respect the total impact of the modules shows. However, environmental processes leading to the rapid and increased release of materials are not always known, anticipated or expected (as in the soil experiments), and thus LCA results (based on the best knowledge) may be too conservative. Further, environmental factors changing the speciation of a pollutant to show increased or decreased toxicity are hard to include in LCA.

4. Conclusions

We conducted field experiments collecting direct, quantitative data on elements released by OPV. The only elements found in elevated quantities in leachates were Zn and Ag (no Al, Sb or any other element were found in contrast to the controls; data not shown). In a rain runoff scenario, the leaching of metals from the OPV modules were observed in modules with a visibly damaged barrier and in OPV that delaminated. Still, apart from a few exceptions, the metal concentrations did not exceed the WHO limit for drinking water. It is important to point out that the quality of the encapsulation and the edge sealing during an outdoor use phase of OPV are essential both for lifetime performance and environmental concerns. The timely replacement of failed modules is thus not only needed from the electricity production point of view, but also to prevent peak concentrations of metals leaching upon delamination. LCA studies could account for the actual amount of Ag and Zn released from OPV.
Only two environmental categories showed impact scores: human toxicity (non-cancer effects) and freshwater ecotoxicity. The contribution of the Ag leaching from damaged modules to these categories are 15% and 30% respectively in terms of the production of the solar cells, and only 1% for both categories when the Ag leaching is from the intact modules, since much less emissions were observed. There are still several challenges of using toxicology indicators in LCA, such as the lack of data in Life Cycle Inventories and model characterisation. With this work, we aim to open the wide road for further investigations on the environmental behaviour of organic photovoltaics.

Acknowledgements

We thank Markus Hösel, Marios D. Chatzisideris and Rafael Garcia-Valverde for assisting in daily monitoring and collection of rainwater and rain water processing. We thank Torben Kjær and Kristian Larsen for constructing the leaching setup and rain runoff. The School of Life Sciences (HLS) of the University of Applied Sciences and Arts Northwestern Switzerland (FHNW) is gratefully acknowledged for internal funding. This work has also been supported by the Danish Ministry of Science, Innovation and Higher Education under a Sapere Aude Top Scientist grant (no. DFF – 1335-00037A). The COST Action MP1307 is thanked for their funding of a short term scientific mission.

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