

## SUNFLOWER

*“Sustainable Novel Flexible Organic Watts Efficiently Reliable”*

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# Deliverable D4.1: Environmental risk assessment and sustainability of OPVs

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## Table of Contents

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1	Summary .....	7
2	Introduction.....	8
2.1	Purpose of this report.....	8
2.2	Existing reference cell and selected benchmark products .....	9
2.2.1	Description of the existing reference cell .....	9
2.2.2	Selected benchmark products for a relative assessment .....	11
2.3	Target markets .....	11
3	Sustainability assessment .....	13
3.1	Introduction .....	13
3.2	Definitive layout of sustainability assessment .....	13
3.2.1	Life Cycle Analysis (LCA), benchmark and eco-efficiency assessment .....	13
3.2.2	Operational Health and Safety (OHS) .....	14
3.2.3	Multi-Criteria Decision Analysis (MCDA) .....	15
3.3	Initial results for existing reference cell - Preliminary LCA, benchmark and eco-efficiency assessment .....	16
3.3.1	Production of existing transparent and flexible single junction OPV cell .....	16
3.3.2	Initial results for existing reference cell - LCA scenario OPV at retrofitted windows. ....	21
3.4	Initial results for existing reference cell - Preliminary OHS assessment results ....	25
3.5	Initial results for existing reference cell - Preliminary MCDA results .....	26
3.6	Summary and initial recommendations .....	27
4	Method setup for fate studies .....	29
4.1	Introduction .....	29
4.2	List of selected priority materials/components to be assessed in definitive tests ..	30
4.3	Selected benchmark product to be assessed for relative assessment .....	31
4.4	Definitive setup for bioavailability assessment tests: Leaching.....	31
4.5	Definitive setup for bioavailability assessment tests: Sorption.....	32
4.6	Definitive setup for bioavailability assessment tests: Biodegradation .....	33
4.7	Definitive setup for bioavailability assessment tests: Fate study .....	33
4.8	Initial results for existing reference cell .....	34
5	Method setup for ecotoxicity.....	36
5.1	Introduction .....	36
5.2	List of selected priority materials/components to be assessed in definitive tests ..	37
5.3	Definitive setup for ecotoxicity assessment tests: General toxicity .....	38
5.3.1	Preliminary results .....	38
5.4	Definitive setup for ecotoxicity assessment tests: Metal-bioavailability and -toxicity	39
5.5	Definitive setup for ecotoxicity assessment tests: Cellular stress response .....	39
5.5.1	Preliminary results .....	40
5.6	Effect Directed Analysis of OPV leachates .....	40
5.7	Summary and preliminary conclusions .....	41
6	References .....	42
7	Appendices.....	45

7.1	Appendix A: Data sources.....	45
7.2	Appendix B: LCA results .....	45
7.3	Appendix C: Valuation and weighting code for the OHS assessment .....	46
7.4	Appendix D: Data source and quality for the Life cycle inventory (LCI) by layers..	47
7.5	Appendix E: Indicators and weighting of the MCDA .....	47

## List of Figures and Tables

### Figures:

- Figure 1: The existing semi-transparent and flexible single junction polymer cell from Konarka has an efficiency of 2.8% and performs at 30 W/m<sup>2</sup> with an active surface of 60%, tested under standard conditions. ....9
- Figure 2: The cradle to gate LCA of the production of the transparent and flexible single junction polymer cell and 1 m<sup>2</sup> of the flexible OPV module includes the step 1 to 4. In the scenario of retrofitted windows with OPV the steps 5 to 8 must be included to calculate the impact of the generation of 1kWh electricity..... 16
- Figure 3: Environmental impacts of the layers of the existing reference OPV cell regarding the chosen 6 indicators. Both electrodes (primary, transparent) showed the highest impact of all layers. Error bars represent the relative error from the deviations of the material flows, emissions and the indicators in a LCA. .... 17
- Figure 4: The process tree of the production of the flexible single junction polymer cell from Konarka shows that the primary silver electrode has the highest environmental impact (42.4%, weighted with the Indicator Recipe (H/A) World total), followed by the transparent ITO electrode (20%), the EBL (12%) and the Encapsulation (11.3%). ....20
- Figure 5: The share of the impact of the BOS – measured with the Indicator Recipe (H/A) world total – of a 3 KWp CdTe façade installation, is dramatically higher (60%) than the PV CdTe laminate (40%). ....21
- Figure 6: The share on the impact of the BOS - measured with the Indicator Recipe (H/A) world total – of a 3 KWp OPV installation in retrofitted windows, is lower (46%) than that of the flexible OPV (54%). If a façade construction was chosen for installation the impact of the BOS would dominate the impact of the plant. ....22
- Figure 7: Under the conditions of the scenario - windows retrofitted with OPV (3kWp) – the CED total, IPCC 2007: climate change and Recipe (H/A) World, Resources, show a significant lower environmental impact per kWh than thin film technologies. Compared with CIS, the indicators show about 60% less impact. Wind energy shows the lowest impact. Compared to the fossil fuel and nuclear based power generation technologies (UCTE and CC) the impact of all PV technologies is up to 80% lower. ....23
- Figure 8: The connection between the clean wind energy and the cheap UTCE electricity is the so called eco-efficiency frontier. PV plants in Southern Europe, already could reach the eco efficiency frontier. ....24
- Figure 9: Initial MCDA results for selected technologies and indicators (see Figure 7). MCDA values were normalised to 1 and weighted as listed in Annex 6.5. Ranges were applied where data was available. ....27
- Figure 10: Different factors can have a deteriorative effect on OPVs leading to ageing of the material and possibly cause the release of compounds into the environment. After partition of those compounds into air, water, soil, and biota, processes such as bioaccumulation or biodegradation determine their fate and ecotoxicological impacts (figure and caption taken from *Zimmermann et al. 2012*). ....30
- Figure 11: Selected priority materials (metals and PCBM) for fate studies highlighted in orange. The different materials were given relative numbers for the mass content in OPV (*Zimmermann et al. 2012*) and relevance for impact in the environment (*Zimmermann et al. 2012*, as well as assessment due to SEC-HPLC results). \* = is intended to be replaced within the framework of the SUNFLOWER project. ....31
- Figure 12: Developed TR-ICP-MS method to distinguish between 0.15 ppb dissolved indium (blue), 0.15 ppb indium in nanoparticulate form as ITO (green) and the ITO particles after dissolution with aqua regia (ARD) (red). ....34

Figure 13: Hatching rate of zebrafish embryos (*Danio rerio*) exposed to 5 mg/L of ZnO nanoparticles for 72 h and 120 h.....38

Figure 14: Comparison of gene expression in zebrafish larvae determined by qRT-PCR (n = 4, 100 larvae pooled) after exposure to 5 mg/L nZnO in Media supplemented with alginate. Asterisk (\*) indicates statistically significant difference to control (p < 0.05). .....40

## Tables:

Table 1: Summary of deliverables for the sustainability assessment and related sections in this report. ....13

Table 2: In different scenarios the benefits and losses in the OPV life cycle will be assessed to support decision making processes of SUNFLOWER partners and of external stakeholders. ....14

Table 3: The MDCA of energy technologies according to Hirschberg C et al. (2010) includes weighting environmental, economical and social sustainability criteria. ....15

Table 4: The EPBT depends on local factors, e.g. the solar radiation and the orientation of the installation. ....22

Table 5: OHS Assessment of the layers of the existing cell with data sources and assessment of completeness of data regarding required personal protection, REACH registration and potential uncertainties and risks. Weighting and evaluations was conducted according to Appendix 7.3. ....25

Table 6: Summary of deliverables for fate studies and related chapters in this report.....29

Table 7: Initial results on metals leached from OPVs during long-term conditions in nanopure water (NPW), artificial lake water (ALW), artificial acidic water (AAW) and artificial sea water (ASW) when OPV are intact or cut into small (2×2 mm) and large (15×30 mm) pieces after 3 month of exposure.....34

Table 8: Summary of deliverables for the ecotoxicity study and related chapters in this report36

## Abbreviations

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Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
BAT	Best Available Technology
BIPV	Building Integrated Photovoltaic
BOS	Balance of System
CC	Combined Cycle
CdTe	Cadmium Telluride
CED	Cumulative Energy Demand
CIS	Copper Indium Sulphide
CIGS	Copper- Indium- Gallium- Selenide
EBL	Electron Block Layer
EPBT	Energy Pay-Back Time
EU	European Union
GHG	Greenhouse Gas Emissions
GHS	Globally Harmonised System
HBL	Hole Blocking Layer
IPCC	Intergovernmental Panel on Climate Change
ITO	Indium Tin Oxide
LCA	Life Cycle Assessment
MCDA	Multi-Criteria Decision Analysis
MSDS	Material Safety Data Sheet
NEEDS	Network for Enhanced Electoral and Democratic Support
kWp	Kilo Watt Peak
OHS	Operational Health and Safety
OHSAS	Occupational Health and Safety Assessment Series
OPV	Organic Photovoltaic
nZnO	Nano Particulate Zinc Oxide
PET	Polyethylene Terephthalate
PCBM	Phenyl-C61-Butyric Acid Methyl Ester
PV	Photovoltaic
REACH	Registration, Evaluation, Authorisation of Chemicals
SiO <sub>x</sub>	Silicon Oxide
SME	Small and medium-sized enterprise
T&D	Transmission and Distribution
UCTE	Union for the Coordination of Transmission of Electricity
VOC	Volatile Organic Compound

# 1 Summary

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Organic photovoltaics (OPV) represent the newest generation of technologies in solar power generation. To achieve the SUNFLOWER targets of increased efficiencies (8-10% on module level), increased expected lifetime (up to 20 years) and at the same time decreased production costs ( $\leq 0.7$  Euro/Wp) different organic and inorganic materials and combinations, e.g. printing inks with nano particles, will be developed and combined into a new OPV cell. The framework described in this work shall help to identify and highlight any potentially significant environmental impact and sustainability risks as early as possible in the development process and support an effective and efficient mitigation. The main objective of this delivery is the presentation of the methodologies for this framework and of initial results gained from a reference OPV.

The main methodologies applied within this framework are Life Cycle Analysis (LCA), benchmark and eco-efficiency assessment, Operational Health and Safety (OHS) assessment, Multi-Criteria Decision Analysis (MDCA), fate studies and ecotoxicological assessment for selected materials.

The initial LCA and eco-efficiency assessment show for a scenario of retrofitted windows with the transparent, reference OPV potential opportunities in the large market for building integrated photovoltaic (BIPV). Within the reference OPV the two layers with the transparent indium tin oxide (ITO) and silver electrodes create the highest environmental impact. While the replacement of ITO is already a key subject of the SUNFLOWER project the LCA on a material layer's level will indicate improvement potentials in relation to the overall environmental impact and potential alternatives. The initial OHS assessment revealed uncertainties for some materials to be considered in an OHS management. MDCA will be used for an overall sustainability assessment of the OPV technology compared with other energy technologies. Concerning fate studies, the experimental set-ups for leaching, sorption and degradation experiments and bioassays covering general toxicity, cellular stress response as well as metal-bioavailability and -toxicity were developed. Preliminary data from leaching experiments suggest that regarding a potential release of inorganic metals, intact OPV appear safe since no leachates or only in absolute trace ranges were found. Detectable concentrations of metals from OPV were only found under harsh conditions (i.e. when cut into pieces) that may arise upon improper disposal of OPVs. Still, these found leachate concentrations have to be put into perspective concerning the relevancy in the environment.

Regarding priority components of OPV, based on their use in the most current development stage and careful literature review, nanoparticulate zinc oxide (nZnO) and phenyl-C61-butyric acid methyl ester (PCBM) were selected for further detailed investigation. ITO – a component of the current reference cell and initially suspected to be cytotoxic – was shown to exert these effects at strongly elevated concentrations (5 g/L and above) only, highly exceeding any environmental levels to be expected. In a preliminary assessment, zebrafish embryos were exposed to nZnO in media containing alginic acid as natural dispersant. First results demonstrate an induction of the oxidative stress marker gene catalase, but not apoptotic marker genes. In addition, the hatching rate was reduced. Overall, the preliminary results indicate a low ecotoxicological potential of nZnO. However, further analyses are needed to assess the environmental safety of this and additional components of OPV and leachates.

Next to single priority OPV components, tests using actual leachates (i.e. containing a cocktail of metals and organics) will be conducted using the developed set-ups. Here, biological activity of leachates will be analysed applying an Effect Directed Analysis (EDA) based on the most promising bioassays. The OPVs can then be evaluated on comparative basis with other emerging, competing thin film technologies (i.e. CIGS).

## 2 Introduction

### 2.1 Purpose of this report

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Organic photovoltaic (OPV) represent the newest generation of technologies in solar power generation, offering the benefits of flexibility, low weight and low cost enabling the development of new consumer nomadic applications and the long term perspective of easy deployment in Building Integrated Photo Voltaics (BIPV) and energy production farms.

Beside all these positive aspects another very important issue is the associated environmental impact of the new materials, OPV modules, production processes in this development. The new technologies and substances of the SUNFLOWER project will require different organic and inorganic materials and combinations, e.g. printing inks with nano particles. About these substances little is known regarding the expected impact on ecosystem quality and human health if released to the environment for example to water in the production phase or leakages in the use phase or at the end of life disposal. It is therefore paramount to follow the development process closely with a framework to identify and highlight any potentially significant environmental impact risks as early as possible to mitigate them effectively and efficiently.

The aim of this work is not only to address the issues mentioned above but also to support the project partners in the challenge of developing a sustainable OPV from cradle to grave. For this purpose environmental, social and economic aspects will be assessed and compared with established and new alternative energy technologies. A special focus is given also to Operational Health and Safety (OHS).

The deliverables at this stage are results of an initial sustainability assessment and initial laboratory tests on PEC, bio-availability, bio-assimilation and (eco-) toxicological effects based on the existing reference cell (see section 2.2). The main deliverables are:

- Definitive layout of sustainability assessment;
- Initial results for existing reference cell and definitive setup for four bioavailability assessment tests, i.e. 1) leaching, 2) sorption, 3) biodegradation and 4) fate study;
- Initial results for existing reference cell and definitive setup for four main (eco-) toxicological assessment tests, i.e. 1) general toxicity, 2) metal-bioavailability and -toxicity, 3) cellular stress;
- List of selected priority materials/components to be assessed in definitive tests based on Milestone 2 results;
- Selected benchmark product to be assessed for relative assessment.

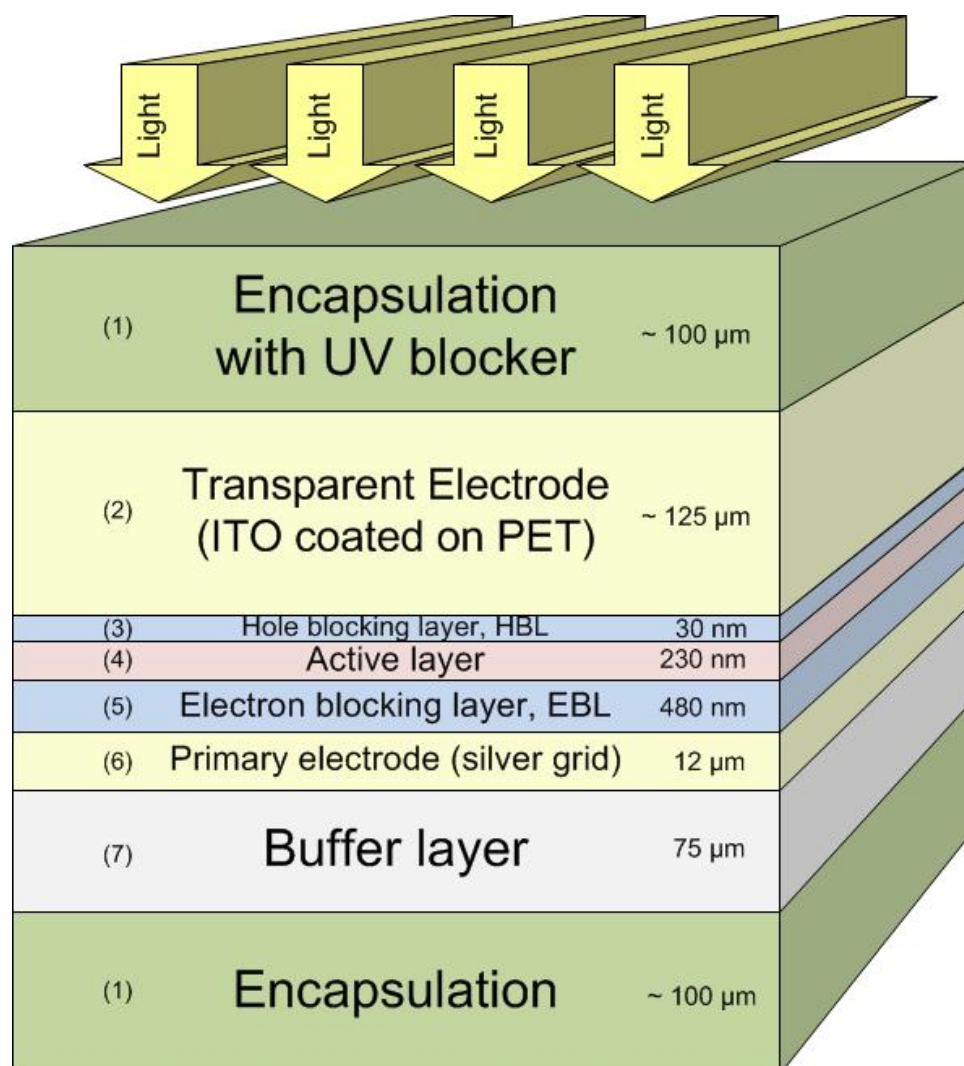
The aim of the Sunflower project is to deliver a printed tandem module (not transparent) with increased efficiencies (8-10% module level), increase expected lifetime (up to 20 years) and at the same time decreased production costs ( $\leq 0.7$  Euro/Wp), while taking into account the environmental impact and footprint. Consequently, the purpose of this delivery is the development of methodologies (both experimentally and LCA) to assess the impact of the to be developed cell and its components. Methods developed are based on the existing transparent flexible single junction polymer cell from Konarka. In a first concrete scenario, (see section 2.3) the hypothesis that the reference cell at retrofitted windows has equal environmental benefits and losses than thin film PV mounted on a façade is investigated.



## 2.2 Existing reference cell and selected benchmark products

### 2.2.1 Description of the existing reference cell

The existing transparent flexible single junction polymer cell from Konarka has an efficiency of 2.8%, performs with  $30 \text{ W/m}^2$  and has an active surface of 60%. The basic structure of its cell stack is composed of ITO/CM<sup>1</sup>/P3HT:PCBM/PEDOT:PSS,CM/CM/Ag which is depicted in Figure 1. The following top to bottom description of the seven main layers provides more detailed information of the functionality, the materials of the single layers, and of the deposition process applied.



**Figure 1:** The existing semi-transparent and flexible single junction polymer cell from Konarka has an efficiency of 2.8% and performs at  $30 \text{ W/m}^2$  with an active surface of 60%, tested under standard test conditions.

#### (1) Encapsulation (with UV filter)

**Function:** The encapsulation is protecting the cell from environmental influences like wetting, oxygen and UV radiation. Some of the other layers are sensitive to these influences and can lose their functionality, if they are affected.

**Material and deposition:** This layer exists mainly of PET substrate coated with SiOx and Al<sub>2</sub>O<sub>3</sub> as barrier, insulation polymers, adhesives (resins) and a triazine compound as UV

<sup>1</sup> CM: Confidential material

blocker, which is directly blended with the PET substrate. The coated PET substrate is processed with roll-to-roll lamination and the adhesives and insulation by UV curing and lamination.

## **(2) Transparent electrode (ITO coated on PET)**

**Function:** The transparent electrode is the anode.

**Material and deposition:** The material of the electrode is a transparent tin-doped indium oxide semiconductor material called indium tin oxide (ITO). It is commercially available and used in the production process as already sputtered on flexible PET foil. The transparent electrode is deposited by roll-to-roll lamination on the previously applied resins from the encapsulation.

## **(3) Hole blocking layer (HBL)**

**Function:** The HBL transports the electrons to the anode, respectively the transparent electrode.

**Material and deposition:** Due to confidentiality reasons the original material cannot be revealed. It is replaced by an alternative component fulfilling the same purpose. The alternative material could be a zinc oxide layer, which is deposited by slot-die coating of zinc oxide ink.

## **(4) Active Layer**

**Function:** Within the active layer electrons are transmitted from the electron donor, which is represented by P3HT. P3HT is excited by light and generates so-called excitons, which are consisting of a pair of a bound electron and a hole. At the junction of P3HT and PCBM (electron acceptor) the excitons are divided into their components, the electrons and the hole. The electrons and holes are then transported via HBL and EBL to the electrodes.

**Material and deposition:** The active layer is composed of a blend of phenyl-C61-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3HT). PCBM is basically a carbon-based nanomaterial, which consists of a fullerene modified with one or two methyl ester functional groups. Synthesis can be carried out with different methods including separation and functionalization steps (Anctil, 2011). P3HT is a semiconducting polymer that requires also several synthesis steps (Anctil, 2011). The active layer is deposited by slot-die coating.

## **(5) Electron blocking layer (EBL)**

**Function:** The EBL blocks the electrons and transports the holes to the cathode, the primary electrode.

**Material and deposition:** The one part of the EBL, Poly(3,4-ethylenedioxythiophene) (PEDOT), is synthesized by using standard oxidative chemical or electrochemical polymerization methods. Because PEDOT was found to be insoluble in water, it was combined with poly(styrenesulfonate) (PSS), which is a water-soluble polyelectrolyte (Garcia-Valverde et al., 2010) and can be therefore provided as an aqueous solution of PEDOT:PSS for the manufacturing process. The EBL exists of an additional component, which is also confidential and therefore cannot be mentioned.

## **(6) Primary electrode (silver grid)**

**Function:** The primary electrode is the cathode.

**Material and deposition:** The primary electrode is a silver (Ag) grid, which is deposited on the EBL. The basic material is a silver paste including silver nanoparticles, which is screen-printed for patterning of the silver grid.

## (7) Buffer layer

**Function:** This layer is buffering the primary electrode and the encapsulation at the back-side of the cell.

**Material and deposition:** The buffer layer is an ethylene copolymer and is deposited by lamination and UV curing.

### 2.2.2 Selected benchmark products for a relative assessment

In a relative assessment benefits and losses of OPV technology shall be compared with benchmark technologies that meet the following criteria:

- **BAT technology:** It should be a Best Available Technology (BAT) of photovoltaic.
- **Similar application:** It should be competitive in the OPV target markets such as BIPV, which means large production volumes and low production costs.

Photovoltaic thin film technologies like the multi-junction thin silicon film (a-Si/ $\mu$ c-Si), Cadmium-Tellurium (CdTe), Copper- Indium- Gallium- Selenide (CIGS) and Copper- Indium- Sulphide (CIS) can be chosen. The database ecoinvent (Swiss Center for Life Cycle inventories) provides scientific and international accepted data of PV Technology for Life Cycle Assessments.

For the relative assessment in the fate study CIGS technology was chosen as benchmark. The detailed reasons (amongst others mechanical flexibility, light-weight and high power conversion efficiencies) for this selection are described in chapter 4.3.

## 2.3 Target markets

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The multitude of market opportunities for polymer photovoltaic is derived from its unique properties of lightweight, flexibility, good low-light performance, semi-transparency and colours. Due to its properties OPV is not expected to displace traditional solar PV technologies, but rather to be able to generate new markets and product opportunities, creating value and revenue for multiple other industries.

The market opportunities for OPV can be classified by the application size and by power generation performance from low to high. The projection is that a whole range of new products will be invented from flexible modules, to rigid glass-packaged laminates for building integration all the way to semi-products that will be integrated by partners to add further functionality and value to existing products. In particular the semi-products of OPV for further integration are expected to be a large driver of the market development, since the thin form factor, flexibility and robustness of OPV allow for simple integration.

As the costs of alternative thin film and Si based PV also decreases it will become more difficult to capture market shares in traditional PV markets. For this reason the Building Integrated Photovoltaic Panels, BIPV market, which to date is only about 1% of the total PV market, but has a large applicable area is a promising high potential market. (Montoro D.F. et al, 2010)

By integration of PV systems into the buildings (BIPV) the initial cost of building materials and labour is offset to a certain extent, as the BIPV modules act as the exterior building envelope. Moreover, the power generated is often consumed at the same location, and hence, there will be significantly reduced transmission and distribution losses. This emerging application has attracted the interest of various real estate developers, urban planners, architects, and the public. In the EU an expected legal harmonization should foster these applications and reduce hurdles to market entry through standardization. Third-generation PV modules are expected to penetrate the BIPV market (windows, walls, and curtains) in

coming years and contribute significantly to its growth, for instance by enabling products to be laminated onto curved building surfaces.

The transparent and flexible single junction polymer cell from Konarka (see chapter 2.2.1) is as electronic charging device already on the market. First experiences in larger markets such as innovative BIPV applications for OPV for industrial buildings made from steel with polyurethane insulation could be gained. In a case study (Konarka, 2012) three promising options for an application on windows are described. These are:

1. Retrofit windows by applying the reference cell to the indoor surface of existing windows;
2. Integrate the reference cell into new construction double-glazed windows;
3. Integrate the reference cell into new construction triple-glazed windows.

The forecasted high potential of the BIPV market for thin film technologies, the non-transparent cell under development in the SUNFLOWER project and the existing transparent reference cell was seen as a suitable starting point for the initial assessment in chapter 3.3.2.

### 3 Sustainability assessment

#### 3.1 Introduction

Table 1 summarizes the deliverables at this stage of the SUNFLOWER project for the sustainability assessment.

**Table 1:** Summary of deliverables for the sustainability assessment and related sections in this report.

<b>D 4.1 Deliverable Description</b>	
Definitive layout of sustainability assessment	Chapter 3.2
Selected benchmark products to be assessed for relative assessment	Chapter 2.2.2
Initial results for existing reference cell	Chapter 3.3/3.4/3.5

The main objective of the sustainability radar is the identification of challenges of environmental, social and economic aspects in an early stage of the development process of the new photovoltaic generation OPV. The results of the sustainability radar shall support decision making of the sunflower partners in the production design of the new OPV and improve transparency of OPV benefits, costs and opportunities.

#### 3.2 Definitive layout of sustainability assessment

The methodologies applied in the sustainability assessment are:

- Life Cycle Analysis (LCA), benchmark and eco-efficiency assessment (chapter 3.2.1);
- OHS Assessments (chapter 3.2.2);
- Multi-Criteria Decision Analysis (MCDA) (chapter 3.2.3);

These are described in the following sections in more details.

##### 3.2.1 Life Cycle Analysis (LCA), benchmark and eco-efficiency assessment

With the frameworks of LCA and eco-efficiency the hypothesis that OPV can be regarded as a green and competitive energy technology will be assessed. The LCA considers recommendations of the IEA Guidelines on LCA (IEA, 2009) for PV-technologies. For the initial LCA the Cumulative energy demand (CED): total, total in MJ-eq, and the IPCC 2007: climate change, GWP 100a in kg-CO<sub>2-eq</sub> were selected therefore. The EPBT will be calculated with the CED and the energy generation over the life time of a PV-plant. The results depend on local factors, e.g. the solar radiation, orientation etc.

To meet the required criteria of the Multi-Criteria Decision Analysis (MCDA) the Recipe 2009 Indicators developed in the Netherlands ([www.lcia-recipe.net/](http://www.lcia-recipe.net/)) were added to the indicator set, i.e. Recipe World (H/A) total, Eco system quality, Human health as well as indicators.

The Recipe Indicators have a stronger weighting of the resources than for example with Eco indicator 99. The development of LCA indicators for nanoparticles is running in international research projects but is not available today. In the LCA results for Eco system quality and

Human health the impacts of nanoparticles will be considered semi quantitative if deemed relevant (chapter 4 and 5).

The system boundary includes all relevant issues in the life cycle of an OPV. In Table 2 the scenarios and objectives are listed. Two main functional units were chosen for the assessment:

- environmental impact per m<sup>2</sup> for the OPV production;
- environmental impact per kWh produced electricity for benchmark with thin film PV – and other electricity generation technologies.

The environmental impact is expressed by the above mentioned environmental impact indicators.

**Table 2:** In different scenarios the benefits and losses in the OPV life cycle will be assessed to support decision making processes of SUNFLOWER partners and of external stakeholders.

Scenario	Objectives	Remarks
Production of OPV	<ul style="list-style-type: none"> <li>• Environmental impact of materials and technologies</li> <li>• Identification of improvement potentials in the supply chain</li> <li>• Benefit of eco-efficient production technologies and energy supply</li> <li>• Recommendations</li> </ul>	Initial assessment: Environmental impact of the existing cell and the different layers (See chapter 3.3.1)
End of life	<ul style="list-style-type: none"> <li>• Impact of Environmental sound such recycling, energy and material recovery and unsound disposal such as landfill, dumping or burning</li> </ul>	Initial assessment: Incineration is considered (See chapter 3.3.2)
Market opportunities	<ul style="list-style-type: none"> <li>• Opportunities of transparent and not transparent OPV in the market</li> <li>• Impacts of BOS</li> <li>• Benchmark</li> <li>• Eco-efficiency of OPV in electricity market</li> </ul>	Initial assessment: Opportunities in BIPV market of windows retrofitted with the existing transparent cell compared to thin film on a façade and eco-efficiency evaluation (See chapter 3.3.2)
Large scale OPV plant of several GW power	<ul style="list-style-type: none"> <li>• Benefits of greener electricity mix to GHG reduction, pollution prevention and rebound to OPV production</li> <li>• Impact on raw material sourcing for OPV production</li> </ul>	No

### 3.2.2 Operational Health and Safety (OHS)

One of the social challenges in the production of new materials such as nanoparticles is also the OHS. Replacement of all toxic substances in the production is a valuable vision but requires a lot of research and might not be achievable at all. In particular small start-up

companies may not be aware of potential risks when developing new products and production processes. A management system e.g. according to OHSAS 18001 contributes to a high OHS standard which includes staff training, availability of information on safety data sheets and suitable personal protection equipment and a design for safety.

The level of OHS will be assessed at the SUNFLOWER suppliers with a questionnaire survey according to OHSAS 18001. The number of hazardous substances used in OPV production, the availability of complete material safety data sheets (MSDS) and the number of REACH registered substances will be assessed to evaluate the OHS level. The OHS level of gaining raw materials and production sites outside developed countries however remains uncertain. The OHS assessment reflects part of the social and individual aspects in the Multi-Criteria Decision Analysis, described in the following section.

### 3.2.3 Multi-Criteria Decision Analysis (MCDA)

To summarize the different parts of the sustainability assessment the results are aggregated in a MCDA based on the three main aspects of sustainability, i.e. environment, society and economy. One outcome of the European research project NEEDS ([www.needs-project.org](http://www.needs-project.org)) were criteria, indicators and new methods to compare the sustainability of electricity supply alternatives (Hirschberg et al., 2010).

**Table 3:** The MDCA of energy technologies according to Hirschberg C et al. (2010) includes weighting environmental, economical and social sustainability criteria.

<b>Environment</b>	<b>RESOURCES</b>	<b>48%</b>
	Energy Resources	
	Mineral Resources	
	<b>CLIMATE CHANGE</b>	
	<b>ECOSYSTEM DAMAGE</b>	
	Impacts from Normal Operation	
	Impacts from Severe Accidents	
	<b>WASTE</b>	
	Chemical Waste in Underground Depositories	
	Radioactive Waste in Geological Repositories	
<b>Economy</b>	<b>IMPACTS ON CUSTOMERS</b>	<b>28%</b>
	Price of Electricity	
	<b>IMPACTS ON OVERALL ECONOMY</b>	
	Employment	
	Autonomy of Electricity Generation	
	<b>IMPACTS ON UTILITY</b>	
	Financial Risks	
<b>Society</b>	Plant Operation Characteristics	<b>24%</b>
	<b>SECURITY &amp; DEPENDABILITY OF ELECTRICAL SUPPLY</b>	
	Political Threats to Continuity of Energy Service	
	Flexibility and Adaptability	
	<b>POLITICAL STABILITY</b>	
	Potential of Conflict induced by Energy System	
	Necessity of Participative	
	Decision-making Process	
	<b>SOCIAL AND INDIVIDUAL RISKS</b>	
	Expert-based Risk Estimates for Normal Operation	
	Expert-based Risk Estimates for Accidents	
	Perceived Risks	
	Terrorist Threat	
	Operational Health and Safety	
	<b>QUALITY OF LIVING CONDITIONS</b>	
	Landscape Quality	
	Noise Exposure	

In a survey from 2009 within the European energy - sector, not representative of the overall population, weighting factors for energy technologies including PV were elaborated that slightly deviate from the common 1/3 weighting. The identified criteria and overall aspect weightings are listed in Table 3. Based on these findings a similar Multi-Criteria Decision Analysis (MCDA) will be applied for a summary assessment of the overall acceptance of OPV compared to other energy technologies.

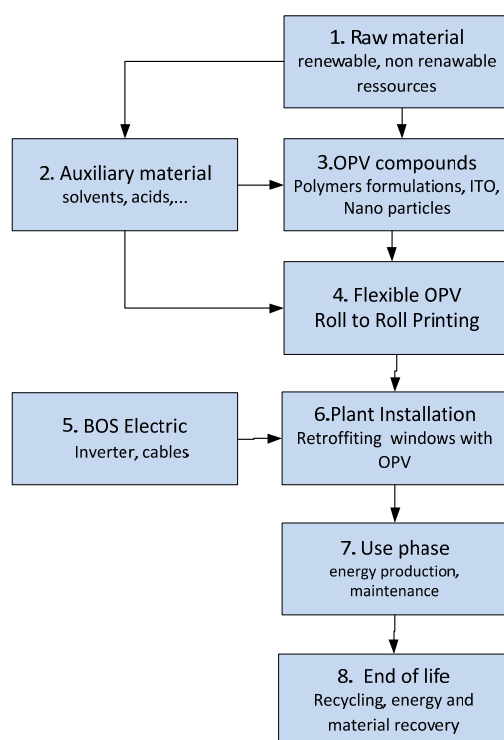
### 3.3 Initial results for existing reference cell - Preliminary LCA, benchmark and eco-efficiency assessment

The preliminary LCA and an eco-efficiency assessment for the existing transparent and flexible single junction OPV cell is split in two parts:

1. Results of the LCA from cradle to gate (step 1 to 4 in Figure 2) of the supply chain for the manufacturing of 1 m<sup>2</sup> module (section 2.3.1).
2. LCA case study and eco-efficiency of a cradle to grave scenario (step 1 to 8 in Figure 2) of windows retrofitted inside with grid connected OPV (section 2.3.2).

#### 3.3.1 Production of existing transparent and flexible single junction OPV cell

OPV compounds such as nanoparticle, polymers, adhesives, resins (see chapter 1.2) and auxiliary materials e.g. halogenated and non-halogenated solvents are produced in chemical processes which are often energy intensive (steps 2 and 3, Figure 2).



**Figure 2:** The cradle to gate LCA of the production of the transparent and flexible single junction polymer cell and 1 m<sup>2</sup> of the flexible OPV module includes the step 1 to 4. In the scenario of retrofitted windows with OPV the steps 5 to 8 must be included to calculate the impact of the generation of 1kWh electricity.

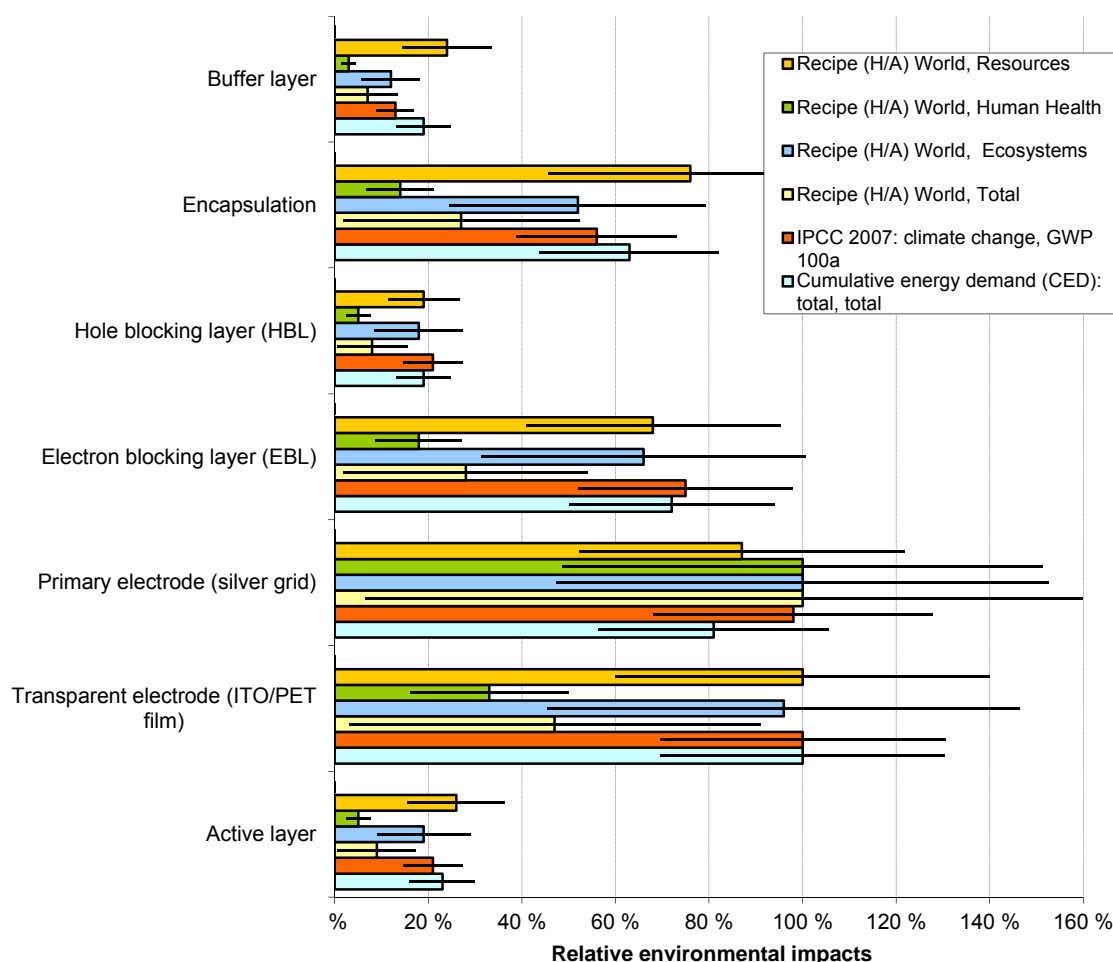
The thermal energy demand such as hot steam for reactions and solvents recovery is dominating. Electrical energy will be used for example for electric drives, drying process but



also for end of pipe treatment of waste streams. Large amounts of VOC-Emissions, halogenated components and heavy metals in waste water, hazardous waste are only a few examples of material flows that need to be treated to meet environmental standards. As far as known the amount of emissions to the environment are considered in the LCA.

The plastic processing industry needs electric energy for melting and forming granulates to polymers films. Depending on their functionality, energy intensive coating processes such as sputtering are applied. Ready mixed inks and the PET films, adhesives and solvents will be supplied to the OPV plant where with roll-to-roll (R2R) processes (step 4, Figure 2) the layers of the module will be printed. Typical waste streams that have to be treated are VOCs emissions, spent solvents, municipal waste and waste water.

**Initial results of LCA for OPV production:** The initially analysed reference cell from Konarka consists of seven layers which are described in chapter 2.2. The different materials used and processed in the layers for the final SUNFLOWER OPV will have different environmental impacts, but these results already give a first indication. The presented LCA results (Figure 3 and Appendix 7.2) show the relative environmental impacts of the layers with regards to six relevant environmental impact indicators (see 3.2.1).



**Figure 3:** Environmental impacts of the layers of the existing reference OPV cell regarding the chosen 6 indicators. Both electrodes (primary, transparent) showed the highest impact of all layers. Error bars represent the relative error from the deviations of the material flows, emissions and the indicators in a LCA.

The error bars represent the relative error from the deviations of the material flows, emissions and the indicators in a LCA, but also includes the data quality (see also appendix 7.4). In Figure 4 the LCA results for the layers are presented as a process tree. It shows the detailed shares of the cell compounds weighted with the indicator Recipe (H/A) world total.

The paragraphs below describe the most relevant impact indicators and initial results for an existing reference cell.

#### *Cumulative energy demand (CED)*

The specific CED calculated in the LCA for the production of the existing cell is 180 MJ/m<sup>2</sup>. For each environmental impact the layer with the highest value was set at 100% and the other layers' impact is calculated relative to this value. The transparent electrode layer creates the highest CED portion and was set at 100% for this indicator as depicted in

Figure 3. The CED of the primary electrode (~80%) has also a major impact, followed by the electron block layer (~70%) and the encapsulation (~65%). The overlapping error bars for these layers indicate that the differences between the average values may not be significant. Several energy intensive processes mainly contributing to the CED were identified, i.e. the sputtering of ITO, the production of the silver paste and the barrier films and the underlying electricity generation for which an UCTE mix is assumed. The main impact of this mix stems from the nuclear energy supply, in particular the fuel elements at the nuclear fuel fabrication plant. To reduce the CED impact indicator value electricity mixes with a higher share of renewable energy, e.g. PV or wind power, could be used in the production processes.

#### *IPCC 2007: climate change, Global Warming Potential (GWP)*

The specific GWP of the production of the reference cell is 8.6 kg CO<sub>2</sub>-eq/m<sup>2</sup>. The source of the maximum GWP per layer is again the transparent electrode which was set at 100% accordingly. The primary electrode has a slightly lower GWP (~95%) followed by the electron block layer (~75%) and the encapsulation (~55%). The overlapping error bars for these layers indicate that the differences between the average values may not be significant. The impact originates from the UCTE electricity mix too. This mix is mainly based on fossil resources like hard coal and natural gas. These fuels are well known for their emissions of CO<sub>2</sub> and its equivalents. To reduce the GWP impact, as before for CED, electricity mixes with a higher renewable share could be used, e.g. PV or wind power.

#### *Recipe (H/A) World Ecosystem*

For this Recipe indicator, the maximum impact of the layers on the ecosystem is generated by the primary electrode which was set at 100%. The transparent electrode has a slightly lower impact (~95%) followed by the electron block layer (~65%) and the encapsulation (~65%). The main sources for the ecosystem impact are emissions from production sites repeatedly the UCTE electricity mix with its fossil energy resources. Their negative influence on the ecosystem along their supply chain, especially from abstraction and use, is obvious, especially from lignite, hard coal and natural gas. More specific data of emissions from the planned production processes must be collected to improve the quality of the results.

#### *Recipe (H/A) World Human Health*

This indicator shows for the primary electrode the maximum impact on human health and was set at 100%. This impact results from the silver paste, more precisely from the exploitation of silver within the methods of refinement. The key production methods regarding the impact on human health are the combined gold-silver production and the silver containing copper production. An even deeper look along the life cycle reveals also the disposal of sulfidic mine tailings within these refinement methods. The transparent electrode, encapsulation, the active layer and the EBL have a lower impact on human health. The UCTE electricity mix also has a key effect on human health mainly due to the use of lignite and hard coal.

#### *Recipe (H/A) World Resources*

Concerning the resources the most relevant impact has again the transparent electrode which was set at 100%. The primary electrode (~85%), the encapsulation (~75%) and the

EBL (75%) are resource intensive as well. Again the same sub-processes as for the other indicators are the main contributors to these impacts.

#### *Recipe (H/A) World Total*

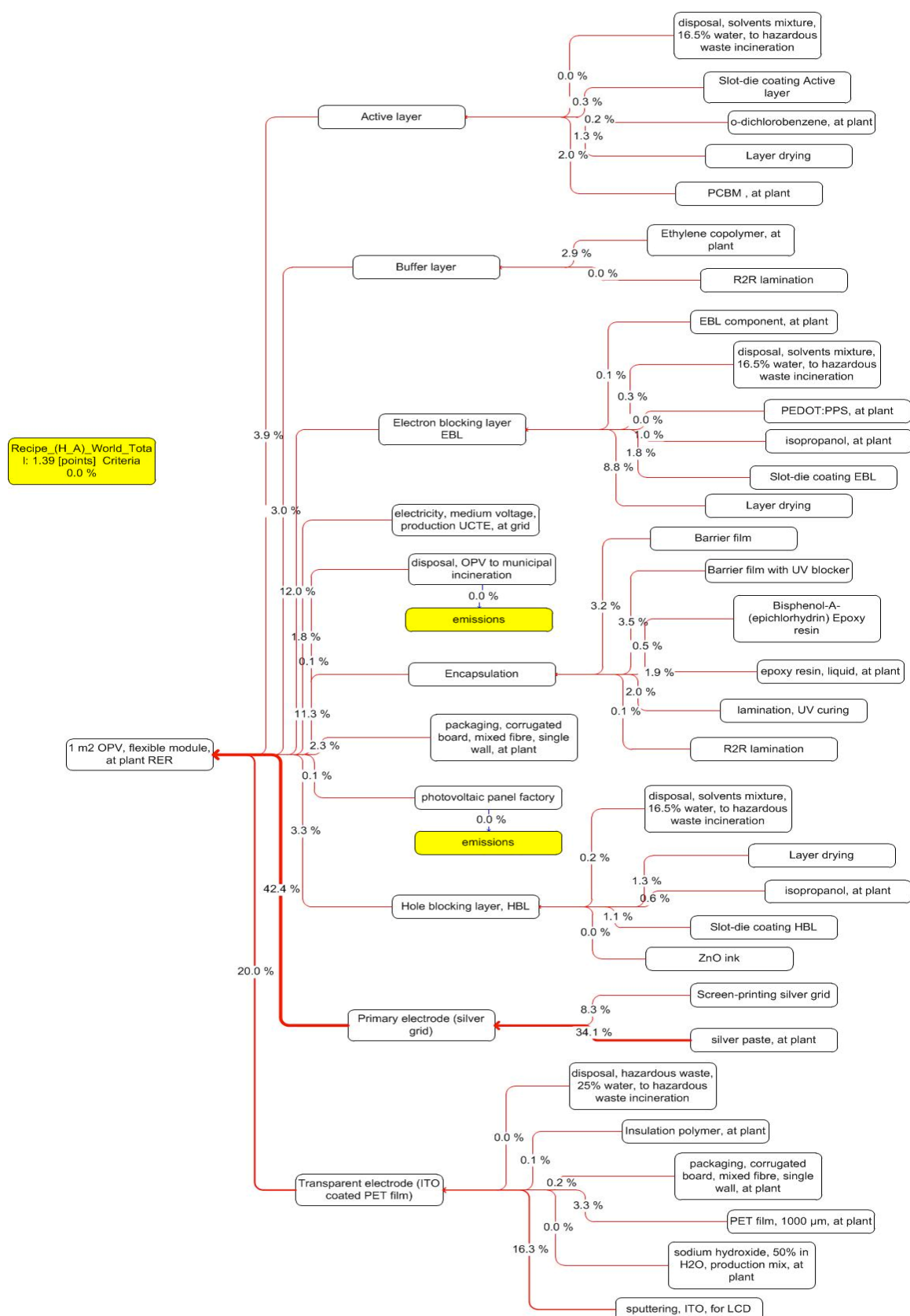
This endpoint indicator summarizes all recipe indicators discussed above. The maximum impact is generated by the primary electrode, while the impacts of other layers are weighted much lower.

As mentioned in the first section of this chapter, Figure 4 shows the detailed share of the compounds in the cell weighted with the indicator Recipe (H/A) world total. The errors of the values are similar to the other indicators and are not presented in Figure 4. The primary electrode contributed with a high share of 42.4<sup>2</sup>% to this impact indicator. 34.1% were stemming from the silver paste. As silver is a scarce material, which remains a compound also during development of the new cell in the frame of SUNFLOWER, it is worthwhile to be assessed more in depth. The impacts of the ITO electrode with a share of currently 20% can be neglected within the next step of the project, since within the SUNFLOWER project it will be replaced. The EBL and the encapsulation have the same moderate share. The impact from the EBL layer (12%) is stemming from the electricity consumption of the layer's drying process. The encapsulation has a share of 11% mainly due to the impact of the two barrier films with a sum of 7%. The impact of the active layer, the buffer layer and the HBL are assessed to be low (between 3% and 4%).

Additional impacts which were not allocated directly to the layers such as the packaging of the final product, emissions, electricity, the factory and the disposal of non-conform products are expected to add up to below 3% of the total impact.

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<sup>2</sup> The number of decimal digits of the values shall help to improve the comprehensibility of Figure 4.



**Figure 4:** The process tree of the production of the flexible single junction polymer cell from Konarka shows that the primary silver electrode has the highest environmental impact (42.4%, weighted with the Indicator Recipe (H/A) World total), followed by the transparent ITO electrode (20%), the EBL (12%) and the Encapsulation (11.3%).

### 3.3.2 Initial results for existing reference cell - LCA scenario OPV at retrofitted windows

The following analysis additionally considers steps 5 to 8 (Figure 2) in the life cycle of an OPV. The impact of potential leakages in the use and end of life phase to water cannot be evaluated in the LCA, because no impact indicators were developed so far. With the results of the laboratory tests (see chapter 3 and 4) useful indications for a semi quantitative evaluation of these impacts within the LCA are expected.

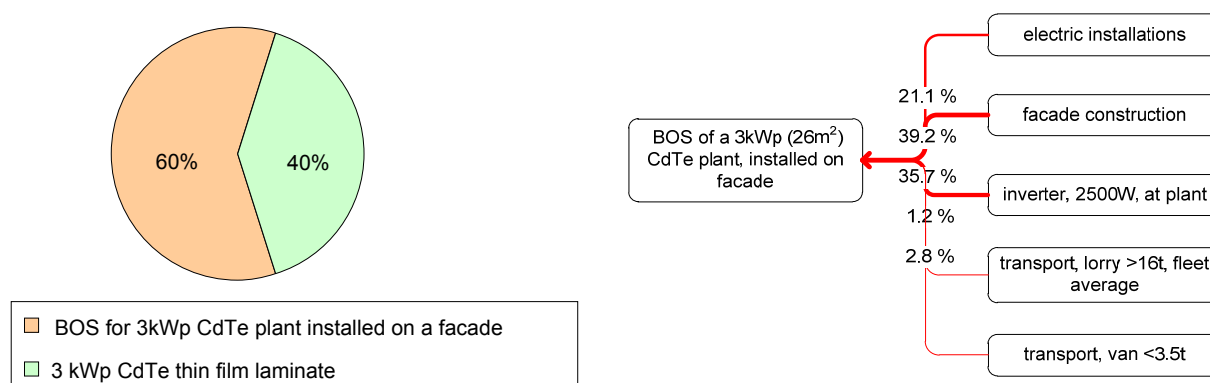
OPV at retrofitted windows is a unique simple and cheap market opportunity requiring adhesive, inverter and electric installations as BOS, solely. A lifetime expectation up to 15 years is realistic compared to outdoor applications with which currently only a life time of 2'000 hours is achievable. An improved insulation of the windows might be an additional benefit to reduce heating or cooling energy. However, common window glass is always reflecting, a disadvantage, which reduces the energy generation between 5 and 10%. OPV may perform better than other thin film technologies in the morning and evening hours or at covered sky. Due to the lack of detailed data of these impacts on the performance, it was assumed that benefits balance the losses.

The scenario compared OPV with thin film PV mounted on a building façade with the standard life time of 30 years. The BOS consist of two inverters, mounting systems, frames and electric installations.

In both scenarios the modules are vertically installed, which reduces the power generation of a PV plant of about 30% (PV Sunrise, 2012) compared to a roof top installation. An average yield of 615 kWh/kWp and year was calculated on the base of the output from 25 thin film roof top installations in Germany (Appendix A: Data sources). The plants are located all over Germany and operate since 2009. The average yearly yield in 2010 and 2011 of 880 kWh/kWp was corrected by a factor 0.7 for façade installation (to 615 kWh/kWp/year).

**LCA Impact of BOS:** The environmental impact of needed BOS has to be considered in the assessment. It is required to install the plant and link it to a grid or store the energy. The material demand depends of the power (kWp) which shall be installed, the efficiency of the cell type, the location e.g. on a building and if the construction is an integrated building part. In the following two scenarios the environmental impact of an extreme high and low share of the BOS of a power installation will be discussed:

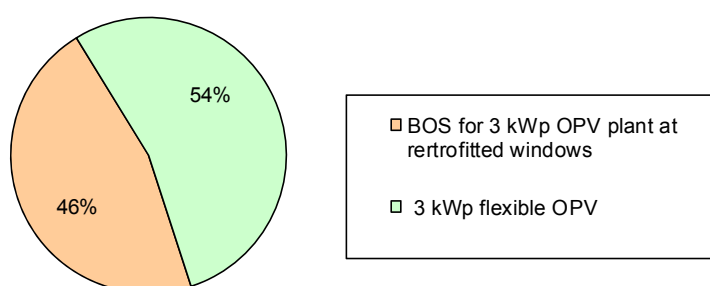
- **Scenario 1 with high share of BOS:** 3 kWp CdTe power installation on façade with mounting system, aluminium construction, inverter and electric installation,
- **Scenario 2 with low share of BOS:** 3 kWp reference cell at retrofitted windows with inverter and electric installation.



**Figure 5:** The share of the impact of the BOS – measured with the Indicator Recipe (H/A) world total – of a 3 KWp CdTe plant on a façade, is dramatically higher (60%) than the PV CdTe laminate (40%).

For the 3 kWp CdTe plant on a façade (Figure 5) it was shown that the BOS had a significantly higher impact (60%) than the CdTe laminate itself (40%). The inverter and the façade construction (made out of aluminium) contribute each >35% to the impact of the BOS, followed by the electric installations with 21%. The rest is transportation and installation energy.

Compared with the CdTe laminate the reference OPV has a lower efficiency. The share of the BOS is therefore higher, because more area per kWp is required for the modules. The environmental impact of the BOS becomes relevant, due the larger amount of frames and mounting systems for modules. This disadvantage increases the environmental impact dramatically and increases the energy payback time of a plant. It can only be lessened if OPV modules substitute as well functions of the facade or they can be fixed directly on the facade. Consequently, the share of the BOS of a transparent OPV at retrofitted windows is with 46% more, because no frames are required (Figure 6). The share of the OPV itself is 54%.



**Figure 6:** The share on the impact of the BOS - measured with the Indicator Recipe (H/A) world total – of a 3 kWp OPV plant at retrofitted windows, is lower (46%) than that of the flexible OPV (54%). If a façade construction was chosen for installation the impact of the BOS would dominate the impact of the plant.

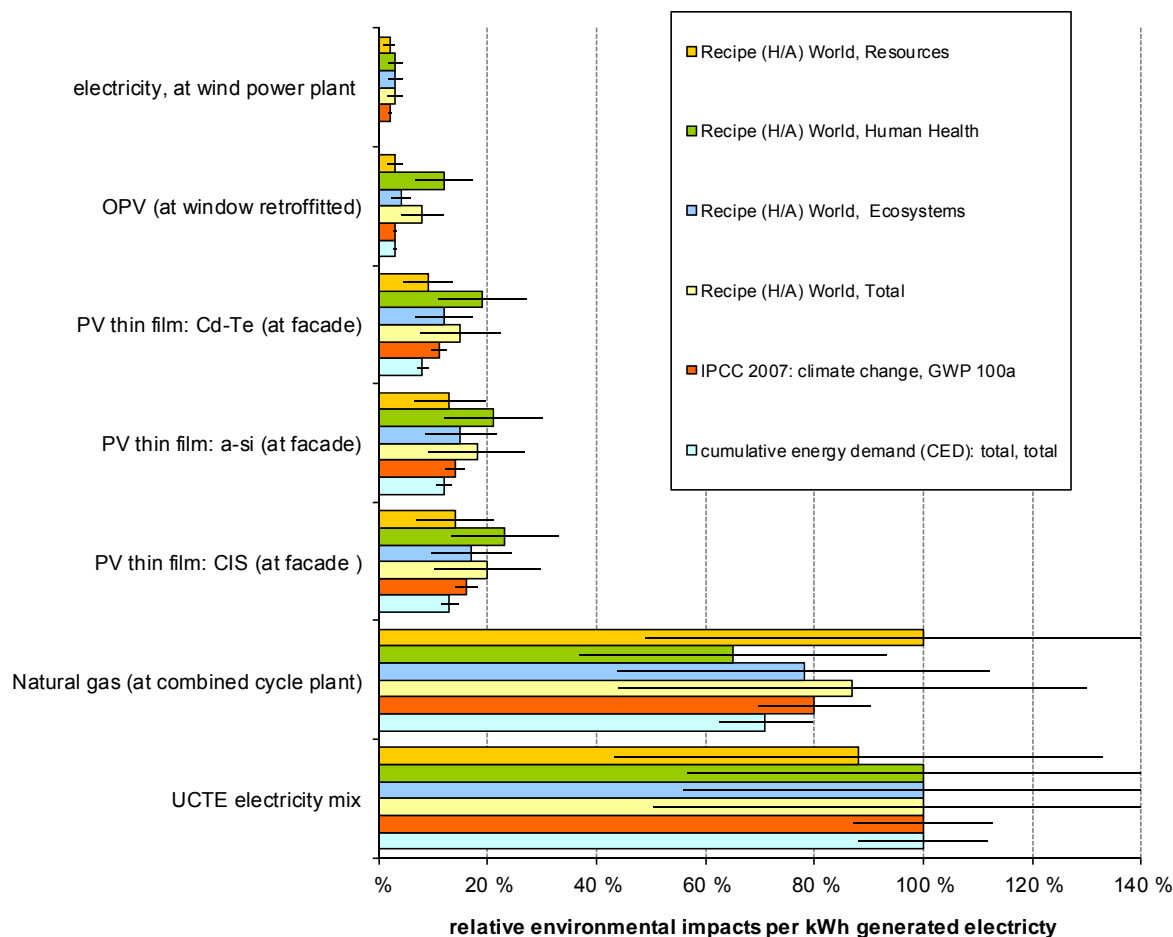
**LCA results for power generation:** Finally the environmental impacts per kWh produced from OPV under the conditions mentioned before was compared with thin film PV, wind, gas and the UCTE power mix. With the results of CED and Recipe (H/A) World, Total, the Energy Pay Back Time (EPBT) was calculated and compared with the thin film technologies. For the OPV, the EPBT is between 3.2 and 5.2 years significantly lower than a-Si thin film with 5.8 to 9.5 years.

**Table 4:** The EPBT depends on the CED of a PV-plant and local factors, e.g. the solar radiation and the orientation of the installation for the electricity generation per year.

PV technology	Electricity generation per kWp and year			CED per kWp (MJ)	EPBT max (yr)	EPBT min (yr)	EPBT av (yr)
	min (MJ)	max (MJ)	av (MJ)				
CdTe PV	1'398	2'307	1'853	19'739	14.1	8.6	10.7
aSi PV	1'398	2'307	1'853	13'317	9.5	5.8	7.2
CIS PV	1'398	2'307	1'853	21'539	15.4	9.3	11.6
OPV	1'398	2'307	1'853	7'292	5.2	3.2	3.9

In Figure 7 all assessed environmental impact indicators are presented. The functional unit is one kWh produced electricity with this technology. Despite of the large deviations of some indicators, OPV seems to generate lower impacts per kWh compared with thin film technologies. The broadly used UCTE electricity mix and natural gas at combined cycle have an up to 5 to 6 times higher impact compared with PV technologies.

The results also were assessed under the aspects of eco-efficiency. The costs of a PV plant with OPV consist of around 40% module costs, 40% area related BOS costs and 20% power related and other costs (Sinke W, 2011). It is assumed that windows retrofitted with OPV have significantly lower relative BOS costs. The area related costs for an installation construction can be nearly disregarded due to the type of installation of the OPV.



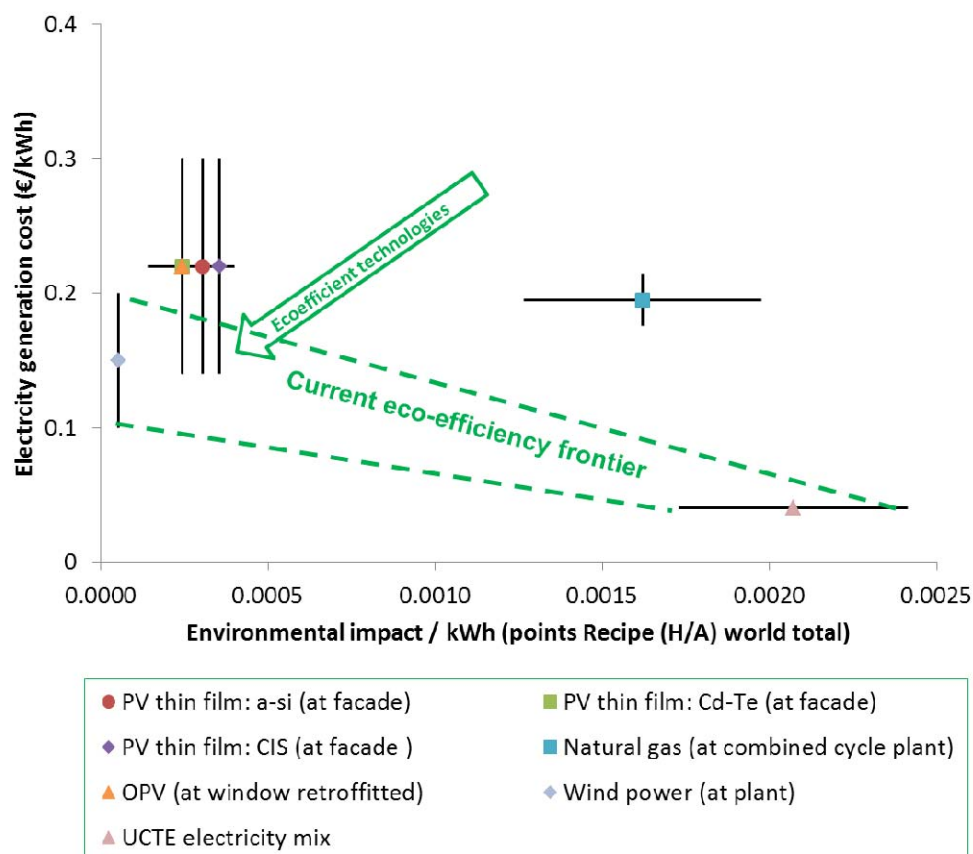
**Figure 7:** Under the conditions of the scenario - windows retrofitted with OPV (3kWp) – the CED total, IPCC 2007: climate change and Recipe (H/A) World, Resources, show a significant lower environmental impact per kWh than thin film technologies. Compared with CIS, the indicators show about 60% less impact. Wind energy shows the lowest impact. Compared to the fossil fuel and nuclear based power generation technologies (UCTE and CC) the impact of all PV technologies is up to 80% lower.

For the installation of thin film PV on a facade these costs must be considered. For that reason as a first approximation the PV installation related costs were estimated to be the same and as well the power generation costs as presented in Figure 8.

PV power generation costs in Southern Europe are currently around 20 €-cent and 40 €-cent in Northern Europe (Baziliana M, 2012), showing large geographical variations. The specific environmental impact per kWh generated at a PV installation as well as the specific costs per kWh are depending on the solar radiation and are therefore lower in Southern Europe in comparison to e.g. Germany.

Under the current market conditions, an UCTE electricity mix is the cheapest electricity to buy, but also the most environmentally problematic. Wind power has the lowest environmental impact per kWh and low power generations costs (off-shore and on-shore). The connection between these types of electricity can be interpreted as an eco-efficiency frontier (see Figure 8).

Under the conditions of the scenario considered, thin film PV and OPV plants could already reach the eco efficiency frontier, if installed in Southern Europe.



**Figure 8:** The connection between the clean wind energy and the cheap UTCE electricity can be interpreted as an eco-efficiency frontier. PV plants in Southern Europe, already could reach this eco-efficiency frontier.



### 3.4 Initial results for existing reference cell - Preliminary OHS assessment results

Fourteen layer materials of the existing OPC solar cell were assessed regarding their operational health and safety. The data sources for the OHS assessment were the Gestis database (Gestis, 2012), the website of the European Chemicals Agency (ECHA, 2012) and Material Safety Data Sheets (MSDS) (Table 2). The provided information of the sources was checked for completeness regarding the required personal protection for the materials. Furthermore, it was investigated if the single materials are registered according the REACH guidelines (Regulation (EC) No 1907/2006).

**Table 5:** OHS Assessment of the layers of the existing cell with data sources and assessment of completeness of data regarding required personal protection, REACH registration and potential uncertainties and risks. Weighting and evaluations was conducted according to Appendix 7.3.

Layer	Material/substance	Data source	Incomplete MSDS data (yes=1, no=0)	Personal Protection				REACH registration (yes = 0, no = 1)	Sum	Uncertainties to be considered in OHS management
				skin	eyes	resp	mean			
<b>Encapsulation (Barrier films)</b>	Cyclophatic epoxy resin	MSDS	1	2	2	0	0.44	0	0.47	low
	Aluminiumoxide	Gestis	0	1	1	2	0.44	0	0.22	insignificant
	Phenoxy Resin PKHJ	Gestis	1	3	2	2	0.78	0	0.64	medium
	Bisphenol-A-(epichlorhydrin) Epoxy resin	Gestis	1	3	2	2	0.78	0	0.64	medium
	Silicon oxide	Gestis	0	1	1	2	0.44	1	0.47	low
<b>Transparent electrode</b>	Insulation polymer	MSDS	0	0	2	3	0.56	1	0.53	medium
	PET	Gestis	0	1	2	2	0.56	1	0.53	medium
	ITO	MSDS	1	2	2	3	0.78	1	0.89	high
<b>HBL</b>	Confidential material	ECHA	1	2	2	2	0.67	0	0.58	medium
<b>Active layer</b>	P3HT	MSDS	1	2	3	3	0.89	1	0.94	high
	PCBM	MSDS	1	2	2	2	0.67	1	0.83	high
<b>EBL</b>	PEDOT:PSS	MSDS	1	2	3	1	0.67	1	0.83	high
	Confidential Material	MSDS	1	3	2	2	0.78	1	0.89	high
<b>Buffer layer</b>	Ethylene copolymer	MSDS	1	2	3	2	0.78	1	0.89	high
<b>Primary elect.</b>	Silver	Gestis	0	1	2	2	0.56	0	0.28	low

The results of this initial OHS assessment based on the reference cell show that for some of the layer materials uncertainties exist which should be considered in a future OHS management (Table 5). In this context uncertainties mean that a lack of information on a material exists or attention on the proper use of personal protection equipment is still required.

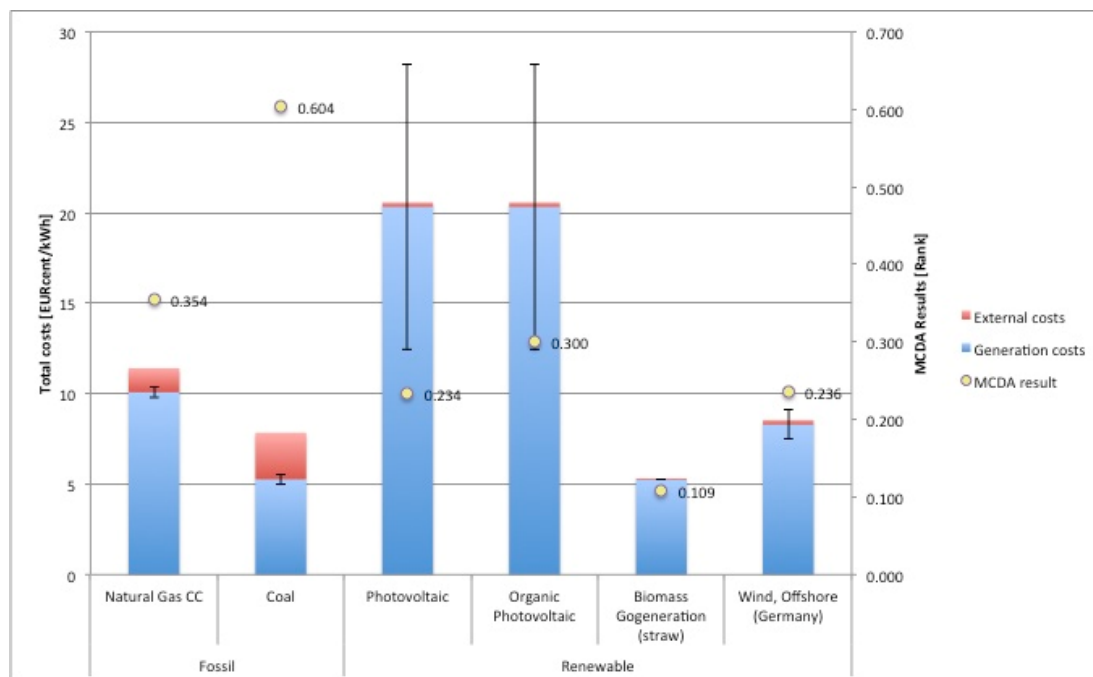
The information on the MSDS of the suppliers of 9 used substances is incomplete and not all (8 of 14) substances are registered according to the GHS and REACH guidelines, what counts as an uncertainty factor. A major source of uncertainties are materials such as PCBM, ITO, PEDOT:PSS, the confidential material of the EBL and the ethylene copolymer of the buffer layer. 5 substances reveal medium potential uncertainties and risks, 3 a low and 1 an insignificant one. 9 out of the 14 substances are classified as hazardous substances according to the current EU regulations.

For a more sustainable production of the OPV solar cells it is recommended to avoid generally hazardous substances and for the suppliers to register the unregistered substances according to the REACH and GHS guidelines and to complete the provided data in the MSDS. For a correct OHS management and for the protection of employees, it is also recommended to provide the complete OHS data to them and to instruct them appropriately.

### **3.5 Initial results for existing reference cell - Preliminary MCDA results**

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The main objective of this initial MCDA was a test of the methodology. A recently published MDCA for energy technologies with estimations for 2030 (Hirschberg et al., 2010) was adapted with the data from the elaborated LCA for the OPV reference cell. It has to be mentioned that the used results of the initial LCA on OPV at retrofitted windows and thin film technology on façades is not representative for the whole PV technology. Based on the used study (Hirschberg et al., 2010) the chosen criteria for the analysis are climate change, ecosystem damage, waste, price of electricity, effects on economy, on utility and social and individual risks. Except for climate change and ecosystem damage the same values as derived for the PV technology were used as well for the OPV technology as a first approximation. Other technologies and their data considered from the above mentioned study were natural gas at combined cycle plant (CC), coal, photovoltaic, biomass cogeneration (straw) and wind energy (offshore, Germany). This allowed an initial comparison of current energy technologies with OPV according to costs and aggregated sustainability criteria as shown in Figure 9.



**Figure 9:** Initial MCDA (rhs) and cost estimation (lhs) results for OPV compared with results from a recent MCDA (Hirschberg et al., 2010) for selected technologies and indicators (see Figure 7). MCDA values were normalised to 1 and weighted as listed in Appendix 7.5 .

In Figure 9, the MDCA results and electricity generation costs for two fossil and four renewable generation technologies are presented using the existing data (Hirschberg et al., 2010) and initial estimates for OPV. The price for electricity generated by photovoltaic is estimated to be still the highest in 2030, followed by natural gas and wind (offshore) (Hirschberg et al., 2010). The lowest prices are expected for biomass cogeneration and coal. For simplicity reasons we assumed for this presentation the same price for OPV as for the estimated price of PV (Hirschberg et al., 2010). However recent developments in the PV as well as the OPV market make these predictions look rather conservative. Coal has the highest impact value (0.6) according to the aggregated MCDA compared to the other technologies. Coal is therefore least sustainable, followed by natural gas according to this metrics. OPV score slightly poorer within this MCDA than other photovoltaic. It has however to be stressed, that this initial MDCA shall rather present the methodology than allow a final rating of the OPV at this stage of the project.

### 3.6 Summary and initial recommendations

In the supply chain of OPV production the used environmental indicators show a relative high impact of the scarce metals in the primary electrode (silver grid) and the transparent electrode (ITO on PET). The SUNFLOWER project target to replace ITO should contribute to the reduction of these environmental impacts. Conducting the LCA on level of the OPV layers indicates improvement potential which can be set in relation to their functionality

The electricity demand in the supply chain of the OPV also has a significant impact. The generation of the UCTE electricity mix, which is the main assumed electricity supply mix for the production processes, requires fossil fuels like coal or nuclear resources and is a main source for GHG and other emissions. Companies in the supply chain of OPV could source an electricity mix with a higher share of renewable energy to mitigate such impacts further.

The preliminary LCA, benchmark and eco-efficiency assessments indicate a unique market opportunity for the transparent and flexible single junction existing cell. It also shows the potential to further reduce the environmental impacts and costs and the importance of the BOS, e.g. with innovative ideas like retrofitting windows with OPV. In the further development

of the SUNFLOWER black tandem cell therefore the environmental and cost aspects of the required BOS should also be considered.

In the supply chain of the existing reference cell some uncertainties regarding the REACH registration and the availability of completely filled out safety data sheets for OHS were identified. From the point of OHS management these gaps should not be neglected, because they are elements to prevent incidents and minimize health risks for employees.

The initial electricity production focused MCDA results based on data from Switzerland for 2030 demonstrate the opportunities for an overall evaluation of the sustainability of OPV and indicate a good acceptance of PV-technologies. Nevertheless it is foreseen to update the MDCA for all technologies and to extend geographical focus with further European countries.

## 4 Method setup for fate studies

### 4.1 Introduction

Table 6 summarizes the deliverables at this stage of the SUNFLOWER project for fate studies.

**Table 6:** Summary of deliverables for fate studies and related chapters in this report.

<b>D 4.1 Deliverable Description</b>	
List of selected priority materials/components to be assessed in definitive tests	Chapter 4.2
Selected benchmark product to be assessed for relative assessment	Chapter 4.3
Definitive setup for four bioavailability assessment tests: <ul style="list-style-type: none"> <li>- 1) Leaching</li> <li>- 2) Sorption</li> <li>- 3) Biodegradation</li> <li>- 4) Fate study</li> </ul>	Chapter 4.4 Chapter 4.5 Chapter 4.6 Chapter 4.7
Initial results for existing reference cell	Chapter 4.8

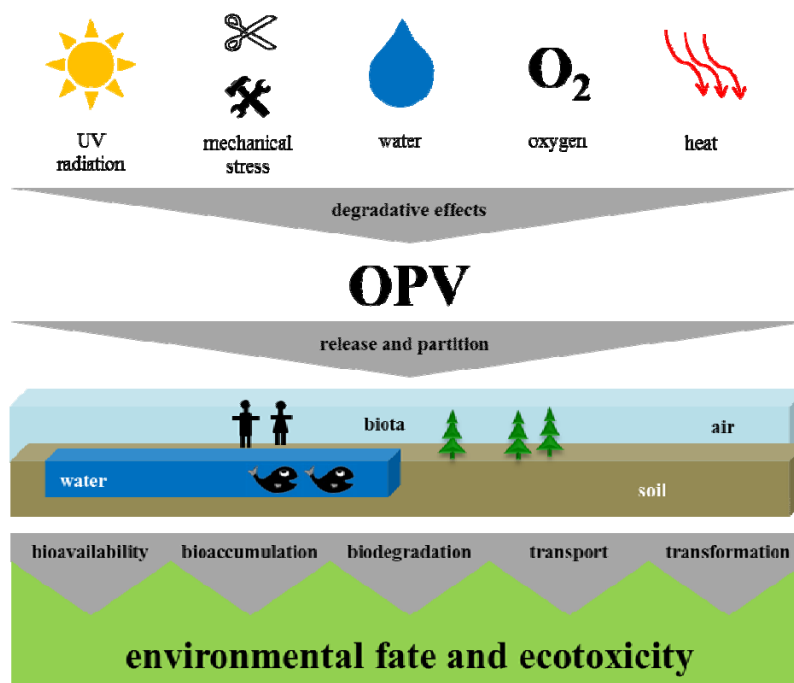
Target of fate studies is to gain insight into the potential environmental impact of organic photovoltaic (OPV) compounds. Current as well as upcoming novel OPV varieties produced by the SUNFLOWER consortium are investigated concerning fate and behavior of their compounds under use-phase and end-of-life scenarios. Besides (theoretical) Life Cycle Assessments (e.g. García-Valverde et al. 2010), until now, the fate of OPVs and their single components in the environment were not experimentally investigated. A schematic chart of OPVs fate and effects in the environment can be seen in Figure 10. From such early research in the OPV development phase relevant conclusions can be drawn about the relevance of the compounds and on how to improve the final product, its application and its ultimate disposal/recycling. As for some novel materials, such as inorganic nanoparticle based wall paints, it was indeed shown that nanoparticles can wash out from outdoor-exposed facades in environmentally relevant concentrations (Kaegi et al. 2010). Therefore, it is necessary to carry out more detailed research and to assess the environmental and health impacts by direct experimental means with conservative approaches in consideration of the safeguard of general public health and the environment. State-of-the-art knowledge on OPV environmental fate and toxicity has been reviewed in Zimmermann et al. 2012.

The following issues were identified to be of specific interest:

- **Relevant influencing factors:** Which use-phase and end-of-life scenarios do enhance release of OPV compounds?
- **Relevant compounds:** Which OPV compounds do actually leach?
- **Expected leachates concentrations:** In which concentrations can those leachates be found?
- **Form of the leachates:** In which physico-chemical form do compounds leach (dissolved vs. particulate, aggregated, complexed)?
- **Bioavailability:** Are these leachates bioavailable for organisms?
- **Sorption behavior:** How does sorption affect the behavior of such leachates in soil?
- **Biodegradability:** Are some OPV compounds biodegradable or not?

A myriad of compounds have already been used during the development of OPVs so far. However, since development made most components obsolete in current models, studies will be constrained to the materials of the priority list (chapter 4.2). These materials were

identified in the frame of WP4 (DL4.1) of the SUNFLOWER project based on their use in the most current development stage, their quantities present, their suspected toxicity, and the lack of data on fate and toxicity. Depending on the outcome of such fate studies, recommendations will be made for possible OPV recycling and recovery of single compounds such as valuable metals.



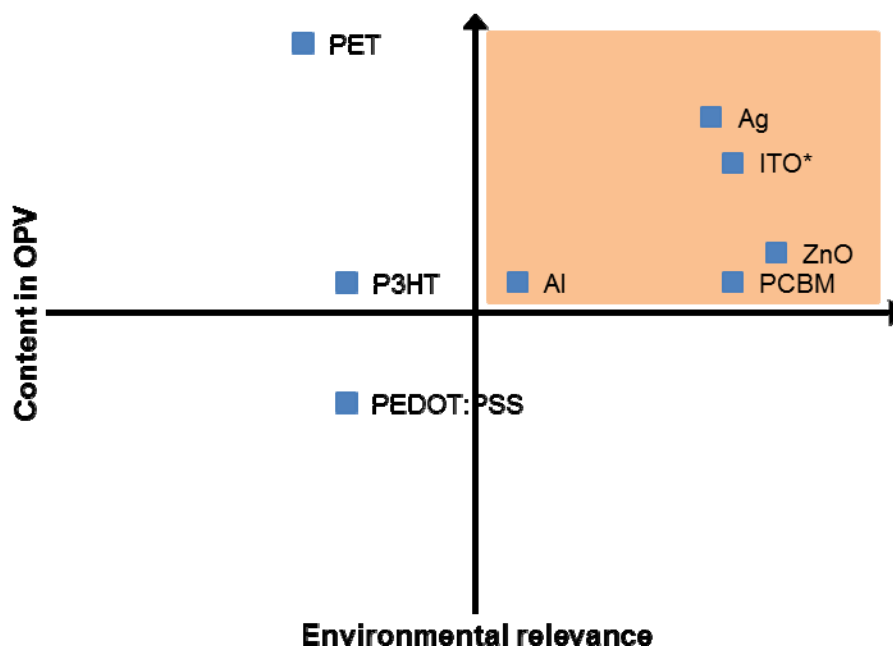
**Figure 10:** Different factors can have a deteriorative effect on OPVs leading to ageing of the material and possibly cause the release of compounds into the environment. After partition of those compounds into air, water, soil, and biota, processes such as bioaccumulation or biodegradation determine their fate and ecotoxicological impacts (figure and caption taken from Zimmermann et al. 2012).

## 4.2 List of selected priority materials/components to be assessed in definitive tests

Concerning the organic fraction of existing reference OPV cells by Konarka Technologies GmbH, which is evaluated at the beginning of the SUNFLOWER project, we will focus on monomeric components. An accelerated solvent extraction of OPV using high temperature and pressure as well as tetrahydrofuran as monopolar solvent did reveal that even under these extreme conditions no polymeric substances in detectable concentrations are dissolving. By means of size exclusion chromatography (SEC-HPLC) we showed that released compounds in the extract are below a molecular weight of 1'250 compared with defined polystyrol standards. Therefore, OPV polymers (such as PET, PEDOT:PSS, P3HT) are not anticipated to be washed out from OPV into the environment under environmentally relevant conditions and are not further considered in this study (Figure 11). Regarding the inorganic fractions, we will study diverse nanoparticles, since insufficient data exists on their environmental fate and they may be present, yet they may pose some concern, if present at high concentrations in nanoparticulate state (i.e. not aggregated as expected) and / or in dissolved form.

For leaching tests (chapter 4.4) as well as fate studies (chapter 4.7), we will focus on metallic components (Figure 11) present in the reference cell, since they are assumed to be leaching to at least some extent under harsh end-of-life conditions but it is not known whether in dissolved or particulate form. For sorption (chapter 4.5) and biodegradation tests (chapter

4.6) we will focus on the fullerene-derivative PCBM, since concerning fate and effects in the environment there was a knowledge gap identified about PCBM (see Zimmermann et al. 2012) and it is contained in OPV in significant amounts (Figure 11). The parent C<sub>60</sub> fullerenes were indeed shown to have adverse effects in the environment (e.g. Lyon et al. 2006). It will be a goal to find a way to fully biodegrade PCBM so that its application in OPV can be continued without raising concerns for the environment. An extensive discussion on commonly used materials in OPV and their effects and further research needs concerning fate in the environment are reviewed in Zimmermann et al. 2012.



**Figure 11:** Selected priority materials (metals and PCBM) for fate studies highlighted in orange. The different materials were given relative numbers for the mass content in OPV (Zimmermann et al. 2012) and relevance for impact in the environment (Zimmermann et al. 2012, as well as assessment due to SEC-HPLC results). \* = is intended to be replaced within the framework of the SUNFLOWER project.

### 4.3 Selected benchmark product to be assessed for relative assessment

As a benchmark product for relative assessment, OPVs leachates will be evaluated against other current best available photovoltaic technologies. So-called CIGS (Cu-In-Ga-Se) cells are promising for the future due to their mechanical flexibility, light-weight and high power conversion efficiencies of up to about 20% (National Renewable Energy Laboratory). OPVs will therefore be compared to CIGS cells as a benchmark. Since CIGS cells do contain a variety of inorganic compounds among which toxic metals such as cadmium and selenium (Bosio et al. 2011), we anticipate that the leachates from CIGS cells should show a larger environmental impact in relative assessments with OPV leachates. Based on initial results we therefore believe that OPVs have a considerable advantage concerning fate and effects in the environment and their impact is significantly less severe compared to other competing thin film technologies.

### 4.4 Definitive setup for bioavailability assessment tests: Leaching

OPV compounds being washed out when exposed to different aqueous solutions will be determined and quantitated in long-term leaching experiments, simulating both use- and end-

of-life scenarios. For the leaching experiments we will simulate the whole possible spectrum of aqueous solutions OPVs can come into contact with in the environment. For this purpose, we will make use of different well-defined artificial waters (i.e. surface waters, marine waters, acidic rain). On the one hand, intact OPV will be tested for their leaching potential simulating the use-phase. On the other hand, OPV will be cut into different sized pieces in order to simulate dismantled, decomposing OPV when potentially disposed on a landfill in the end-of-life phase.

Regarding the leaching of metals it is expected that the more decomposed the OPV the more metals will leach due to the increased interface of OPV layers in contact with environmental media. Additionally, the more corrosive the solution (salt concentration, pH), the easier metals are thought to be leaching out. Intact OPV are not expected to release compounds due to their PET encapsulation and the fact that they are operational (i.e. delivering electricity) over periods of years. However, we expect that at least some compounds (inorganic and organic) will be released from damaged OPV, which possibly could occur when disposed on a landfill. Whereas inorganics are detected by ICP-MS, the detection of organics will be done by a variety of analytical methods such as SEC-HPLC, RP-HPLC, qTOF and GC-MS.

Furthermore, leachates will be compared on the one hand to CIGS cell leachates (see chapter 4.3) for a relative assessment, and on the other hand to OPV which were applied to an accelerated ageing test (simulating sunlight and rain; ISO 4892-2 A2:2006) beforehand in order to see whether leaching kinetics as well as polymer/monomer patterns might be different.

#### 4.5 Definitive setup for bioavailability assessment tests: Sorption

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When leachates are transported by surface waters it has to be assessed whether they remain in an available form for organisms or whether they sorb to other ambient substances such as soil and remain retained. So far, there is a complete gap of knowledge about the fullerene-derivative PCBM identified as priority material (chapter 4.2) concerning behavior and fate in the environment (Zimmermann et al. 2012). In order to analyze and predict the behavior of PCBM in the environment, different aspects will be investigated in the following three setups:

- **Water solubility:** The amount of PCBM maximally soluble in water will be determined in order to estimate whether PCBM preferentially aggregates to particles or dissolves in the water phase after leaching. As a comparison, for C<sub>60</sub> the aqueous solubility was determined to be about 8 ng L<sup>-1</sup> (Jafvert and Kulkarni 2008). Due to the monopolar side chain of PCBM, its solubility is expected to be slightly higher. The setup for the determination of the water solubility consists of prolonged stirring of PCBM in water, filtration and centrifugation to remove remaining particles and detection of the dissolved PCBM using RP-HPLC (modified from OECD guideline 105).
- **Log K<sub>ow</sub>:** The water-octanol partition coefficient will be determined in order to assess whether PCBM tends to remain in the water phase or preferentially adsorbs to organic phases (i.e. those of soils or sediments). For C<sub>60</sub> (Jafvert and Kulkarni 2008), the log K<sub>ow</sub> was determined to be 6.67 (i.e. strong tendency to adsorb to organic material) and is assumed to be lower for PCBM due to its monopolar side chain. The setup for the determination of log K<sub>ow</sub> consists of shaking PCBM in a water-octanol 2-phase mixture and detection of PCBM in both phases by means of RP-HPLC (modified from OECD guideline 123).
- **Adsorption – desorption:** Adsorption behavior to fully characterized soils (different pH, sand content, clay content, organic material content) will be tested. Different soils will be provided by the ETH Zurich (Switzerland). Due to PCBM's overall hydrophobic



character it is thought to be adsorbing to a large extent. The setup consists of shaking PCBM in a water-soil suspension and subsequent detection of PCBM in the water-phase using RP-HPLC (modified from OECD guideline 106).

#### **4.6 Definitive setup for bioavailability assessment tests: Biodegradation**

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Since the fullerene-derivative PCBM was defined as a priority material (chapter 4.2), this compound will also be applied to microbial degradation studies. Different bacterial strains such as *Sphingomonas* sp. (Kolvenbach et al. 2007) and *Microbacterium* sp. (Bouju et al. 2012) will be tested for possible degradation abilities since they were shown before to be capable of degrading organic micropollutants containing aromatic rings. Furthermore, different fungi will be tested whether they can degrade PCBM, since white-rot fungi were already found to succeed in degrading C<sub>60</sub> fullerol (Schreiner et al. 2009). For this purpose, different fungal strains producing different classes of degrading enzymes will be provided by the Internationales Hochschulinstitut Zittau (Germany). At first, PCBM as a pure substance will be tested. If such degradation studies are successful, <sup>14</sup>C-labelled PCBM may be tested in order to elucidate degradation mechanisms. If PCBM can be shown to be biodegradable into harmless residues, this would significantly decrease the expected environmental impact of OPV.

#### **4.7 Definitive setup for bioavailability assessment tests: Fate study**

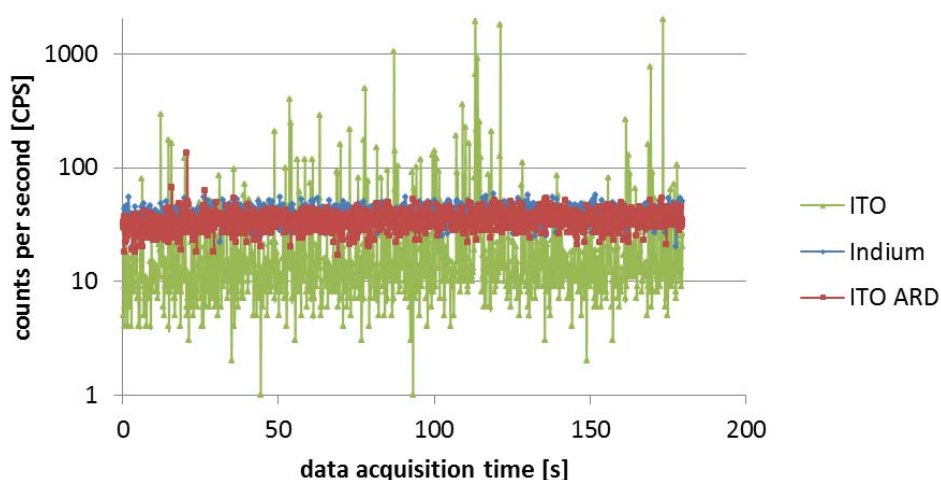
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In order to assess the bioavailability of metals leaching from OPV, a method distinguishing dissolved from particulate fraction using ICP-MS was developed. As an example, dissolved silver ions in the environment are highly toxic to prokaryotes and many freshwater and marine invertebrates and fish whereas the toxicity of nanoparticulate silver is poorly understood but is assumed to cause additional toxic effects above that caused by dissolved silver ions (Fabrega et al. 2011). Therefore, it is particularly crucial to know whether metals present in OPVs are leaching in dissolved or particulate form.

For this, ICP-MS was operated in time-resolved analysis mode (TR-ICP-MS). The method makes use of the fact that, when suspensions are diluted to concentrations sufficiently low, single nanoparticles appear as a single peak event on the baseline of dissolved metal (compare Figure 12). When all particulate materials are dissolved upon addition of aqua regia, the difference between the dissolved metals baseline (nanoparticle peaks excluded) and the baseline observed after aqua regia treatment corresponds to the amount of nanoparticulate metal.

As proof of principle it was demonstrated that dissolved and nanoparticulate indium (from ITO) can be distinguished (Figure 12). Whereas the baseline of dissolved indium is found at 38.5±6.2 counts per second, the ITO nanoparticles measured at the same concentration of indium have a baseline at CPS=12.6±5.6 (peaks eliminated) only. Here, peaks reflect the particles, since after aqua regia treatment, the resulting baseline of indium corresponds well to the baseline of the dissolved standard (CPS=34.3±6.0, expected at 38.5). Peak elimination for calculation of the baseline of particulate suspensions was done as described in Mitrano et al. 2012 (exclusion of mean + 3SD until no further decrease) with an automated macro. In a next step we will extend the TR-ICP-MS method to all priority metals present in OPV (including silver, aluminum and zinc).

Fully developed, this method will be an invaluable tool to check whether leachates from OPV are released as dissolved or particulate species. From this it will be possible to model their bioavailability, uptake behavior into different organisms as well as transport pathways along surface waters and soils.



**Figure 12:** Developed TR-ICP-MS method to distinguish between 0.15 ppb dissolved indium (blue), 0.15 ppb indium in nanoparticulate form as ITO (green) and the ITO particles after dissolution with aqua regia (ARD) (red).

#### 4.8 Initial results for existing reference cell

For intact OPV in the use-phase of the product, leaching of OPV compounds is assumed to be negligible due to almost impermeable barrier films used as encapsulation for the modules without which OPV would not be functional over several years. However, when OPV are dismantled and disposed on a landfill, over long periods of time OPV might decompose and the ambient conditions can affect the inner layers possibly leading to relevant leaching. Initial results indeed confirm that metals may leach out of decomposed OPVs (i.e. cut into differently sized pieces; see chapter 4.4) under harsh conditions. The extent, however, appears to be very low and metals are found only in very low trace concentrations in the tested leachate (i.e. low  $\mu\text{g/L}$ ) (Table 6).

		Al	Zn	Ag	In	Sn
NPW	small					
	large					
	intact					
ALW	small					
	large					
	intact					
AAW	small					
	large					
	intact					
ASW	small					
	large					
	intact					

No release	Marginal release	Minor release	Medium release	Not available
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**Table 7:** Initial results on metals leached from OPVs during long-term conditions in nanopure water (NPW), artificial lake water (ALW), artificial acidic water (AAW) and artificial sea water (ASW) when OPV are intact or cut into small (2×2 mm) and large (15×30 mm) pieces after 3 month of exposure.

Therefore, our preliminary data suggests that leaching of environmentally relevant concentrations of metals from OPV might only occur under harsh conditions upon improper disposal. The found leachate concentrations can be put into perspective concerning the relevancy in the environment. Leachate concentrations will be compared to toxicity data from literature in order to see whether these concentrations might pose a threat to living organisms or not.

## 5 Method setup for ecotoxicity

### 5.1 Introduction

Table 8 summarizes the deliverables at this stage of the SUNFLOWER project for the ecotoxicity study.

**Table 8:** Summary of deliverables for the ecotoxicity study and related chapters in this report

D 4.1 Deliverable Description	
List of selected priority materials/components to be assessed in definitive tests	Chapter 4.2
Definitive setup for ecotoxicity assessment tests: - 1) General toxicity - 2) Metal-bioavailability and -toxicity - 3) Cellular stress response	Chapter 4.3 Chapter 4.4 Chapter 4.5

An evaluation of potential ecotoxicity is performed for two forms of releases:

- (i) Potentially critical single components of OPVs, and
- (ii) OPV leachates from weathering tests (Chapter 4.4).

As mentioned before OPV cells are encapsulated and need to function until their end of life. Therefore, a release of large concentrations of harmful substances under normal, use-phase conditions is not expected. Nevertheless, during the ageing process, factors such as UV irradiation, pollutants, high surface temperatures, hot-cold and dry-wet cycles as well as mechanical damage (due to hale for example, Manceau et al. 2011) could lead to leachates that may have ecotoxicological activity. In the end of life scenarios including deposition on landfills, shredding or burning, the release of ecotoxicological active compounds into the environment may take place. Whether or not a potential hazard and risk for the environment the different components used in OPVs (pure compounds as well as weathering products), need to be assessed by appropriate bioassays.

The biological activity of the pure chemicals/metals and leachates will be analysed in fish cell systems (*in vitro*) and early-life-stages of zebrafish (*in vivo*). Three compounds of interest are chosen based on existing literature data and the amount used in OPVs. Potential ecotoxicological activities are determined by biomarkers and targeted gene expression analysis. This approach will yield relevant novel information not available as of now.

To get a comprehensive view of the potential ecotoxicity we will employ the following five main ecotoxicological assays:

1. MTT assay for cytotoxicity assessment yielding information on general toxicity,
2. Quantitative real time PCR (qRT-PCR) for gene expression analysis yielding information on cellular stress response,
3. Assay for determining oxidative stress (cellular stress response): H<sub>2</sub>DCF-DA assay,
4. *In vivo* analysis in zebrafish eleuthero-embryos yielding information on cellular stress response as well as metal-bioavailability and –toxicity,
5. Effect Directed Analysis (EDA) of leachates.

We will analyse ranges of different concentrations, from expected environmental levels up to toxicological levels to determine full range dose-response curves. The leachate samples from our fate studies (see section 3) will undergo an Effect Directed Analysis (EDA).

The risk assessment of OPV and its materials is a major component in the development of environmentally safe new OPV within the SUNFLOWER project. These analyses aim to identify safe components and components of potential ecotoxicity.

## 5.2 List of selected priority materials/components to be assessed in definitive tests

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Chemicals and compounds that are bioavailable for uptake will be analysed. Nanoparticles used for OPV production are of interest as they may potentially leach into the environment and subsequently may be taken up by organisms. In contrast, polymers are too large molecules to be taken up into the cell, therefore toxic effects are not expected. However, UV-irradiation and degradation mechanisms (Hintz et al. 2011) could lead to smaller-sized molecules (e.g. monomers), which may be taken up by organisms in the environment. Based on our initial analysis we select the following materials for the detailed ecotoxicological analysis (Figure 11):

- (1) **Nanoparticulate ZnO (nZnO).** This nanoparticle serves as a major compound of OPV and therefore needs ecotoxicological assessment. Particle dissolution and  $\text{Zn}^{2+}$  shedding of nZnO can lead to pro-inflammatory and cytotoxic effects, which lead to lysosomal damage, triggering of intracellular  $[\text{Ca}^{2+}]$  flux, mitochondrial perturbation and cytotoxicity (George et al. 2010; Xia et al. 2008). FDA's National Center for Toxicological Research (NCTR) is investigating nanomaterials in products for human use. Currently, nZnO is assessed by NCTR due to insufficient information on the skin penetration and uptake of nanoscale materials from the gut (FDA 2012). Even though different nZnO has undergone several ecotoxicological assessments before (Bai et al. 2009; Yu et al. 2011), knowledge about the effects and risks of nZnO in environmentally relevant media (aquatic systems) is lacking. Another knowledge gap exists on uptake and ecotoxicological target organs of nZnO in fish. Knowledge of target organs is particularly crucial when potential effects and chances for metabolism need to be assessed.
- (2) **PCBM.** This compound was not evaluated for potential environmental risks so far. Other fullerenes were studied, but results cannot be translated to PCBM. It needs particular analysis, as the fate and toxicity are dependent on the surface derivatisation and environmental conditions.

nZnO and PCBM are selected for further investigations on their biological activities. As ITO is intended to be replaced in the novel OPV, it is not chosen for further investigations. Furthermore, our initial screening results demonstrated that effects cytotoxic effects were only observed at extremely elevated concentrations of more than 5g / L (Human hepatoma cells). From literature there is evidence that nanoparticles including nZnO and PCBM potentially generate **reactive oxygen species (ROS)** (nZnO, C60) and induce **inflammatory effects** (nZnO). Accumulation and bioavailability of nanoparticles are influenced by environmental matrices such as amount of organic material (NOM), ionic strength, pH, surface area and shape (Handy et al. 2008b). Furthermore, the small size enhances uptake and interaction with biological tissues. Presently, the fate and behaviour of nanomaterials in the environment and its potential adverse effects are very limited and therefore need expert ecotoxicological investigation (Fent 2010; Kahru and Dubourguier 2010; Nowack and Bucheli 2007).

### 5.3 Definitive setup for ecotoxicity assessment tests: General toxicity

Ecotoxicological assessments are frequently conducted with fish cell lines (*in vitro*) or fish (*in vivo*). Data obtained by fish cell lines are more reproducible, less costly, and ethically justified. For the same reasons early-life-stage tests with zebrafish embryos have gained widespread use.

In order to identify the acute toxic potential of selected components used in different OPV layers, cytotoxicity is measured by several different methods including the **MTT test**. The test is based on the reduction of the yellow tetrazolium salt 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) into a blue formazan product by the mitochondrial succinate dehydrogenase (Mosmann 1983). The reduction only takes place in viable cells and therefore this assay will be used to assess the acute toxic potential of the different OPV components.

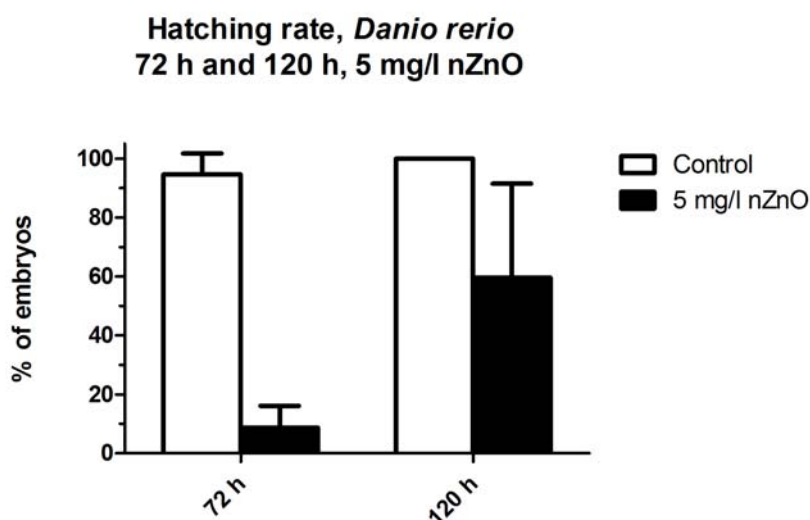
For nanomaterials, an additional alternative assay should be performed (Wörle-Knirsch et al. 2006). Therefore, data derived from the MTT test with nanoparticles (ZnO, PCBM) will be verified by the **lactate dehydrogenase (LDH) assay**, which measures the membrane integrity. Cellular membrane damage results in subsequent leakage of the cytosolic enzyme LDH into the extracellular fluid, which is a measure of cell membrane damage. Cytotoxicity of pure compounds and leachate will be analysed in *zebrafish liver or fibroblast like cell lines (zfl, zfl4) and human hepatoma cell line (Huh7)*.

In *early-life-stage tests with zebrafish*, eggs are exposed to the test substance until 96 hours post fertilisation. Assessed endpoints are **hatching and mortality rate**.

Both the *in vitro* assays and the *in vivo* assay (zebrafish embryos) will be used for assessment of different leachates produced during evaluation of the environmental behaviour of OPV and its constituents (section 4.4).

#### 5.3.1 Preliminary results

Zebrafish embryos were exposed to 5 mg/l nZnO. The hatching rate was assessed after 72 and 120 hours post fertilisation. nZnO led to a reduction in the hatching rate (Figure 13).



**Figure 13:** Hatching rate of zebrafish embryos (*Danio rerio*) exposed to 5 mg/L of ZnO nanoparticles for 72 h and 120 h.

## 5.4 Definitive setup for ecotoxicity assessment tests: Metal-bioavailability and -toxicity

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The bioavailability of metals and its potential toxicity will be assessed *in vivo* in zebrafish embryos.

**Toxicity assessment:** Prior to studying effects of nanoparticles, key questions such as how to suspend nanoparticles (PCBM, nZnO) homogeneously in water and whether they are taken up by fish embryos need to be answered. Alginate acid added to the zebrafish media is expected to positively influence the nanoparticle dispersal and dissolution of nZnO. We will therefore use alginate acid as a supplement in the fish embryo media. In addition to nZnO, zebrafish embryos will be exposed to ZnCl<sub>2</sub> to assess whether effects are induced by nanoparticles or metal ions, or a combination thereof. Exposure concentrations will be confirmed by ICP-MS.

**Bioavailability and uptake:** The accumulation of zinc or indium in zebrafish embryos exposed to nZnO or ZnCl<sub>2</sub>, will be assessed by ICP-MS. After exposure, the larvae are anaesthetised, washed and dissolved in aqua regia. The comparison will allow delineating the effect of the nanostructure versus dissolved Zn metal ions.

In order to assess whether and in which tissues zinc and indium is accumulated, zebrafish embryos will be embedded after the exposure, cut into thin layers and analysed by Laser Ablation ICP-MS. The laser will be directed on the target organ, where it is ablating with pulsed laser beam, creating an aerosol transported directly to the ICP-MS. This method was already successfully applied in our laboratory to detect the accumulation of metals in *Daphnia magna*. Transmission electron microscopy (TEM) will be used to assess the accumulation of nanoparticles in the cell.

## 5.5 Definitive setup for ecotoxicity assessment tests: Cellular stress response

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The selected components are analysed for various toxicological activities including oxidative stress, apoptosis and metabolic activity. Induction of apoptosis, inflammation, CYP1A and oxidative stress by nanoparticles (nZnO, PCBM) will be analysed by gene expression analysis and a H<sub>2</sub>DCF-DA assay in fish cell lines and *in vivo* in zebrafish embryos.

Gene expression analysis in fish exposed to contaminants is an appropriate procedure, particularly when mechanisms of action are unknown (Handy et al. 2008a). In our laboratory, an established technology to examine the differences in gene expression between exposed and non-exposed cells or organisms is used. It is the SYBR<sup>®</sup> Green based quantitative real-time polymerase chain reaction (qRT-PCR).<sup>3</sup>

Expression of inflammation and apoptosis related genes (e.g., *bax*, *nox*, *p53*, *p21*, *bcl2*) will be focused on in zfl or zf4 and in Huh7 after different incubation time with nZnO and ZnCl<sub>2</sub>. Additionally, marker genes for oxidative stress (Cat, SOD, Nrf2) will be assessed. Further, intracellular ROS will be detected by a H<sub>2</sub>DCF-DA assay (Wang and Joseph 1999).<sup>4</sup>

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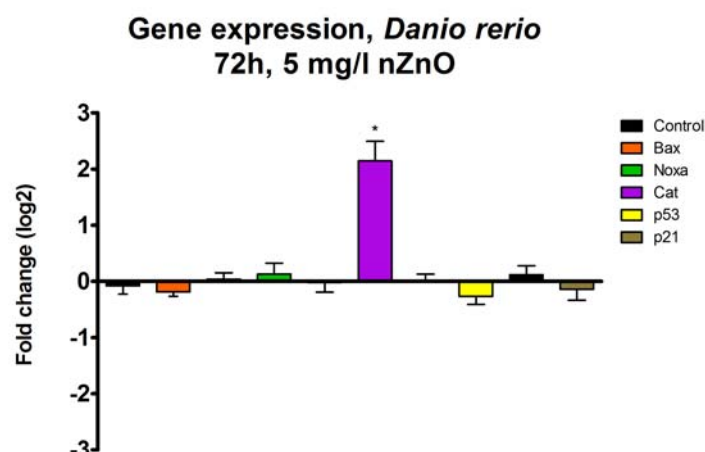
<sup>3</sup> The procedure starts with extraction of the RNA and is followed by a conversion of the mRNA to cDNA by reverse transcriptase using an oligonucleotide primer (random hexamer). During a process of repeated heating and cooling a chain reaction (PCR) is set in motion, in which the DNA template is exponentially amplified. A previously added primer, containing sequences complementary to the target region, enables a selective and repeated amplification. The amount of DNA theoretically doubles with every cycle of PCR, but finally it is limited due to the exhaustion of the reaction components and reaches a plateau phase. In contrary to the normal PCR (where the detection of PCR amplification takes place at the final phase of the PCR reaction), the Real-Time chemistries allow for the detection of PCR amplification during the early phase of the reaction. The data is taken at the exponential phase of the PCR reaction, which makes quantification of DNA and RNA easier and more precise. The SYBR<sup>®</sup> Green is an unspecific dye that binds to double stranded DNA. As more double stranded DNA is produced, the intensity of the fluorescent emission of SYBR<sup>®</sup> Green increases.

<sup>4</sup> Basically, the treated and untreated cells are incubated in PBS containing the dye H<sub>2</sub>DCFDA (2,7-dihydrodichlorofluorescein diacetate). This lipophilic and non-fluorescent dye can pass through the plasma membrane, where acetate groups are de-esterified by cellular esterase to a hydrophilic alcohol (H<sub>2</sub>DCF). The reaction of H<sub>2</sub>DCF with ROS results in the fluorescent molecule DCF. The fluorescence will be then measured by flow cytometry or a microplate reader.

Active compounds are subsequently analysed *in vivo* in zebrafish embryos for various toxicological activities including general toxicity, oxidative stress, metabolic activity and bioaccumulation. Early-life-stage tests with zebrafish embryos and larvae will be suitable to determine whether the compound will be taken up into the organism and to confirm the results from *in vitro* studies. The RNA extracted from exposed eleuthero-embryos will be used for gene expression analysis as in *in vitro* studies by qRT-PCR.

### 5.5.1 Preliminary results

We performed a gene expression analysis using RNA extracted from embryos exposed to 5 mg/L nZnO (Figure 14). Target genes involved in the pathways of **apoptosis** (*Bax*, *Noxa*, *p53*, *p21*) and **oxidative stress** (*Cat*) were chosen. Only *Cat* is significantly up-regulated.



**Figure 14:** Comparison of gene expression in zebrafish larvae determined by qRT-PCR (n = 4, 100 larvae pooled) after exposure to 5 mg/L nZnO in Media supplemented with alginate. Asterisk (\*) indicates statistically significant difference to control (p < 0.05).

## 5.6 Effect Directed Analysis of OPV leachates

Effect Directed Analysis (EDA) combines chemical fractionation and chemical analytics of environmental samples with toxicity testing, preferably by *in vitro* assays. This is an appropriate approach to assess the environmental consequences of ageing and weathering processes of OPV. Toxic fractions are identified by determining the toxic response of each (sub)-sample with appropriate bioassays (cytotoxicity, selected gene expressions). The basic structure of an Effect Directed Analysis involves three phases.

In **Phase 1**, the complex mixture (here: leachate from OPV cell) is fractionated in to broad groups (e.g. NOCs, cationic or anionic metals, polar or hydrophilic substances).

In the case of an OPV cell, an accelerated solvent extraction with different solvents (e.g. water, acids, organic solvents) is conducted, followed by a filter process to remove particulates, and if necessary, a solid phase extraction to remove organics. Then a first screening is performed to assess the cytotoxicity of the different fractions.

**Phase 2** is conducted to identify specific active toxicants. For example, if Phase 1 concluded toxicity was being caused by cationic metals, Phase 2 would determine which specific metal (in case of OPV: Ag, Al, Zn) is responsible for the observed toxic effect. For further fractionation a Cation Exchange Column Chromatography could be used. The new fractions are again tested by *in vitro* bioassays and chemical analysis (using ICP-MS) to identify the compound with the toxic response.



In **Phase 3**, the activities of individual and copy-mixtures of the identified compounds in the original sample are confirmed by using the same bioassays. This approach will allow a characterisation of the ecotoxicological potential of the OPV leachates and identify responsible compounds.

## **5.7 Summary and preliminary conclusions**

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The potential hazard and risk for the environment of different components used in the existing OPV reference cell will be assessed. The chosen bioassay will cover general toxicity, cellular stress response as well as metal-bioavailability and –toxicity. Based on the use in the most current development stage and lack of data according to literature review, nZnO and PCBM are selected for further detailed investigation. Furthermore, the biological activity of leachates derived from fate studies will be evaluated applying an Effect Directed Analysis based on the most promising bioassays.

In a preliminary assessment, zebrafish embryos were exposed to nZnO in media containing alginic acid as natural dispersant. First results demonstrate an induction of the oxidative stress marker gene catalase. Transcripts of genes involved in the apoptosis pathway were neither induced nor repressed. Furthermore, embryo hatching was reduced.

Overall, the preliminary results show potential ecotoxicity of the investigated compounds only at high concentrations. Further analyses are needed to assess the environmental safety of components and leachates.

## 6 References

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- Anctil, A. (2011). Fabrication and Life Cycle Assessment of Organic Photovoltaics. PhD Thesis, Rochester Institute of Technology.
- Bai W., Zhang Z., Tian W., et al. (2009) Toxicity of zinc oxide nanoparticles to zebrafish embryo: a physicochemical study of toxicity mechanism. *Journal of Nanoparticle Research* (12): 1645-1654. doi: 10.1007/s11051-009-9740-9.
- Baziliana M., Onyejia I., et al. (2012) Re-considering the Economics of Photovoltaic Power. UNIDO and others
- Bosio A., Romeo A., Menossi D., Mazzamuto S., and Romeo N. (2011) Review: The second-generation of CdTe and CuInGaSe<sub>2</sub> thin film PV modules. *Crystal Research and Technology* (46): 857-864.
- Bouju H., Ricken B., Beffa T., Corvini P. F. X., and Kolvenbach B. A. (2012) Isolation of bacterial strains capable of Sulfomethoxazole mineralization from an acclimated membrane bioreactor. *Applied and Environmental Microbiology* (78): 277-279.
- Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. (2010, 10). Technische Regeln für Gefahrstoffe (TRGS 510). TRGS 510 - Lagerung von Gefahrstoffen in ortsbeweglichen Behältern . Germany.
- Dupont S. R., O. M. (2012). Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells. *Solar energy materials and solar cells* , 97.
- Dyer-Smith C., N. J. (2012). Organic Solar Cells. In T. M. A. McEvoy, *Practical Handbook of Photovoltaics - Fundamentals and Applications* (pp. 543-569). Oxford, UK: Elsevier Ltd.
- Espinosa, N. G.-V. (2010). A life cycle analysis of polymer solar cell modules prepared using roll-to-roll methods under ambient conditions. *Solar Energy Materials and Solar Cells* .
- European Union. (2006). Regulation (EC) No 1907/2006 of the European Parliament and of the council. *Official Journal of the European Union* .
- Fabrega J., Luoma S. N., Tyler C. R., Galloway T. S., and Lead J. R. (2011) Silver nanoparticles: Behaviour and effects in the aquatic environment. *Environment International* (37): 517-531.
- FDA – U.S. Food and Drug Administration:  
<http://www.fda.gov/downloads/AboutFDA/ReportsManualsForms/Reports/BudgetReports/UCM301515.pdf>, visited July 16 2012
- Fent K. (2010) Ecotoxicology of engineered nanoparticles. In: Frimmel FH, Niessner R (eds) *Nanoparticles in the Water Cycle*. Springer-Verlag, Berlin Heidelberg, pp 183-205.
- Fthenakis V., F. R.-S. (2011, November). Methodology Guidelines on Life Cycle Assessment of Photovoltaic Electricity, 2nd edition, IEA PVPS Task 12. *Methodology Guidelines on Life Cycle Assessment of Photovoltaic Electricity* , 2. USA: IEA International Energy Agency.
- García-Valverde R., Cherni J. A., and Urbina A. (2010) Life cycle analysis of organic photovoltaic technologies. *Progress in Photovoltaics: Research and Applications* (18): 535-558.
- Gaudiana R., B. C. (2008). Fantastic plastic. *Nature: Naturphotonics* , 2.
- George S., Pokhrel S., Xia T., et al. (2010) Use of rapid cytotoxicity screening approach to engineer a safer zinc oxide nanoparticle through iron doping. *ACS Nano* (4): 15-29.
- Handy R. D., Henry T. B., Scown T. M., et al. (2008a) Manufactured nanoparticles: their uptake and effects on fish--a mechanistic analysis. *Ecotoxicology* (17): 396-409. doi: 10.1007/s10646-008-0205-1.

- Handy R. D., Owen R., Valsami-Jones E. (2008b) The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges, and future needs. *Ecotoxicology* (17): 315-325. doi: 10.1007/s10646-008-0206-0.
- Hintz H., Egelhaaf H.-J., Lürer L., et al. (2011) Photodegradation of P3HT–A systematic study of environmental factors. *Chemistry of Materials* (23): 145-154. doi: 10.1021/cm102373k.
- Hirschberg, C. Bauer, Schenler W. Burgherr P. (2010) Facts for the energy decisions of tomorrow. *Energie-Spiegel* (20). Paul Scherrer Institut
- International Energy Agency, IEA (2009). Methodology Guidelines on Life Cycle Assessment of Photovoltaic Electricity. Report IEA-PVPS T12-01:2009
- Jafvert C. T., and Kulkarni P. P. (2008) Buckminsterfullerene's (C<sub>60</sub>) Octanol-Water Partition Coefficient (K<sub>ow</sub>) and Aqueous Solubility. *Environmental Science and Technology* (42): 5945-5950.
- Kaegi R., Sinnet B., Zuleeg S., Hagendorfer H., Mueller E., Vonbank R., Boller M., and Burkhardt M. (2010) Release of silver nanoparticles from outdoor facades. *Environmental Pollution* (158): 2900-2905.
- Kahru A., Dubourguier H.-C. (2010) From ecotoxicology to nanoecotoxicology. *Toxicology* (269): 105-119. doi: 10.1016/j.tox.2009.08.016.
- Kolvenbach B., Schlaich N., Raoui Z., Prell J., Zühlke S., Schäffer A., Guengerich F. P., and Corvini P. F. X. (2007) Degradation Pathway of Bisphenol A: Does ipso substitution apply to phenols containing a quaternary  $\alpha$ -carbon structure in the para position? *Applied and Environmental Microbiology* (73): 4776-4784.
- Konarka Technologies, Inc. (2012): <http://www.konarka.com>
- Krebs F. C., F. J. (2010, August). Product integration of compact roll-to-roll processed polymer solar cell modules: methods and manufacture using flexographic printing, slot-die coating and rotary screen printing. *Journal of Materials Chemistry* .
- Krebs F. C., T. T. (2010, May). Upscaling of polymer solar cell fabrication using full roll-to-roll processing. *Nanoscale* .
- Krebs, F. C. (2008, November). Fabrication and processing of polymer solar cells: A review of printing and coating techniques . *Solar energy materials and solar cells* .
- Krebs, F. C. (2009). Polymer solar cell modules prepared using roll-to-roll methods: Knife-over-edge coating, slot-die coating and screen printing . *Solar energy materials and solar cells* , 93.
- Lenzmann F., K. J.-V. (2011). Refined life-cycle assessment of polymer solar cells. 26th European photovoltaic solar energy conference and exhibition. Hamburg.
- Lyon D. Y., Adams L. K., Falkner J. C., and Alvarez P. J. J. (2006) Antibacterial activity of fullerene water suspensions: Effects of preparation method and particle size. *Environmental Science and Technology* (40): 4360-4366.
- Manceau M., Rivaton A., Gardette J.-L., et al. (2011) Light-induced degradation of the P3HT-based solar cells active layer. *Solar Energy Materials and Solar Cells* (95): 1315-1325. doi: 10.1016/j.solmat.2010.09.021.
- Mitrano D. M., Leshner E. K., Bednar A., Monserud J., Higgins C. P., and Ranville J. F. (2012) Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry. *Environmental Toxicology and Chemistry* (31): 115-121.
- Montoro D.F., Vanbuggenhout P. and Ciesielska J.(2010) Building integrated Photovoltaics. Photovoltaic Industry Association. [www.pvsunrise.eu](http://www.pvsunrise.eu)
- Mosmann T. (1983) Rapid colorimetric assay for cellular growth and survival: Application to proliferation and cytotoxicity assays. *Journal of Immunological Methods* (65): 135-147.

Moulé, A. J. (2010). Power from plastic. *Current Opinion in Solid State and Materials Science*, XIV.

National Renewable Energy Laboratory (NREL): <http://www.nrel.gov>

NEEDS project: <http://www.needs-project.org/>

Nowack B., Bucheli T. D. (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environmental Pollution* (150): 5-22. doi: 10.1016/j.envpol.2007.06.006.

OECD guidelines:

[http://www.oecd.org/document/40/0,3746,en\\_2649\\_37465\\_37051368\\_1\\_1\\_1\\_37465,00.html](http://www.oecd.org/document/40/0,3746,en_2649_37465_37051368_1_1_1_37465,00.html)

Raw materials supply group. (2010). Critical raw materials for the EU. Working group report, European Commission.

ReCiPe methodology for Life Cycle Assessment Impact Assessment:

<http://www.lcia-recipe.net/>

Roes A. L., A. E. (2009). Ex-ante environmental and economic evaluation of polymer photovoltaics. *Progress in photovoltaics: research and applications*, 17, 372-393.

Schreiner K. M., Filley T. R., Blanchette R. A., Beitler Bowen B., Bolskar R. D., Hockaday W. C., Masiello C. A., and Raebiger J. W. (2009) White-rot basidiomycete-mediated decomposition of C60 fullerol. *Environmental Science and Technology* (43): 3162-3168.

PV Sunrise: sunrise toolbox.xls downloaded from [www.pvsunrise.eu](http://www.pvsunrise.eu), visited June 2012

Søndergaard R., H. M.-O. (2012). Roll-to-roll fabrication of polymer solar cells. *Advances functional materials*, 15.

Schaller, A. (2010, 11). From sustainable electronics to green services. Internet of things .

Sinke W (2011), Photovoltaic solar energy, progress beyond expectations. ECN Solar Energy & European Photovoltaic Technology Platform. IEA EGRD Meeting – Paris – 16-17 November 2011

Swiss center for Life Cycle inventories: [www.ecoinvent.org](http://www.ecoinvent.org), database ecoinvent data v2.2

The large international photovoltaic database: [www.sonnenertsag.eu](http://www.sonnenertsag.eu), visited June 2012

Umweltbundesamt, Berlin. (2003). Integrierter Umweltschutz bei bestimmten industriellen Tätigkeiten: Teilband II "Bedrucken" . Final report, Berlin.

Wang H., Joseph J. A. (1999) Quantifying cellular oxidative stress by dichlorofluorescein assay using microplate reader. *Free Radical Biology & Medicine* (27): 612-616.

Wörle-Knirsch J. M., Pulskamp K., Krug H. F. (2006) Oops they did it again! Carbon nanotubes hoax scientists in viability assays. *Nano Letters* (6): 1261-1268. doi: 10.1021/nl060177c.

Xia T., Kovochich M., Liong M., et al. (2008) Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties. *ACS Nano* (2): 2121-2134.

Yu L.-P., Fang T., Xiong D.-W., et al. (2011) Comparative toxicity of nano-ZnO and bulk ZnO suspensions to zebrafish and the effects of sedimentation,  $\cdot\text{OH}$  production and particle dissolution in distilled water. *Journal of Environmental Monitoring* (13): 1975-1982. doi: 10.1039/c1em10197h.

Zimmermann Y. S., Schäffer A., Hugli C., Fent K., Corvini P. F.-X., and Lenz M. (2012) Organic photovoltaics: Potential fate and effects in the environment. Submitted.

## 7 Appendices

### 7.1 Appendix A: Data sources

#### Database and assumption for the calculation of the electricity production for the LCA Scenarios

	Roof top application	Source	This study façade application	Source
Electricity generation with thin film	per kWp: Min: 665 kWh/yr Max: 1099 kWh/yr Average: 878 kWh/yr	www.sonnenertrag.eu. Plants build in 2009. Electricity production 2010 and 2011.	per kWp: Min: 466 kWh/yr Max: 769 kWh/yr Average: 615 kWh/yr	Conversion roof top to façade factor 0.7 (sunrise toolbox.xls)

### 7.2 Appendix B: LCA results

#### Initial results of LCA for OPV production

Indicator	OPV Total	Encapsulation	Transparent Electrode	HBL	Active layer	Primary electrode	Buffer layer	EBL
CED total in MJ-eq	180.3	28.2	44.8	8.61	10.1	36.2	8.37	32.1
IPCC 2007: GWP 100a in kg-CO <sub>2</sub> eq	8.58	1.17	2.1	0.43	0.45	2.07	0.27	1.59
Recipe (H/A) World, Total in points	1.39	0.16	0.28	0.046	0.054	0.59	0.041	0.17
Recipe (H/A) World, Ecosystems in points	0.04	0.0048	0.0089	0.0017	0.0017	0.0093	0.0011	0.0062
Recipe (H/A) World, Human Health in points	0.88	0.066	0.16	0.023	0.023	0.48	0.14	0.085
Recipe (H/A) World, Resources in points	0.47	0.085	0.11	0.022	0.029	0.097	0.026	0.075

**LCA scenario of windows retrofitted with OPV**

Indicator	OPV	a.s.i	CIS	Cd-Te
Cumulative energy demand: total, total in MJ-eq	0.945000	1.279000	1.396000	0.867000
IPCC 2007: climate change, GWP 100a in kg-CO <sub>2</sub> eq	0.053200	0.073000	0.086500	0.055800
Recipe (H/A) World, Total in points	0.009530	0.009840	0.010800	0.008360
Recipe (H/A) World, Ecosystems in points	0.000248	0.000304	0.000355	0.000244
Recipe (H/A) World, Human Health in points	0.006710	0.006000	0.006510	0.005570
Recipe (H/A) World, Resources in points	0.002570	0.003540	0.003900	0.002550

**7.3 Appendix C: Valuation and weighting code for the OHS assessment**

Validation of the amount of handling measures	Points
Insignificant	0
Low	1
Medium	2
High	3

Indicator		Weighting
Incomplete data		0.75
Personal protection	Skin	1.5
	Eyes	
	Respiratory	
REACH registration		0.75

Summed up and normalized values of the indicators	Validation of handling measures
0-0.25	Insignificant
0.26-0.5	Low
0.51-0.75	Medium
0.76-1	High

#### 7.4 Appendix D: Data source and quality for the Life cycle inventory (LCI) by layers

Layers	Contributing Partners	Further Data source	Data Quality
R2R,Production	KONA	(Umweltbundesamt, Berlin, 2003)	+- (no access to data)
Encapsulation (Barrier films)	AMC, FhG, DTF, KONA,SAES	Ecoinvent, (Espinosa N. et al., 2010)	++-
Buffer layer	KONA	Ecoinvent,	++-
HBL	KONA	Ecoinvent, (Espinosa N. et al., 2010)	++-
EBL	KONA, AGFA, BASF	Ecoinvent, (Roes A. L., 2009) (Espinosa N. et al., 2010)	++-
Active layer	KONA	Ecoinvent, (Anctil, 2011), (Espinosa N. et al., 2010)	+-
Transparent electrode	KONA	Ecoinvent, (Espinosa N. et al., 2010)	+-
Primary electrode	KONA,GINK	Ecoinvent (Espinosa N. G.-V. R., 2010)	++-

#### 7.5 Appendix E: Indicators and weighting of the MCDA

Sustainability focus with weighting	Indicators	Weighting of indicators
Environment 48%	Greenhouse Gas Emissions	20.20%
	Ecosystem Damages	7.70%
	Severe Accidents	7.70%
	Waste, in underground depository	6.20%
	Waste, Radioactive	6.20%
Economy 28%	External Costs	6.50%
	Generation Cost	6.50%
	Fuel Price sensitivity	7.00%
	Capital costs	8.00%
Society 24%	Max. Accidental Consequences	12.00%
	Health Damages	12.00%