Paula L. Pedigo
1615 Payne Loop Road
Smiths Grove, KY 42171

August 8, 2025

RECEIVED
AUG 1 8 2025
PUBLIC SERVICE
COMMISSION

Kentucky State Board on Electric Generation
211 Sower Boulevard PO Box 615
Frankfort, KY 40602

Case: Wood Duck Sola 2024-00337

RE: Threats to the waterways and delicate ecosystem – Contaminates, Quality of Life , Health and Economic impact

Dear Commissioners:

I would like to provide the following information on potential contaminates and the economic and quality of life issues this solar project could bring to our residential and farming area. I ask that the Siting Board consider this information with the upmost consideration and admonishment that I am not a scientist, nor does the community advocates have the financial resources to hire expert witnesses. We have worked diligently to learn everything that we can about the solar panels and have finally been given the opportunity to bring our concerns to you and for that, we are grateful and we appreciate your consideration.

We believe the threat of contamination is real and it would have a detrimental impact on the economic viability of our community and our state. We believe it will affect the health and well-being of our community. We believe it could harm Mammoth Cave and the Amish community; as well as, the many people who fish and hunt the land. We believe it will harm our soil, removing the potential for future farming.

On April 15, 2025 Mammoth Cave National Park issued a letter of opposition about the Wood Duck Solar Project. I have attached a copy for reference. The letter addressed batteries as a specific concern, but also addressed in #3, **"any contamination."**

Eventually there was a meeting between Geenex Solar/Wood Duck and Mammoth Cave resulted in a statement by the developer that there **will not be any batteries** in the development. As a community member, I find this hard to believe and have requested via a previous letter that the PSC have this statement verified by an independent engineer and obtain a signed statement from the owner of Geenex, Juergen Fehr. We obviously do not want the letter from Wood Duck as they do not have any financial resources or assets and if they continue as in the past, they will sell the project before it is producing energy.

In the applicant's response to questions (page 133 of response 1), they submitted an email of documentation that they agreed **to stormwater and karst setbacks in their meeting, there is no written record addressing contaminants**. This letter to you is attempting to address what Wood Duck has failed to do. **The facts remain, there are contaminants and heavy metals in solar panels and the potential for rust and corrosion are greatly increased in this area providing a promised threat to the water systems.**

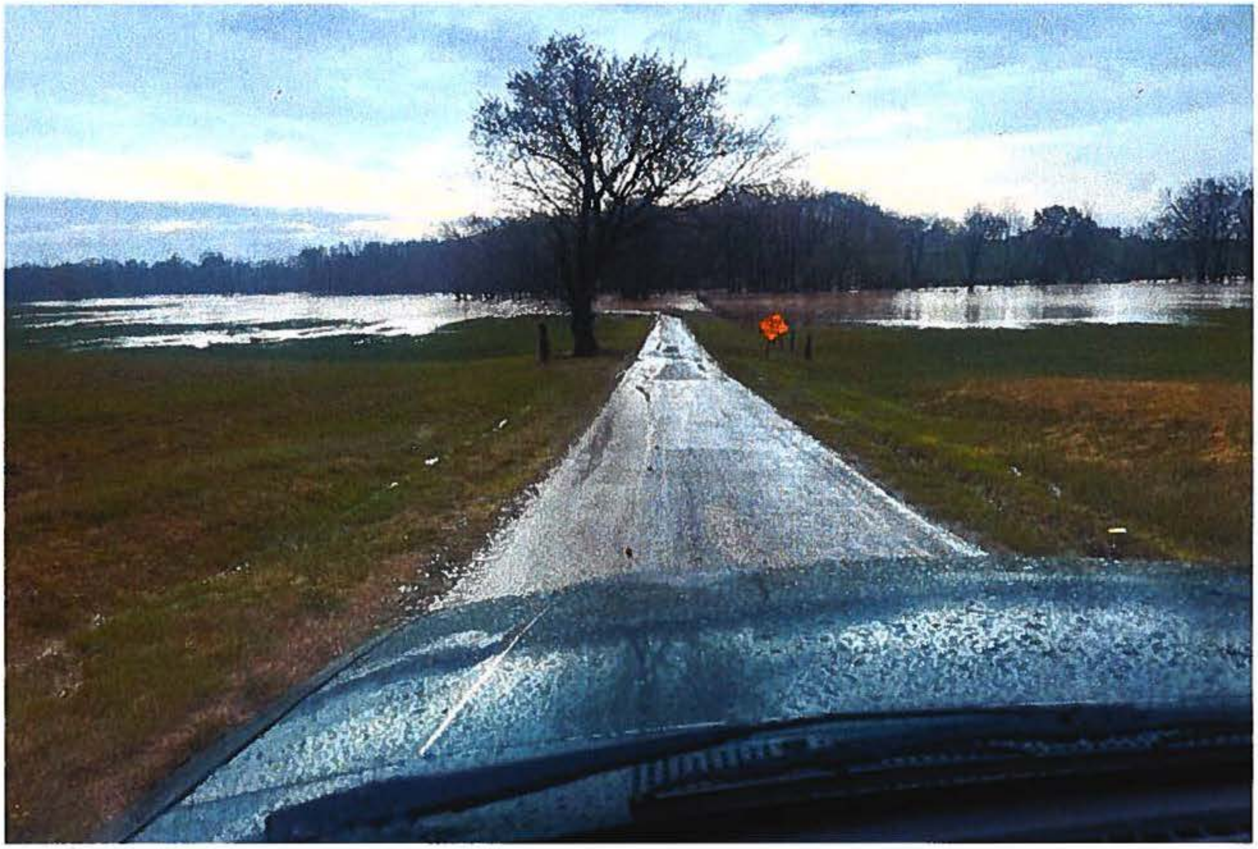
We must address a written response from Wood Duck to County Judge Executive Byrd in May 2025. The question was asked: "***Will your company seek and obtain approval from the US Department of the Interior before further development proceeds?"***

Response: "Wood Duck is committed to seeking and securign approvals from all local, state and federal agencies with permitting authority over the project. As the Department of Interior does not have an approval/disapproval process for project like Wood Duck, no approval can or will be sought."

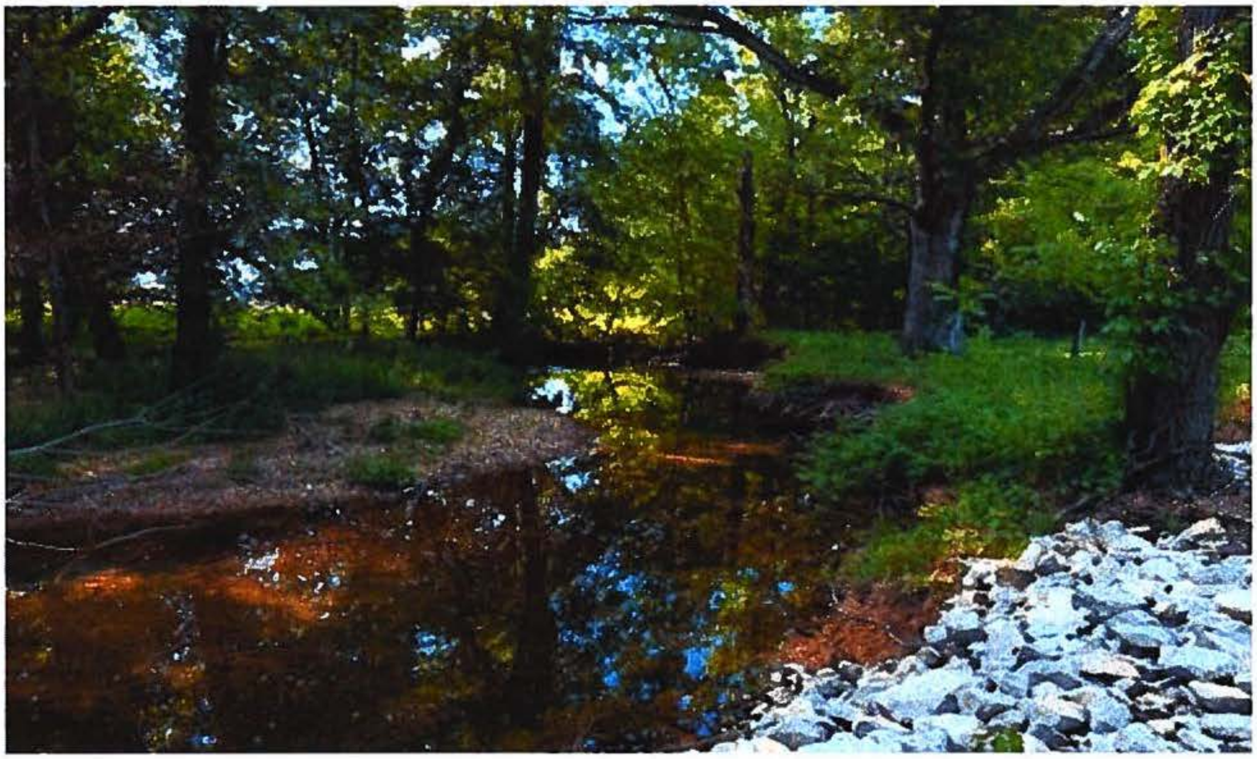
As a community member, I am upset with this response as Mammoth Cave is a national treasurer. It is the economic backbone of Park City and Cave City, with other communities reaping tremendous rewards. It means hundreds of thousands of tourism dollars into our communities. How dare this company come into our area and disrespect the cave!

I live in this community and Little Sinking Creek (WOTUS) floods really bad. There is no mitigation, no plastic screened fences that can protect this watershed and all of the properties around it.

This is a federal watershed that must be protected. I submit to you a photo from the April 2025 flood.



How is normally looks –



Contaminates, quality of life, health and economic impact

Mammoth Cave is mentioned numerous times in the Critical Issues Analysis that the underground water percolates to Mammoth Cave and then to Green River. The report references dye tests, etc. There is no disputing the science. The Wetlands study **identifies 83 underground water tributaries** and over **80 acres in the 100-year flood plain** and the project area is in **Tornado Alley. It includes two creeks that fall under WOTUS.**

Isn't it ironic in the coal mines, we are extracting minerals. In this case, we are trying to protect the mineral of water, not only for the cave, but for every person who lives and farms in this community. These solar panels do not need to sit on top of a precious mineral that they could contaminate.

It is important to note that there are 3 ways in which panels can leach from damaged encapsulation: 1 – panel production 2 – panel use in midlife 3 – end of life disposal. I have not addressed the production phase, only to identify the heavy metals and toxins that are encapsulated inside of the panels: What goes in, must come out. I am concerned with midlife, and what happens to indidivual panels that have advanced to the end of life due to breaks/leachs/damages.

It is also noted that wind and snow loads and temperature changes can cause microcracks or breakage to panels. These undiscovered cracks on panels pose potentiarisks of lead leakage. (Journal of Hazardous Materials, page 5). In 2024 and 2025, Barren County experienced some of the coldest temperatures on record. Wonder if that will break any panels and cause leakage?

Dr. Danna Baxley, Director of Conservation with the Nature Conservancy in Lexington has encouraged the state to develop a policy for alternative energy focusing on non developable land. Farmland and residential communities are off-limits.

The American Farmland Trust encourages communities to find alternative locations to preserve the American farm.

To evaluate **contaminates,** we must consider batteries and all other things that could potentially contaminate the soil and the underground waterways. This project is on karst land and the delicate ecosystem. The panels are a combination of glass, heavy metals and rare earth elements.

We must riase the issue of **fire safety and fire concerns**. The thermal runaway it creates, the flammable gas releases, the explosions, the complex chemical reactions are difficult to extinguish. Fires can happen due to many reasons, everything from glass breakage, overheating, lightning, tornado damage and rodent damage to the cabling and wires, as not all wires are underground.

In Barren County, the panels are so close to neighboring properties, fire transference and damage from heat and water will be guaranteed.

It is also known in Barren County that the majority of this project is on 4 inch waterlines with insufficient fire hydrants. The fire toxins are hazardous and will cause a community to shelter in place. The toxins that go up, will come down and will land on crops, gardens, residential neighborhoods and our creeks and underground waterways.

There is little research on the toxins released when panels burn and the combustible cocktail they create, but communities generally shelter-in-place. With all of the chemicals encapsulated into the panels, those chemicals are being released.

This illustration from the Journal of Clearer Production shows the water, soil and underground waterways and just how closely they are aligned. This would apply to any toxin that could leak and/or leach from any product in the development whether a battery, a panel, rust from metal, etc.

performance of the energy production must be considered but also the imposed heat stress on the connections and inverters and other parts of the array must be noticed. Therefore, heatwaves, wildfires and unusual temporary hot climate situations can easily increase the temperature of the parts of the panel surfaces, which are already at a thermally excited state. In this way, an unpredictable area of the PV module may have the potential to ignite and start a fire.

4. Fire characteristics

Once ignited by an external fire source or a system fault, PV panels burn since they are combustible. PV panels are usually layered and made of silicon as semiconductors and other layers such as PET (polyethylene-vinyl acetate), TPT (tedlar-polyester-tedlar), EVA (ethylene-vinyl acetate) and some cover layers etc. Each of these materials contributes to the fire characteristics and smoke/toxic gas emissions, affecting people and the environment. A schematic of various impacts associated with a PV fire on the immediate environment is illustrated in Fig. 3. The main aspects of fire production are:

a) Flame: the extent of the flame propagation depends on the thermal properties of the burning PV and environmental conditions such as air temperature and wind affecting the burning.
b) Emissions: this varies with the PV type and burning rate. For instance, the composition of gas effluents (CO, CO_2 and toxic gases) is completely different for the PV type and materials used for back-sheets or cover layers.
c) Fire residues and debris: the amount and the toxicity of the fire residues is different for each of the burnt specimens. Therefore, extensive and comprehensive investigations and fire tests are required.
d) The interaction of water from the suppression system and the combustion residues: This is a critical point to be considered while it seems that there have not been enough studies conducted on the effectiveness of the use of water for putting out PV fires.
e) Smoke and its distribution: One of the major and most visible and sensible outcomes of a fire incident is smoke. In some stages of ignition, there is no visible flame, but smoke is produced. This can lead to the degradation of air quality when there is poor ventilation.

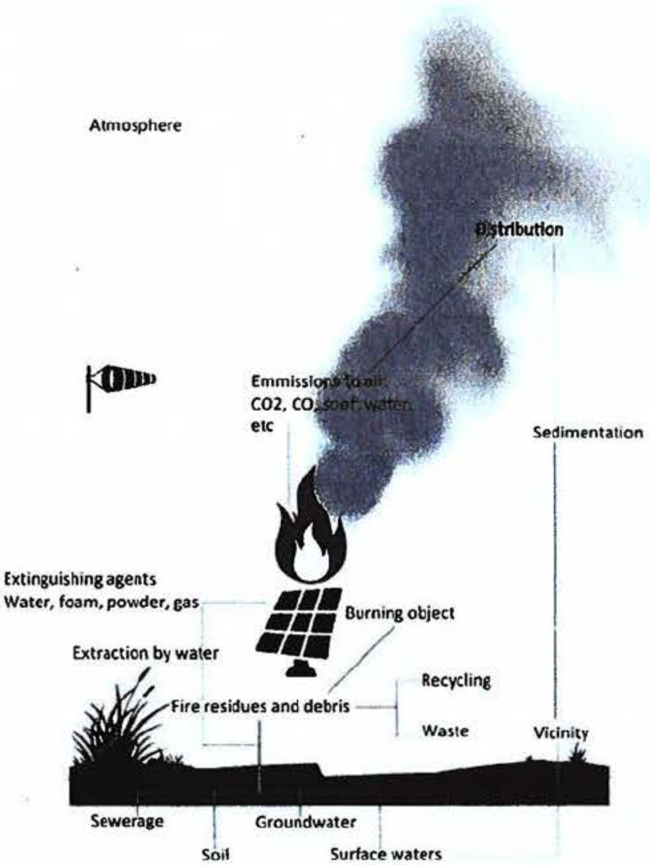
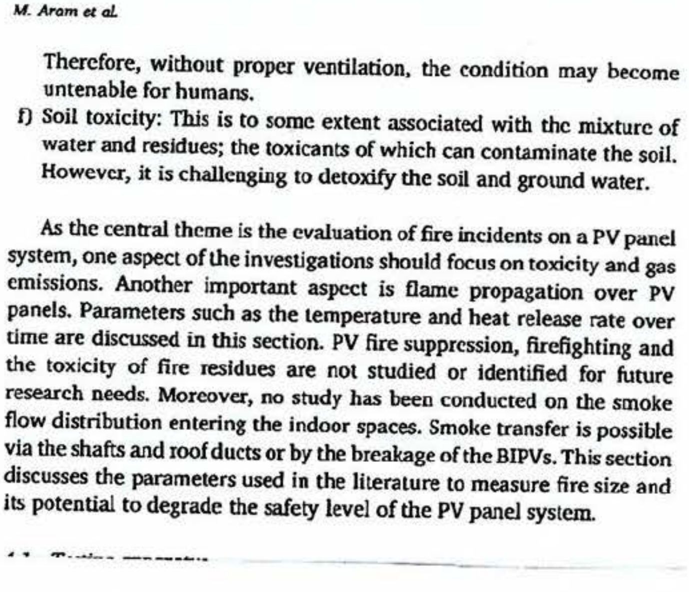


Fig. 3. Illustration of environmental aspects associated with a fire event of PV.



M. Aram et al.

Therefore, without proper ventilation, the condition may become untenable for humans.

f) Soil toxicity: This is to some extent associated with the mixture of water and residues; the toxicants of which can contaminate the soil. However, it is challenging to detoxify the soil and ground water.

As the central theme is the evaluation of fire incidents on a PV panel system, one aspect of the investigations should focus on toxicity and gas emissions. Another important aspect is flame propagation over PV panels. Parameters such as the temperature and heat release rate over time are discussed in this section. PV fire suppression, firefighting and the toxicity of fire residues are not studied or identified for future research needs. Moreover, no study has been conducted on the smoke flow distribution entering the indoor spaces. Smoke transfer is possible via the shafts and roof ducts or by the breakage of the BIPVs. This section discusses the parameters used in the literature to measure fire size and its potential to degrade the safety level of the PV panel system.

A fire will deposit toxins in the ground and the soil will need to be removed immediately to secure our residential and farming community. How can the community be assured that Wood Duck will be responsible to this **haz mat situation**? What if they sell to a company who isn't responsive and we are left with contaminated soil that washes to other properties? What if it does contaminate Mammoth Cave?

When studying the toxins within solar panels, I read the **differences between "leak" and "leaching."** In solar panels, "leak" generally refers to the unintended flow of water, potentially causing roof damage or electrical issues, while "leaching" refers to the release of hazardous substances from the panel, typically due to damage or improper disposal.

Leak in Solar Panels: **Definition:** A leak in a solar panel system refers to the unwanted intrusion of water, usually due to improper sealing or installation issues around the mounting hardware.

Causes:

- **Improper sealing:** Gaps or poorly sealed areas around mounting brackets or other penetrations can allow water to seep in, especially during rain or snow.
- **Damaged flashing:** Flashing, which is used to direct water away from roof penetrations, can be damaged during installation or deteriorate over time, leading to leaks.
- **Incorrect installation:** Mounting brackets that are too tight or too loose can crack the roofing material or shift, creating paths for water to enter.
- **Interrupted water flow:** Solar panels or mounting systems can sometimes interfere with the natural flow of water off the roof, causing pooling and potential leaks.

- **Consequences:**

Roof damage, structural issues, electrical hazards, and reduced panel efficiency can result from leaks.

Leaching in Solar Panels: Leaching in solar panels refers to the release of hazardous materials from the panel's components into the environment, typically due to panel damage or improper disposal. As we have recently learned, solar panels are breaking for no reason, except the glass is too thin. They also break from lightning, hail, overheating, animal damage, gun shot damage, tornados, etc.

Causes:

- **Panel damage:** Cracked or broken panels, especially those with compromised seals, can allow rainwater to contact and dissolve hazardous materials within the panel, such as lead or cadmium.
- **Improper disposal:** Solar panels ending up in landfills can leach hazardous materials into the soil and groundwater if not handled properly.
- **Consequences**: Potential contamination of soil and water sources with toxic materials.
- **Safety:** Properly installed and functioning solar panels are generally considered safe and do not leach hazardous materials **under normal operating conditions**, according to the U.S. Environmental Protection Agency. The materials are typically encapsulated in glass and other non-reactive substances. But, what if normal fails and out of the 204,525 panels, we get a batch that is inferior? What happens if the glass is thin and they break and shatter and the leaching begins before the solar company even knows they are broken.

According to the leases signed between Wood Duck and the landowners, the landowner cannot enter the locked/fenced facilities. So, there will be no random checking of panels.

List of contaminates in a solar system:

1. Batteries for energy storage
2. Batteries for the racking systems
3. Glass shards
4. Heavy metals inside of the panels including: (not a complete list)
    - Lead
    - Silicon
    - Ethylene Vinyl Acetate
    - Cadmium
    - Silver
    - Gallium
    - Phosphorus
    - Copper
    - Cadmium Telluride

5. Metal racking system frames
6. Metal fence wire
7. Metal posts
8. Wood posts
9. Rubber wire conduit
10. Fire Toxins
11. Concrete
12. Gravel

According to the decommissioning plan submitted with the application, Wood Duck is going to have at least 204,525 solar panels with 2,351 tracking system metal frames, over 28,512 metal posts, 159,740 linear feet of fences, 59,141 linear feet of cables and conduits. There is no estimate provided for fence posts, whether metal or CCA treated posts.

Batteries for Energy Storage

Solar batteries, particularly lithium-ion batteries, can leak. Leakage can be caused by various factors, including overcharging, overheating, physical damage, and aging. Proper storage, handling, and maintenance are crucial to prevent leakage and ensure battery safety and longevity. Where are these batteries going to be stored and who is checking them on a daily/weekly basis to ensure there are no problems? Are these going to be in the 35 inverter stations? How are the inverter stations going to be cooled?

Lithium-ion batteries are commonly used due to their high energy density, long lifespan, and relatively low maintenance requirements. Lead-acid batteries are also an option, particularly for those seeking a more affordable solution. What are the dangers for these?

The community does not know the types of batteries that will be used.

Causes of Leakage:

- **Age and Degradation:** Like any battery, solar batteries age and degrade over time, leading to a decrease in stability of internal components and potential leakage.
- **Overcharging:** Overcharging, often due to a faulty battery management system (BMS) or improper configuration, can cause overheating, gassing, and eventually leakage.
- **Physical Damage:** Damage to the battery casing, such as from impacts or improper handling, can compromise the seals and lead to leaks.
- **Improper Maintenance:** Poor maintenance practices, such as using incorrect charging methods or neglecting regular inspections, can also contribute to leakage.

- **Electrolyte Leakage:** Electrolyte leakage, especially in older batteries or those subject to harsh conditions, can cause corrosion and further damage to the battery and surrounding components.

Consequences of Leakage:

- **Reduced Battery Performance:** Leaks can significantly reduce the battery's capacity and overall performance.
- **Safety Hazards:** Leaked battery acid or other chemicals can be corrosive and pose health and safety risks, including burns and electrical faults.
- **Property Damage:** Leaks can damage surrounding components, including the battery enclosure, wiring, and other equipment.

As of this writing, the developer has **not provided to the community** the number and size of batteries that will be used in the development or where they will be located. There is no plan for frequent observation management by the developer.

Batteries in the tracking systems

To move solar panels, motors and batteries are needed to create a solar tracking system. The motors, often DC motors, adjust the panel's position to follow the sun, maximizing energy capture. Batteries store the energy generated by the panels, allowing the system to operate even when the sun isn't shining. A charge controller regulates the power flow between the panels, batteries, and motor.

Motors:

DC Motors: Common choice for solar panel tracking, available with or without gearboxes.

Brushless DC (BLDC) Motors: Versatile and suitable for various tracking applications.

Motor Selection: Consider factors like torque, speed, and voltage requirements based on the solar panel size and tracking system design.

Motor Control: PWM (Pulse Width Modulation) controllers can be used to adjust motor speed, providing precise control.

As of this writing, the developer **has not provided to the community** the number and size of batteries to be used in the tracking systems. Is it one per panel? Who is responsible for inspections? How long do they last? What is the maintenance and replacement schedule? Will they be recycled? Please make that a requirement.

Glass shards : There has been much written about glass shards, the most notable from Michigan State Representative Cam Cavitt who talks about glass shards in his district that grow potatos for the potato industry. He states that farmers in his district have received letters from the potato industry telling the farmers that they can NEVER grow potato crops on land where solars have been.

While potatoes grow beneath the surface, it can be inferred that grass shards can reach the leaves and roots of soybeams and the stalks of corn and be inhaled by large combines and harvesting machinery which will contaminate the entire crop and no one would know. But MOST importantly, it can reach the **gardens of neighbors and ruin their potatoes, beets, carrots and basically anything that a piece of glass could adhere to.** It could cut the feet of the little children walking in their yards or playing in the creeks. The shards are also a risk to animal feet and the potential of injesting a shard in water or food.

With the flooding in this area, especially along Little Sinking Creek, a WOTUS, the glass could end up any where. Roads, yards, gardens, crops, livestock pins and there is documented research the panels are breaking from Texas to Thailand. (see attached article)

Here is the statement from the Potato Growers of Michigan, which applies directly to Barren County, Kentucky. This could devastate our agriculture industry, not only to the farmers, but to the tenant farmers and those who participate in share-cropping. It will affect our families who raise gardens to feed their families.

6. The following is a public statement from the Potato Growers of Michigan, Inc. on Solar Energy Development and Land Use. It is a good summary of this important issue.
   "The Potato Growers of Michigan, Inc. (PGMI) recognizes the growing role of renewable energy in our state's future and supports the rights of landowners to make decisions about how their property is used. As strong proponents of personal property rights, we respect each landowner's freedom to enter into agreements that align with their values and needs. That said, PGMI believes solar energy development must be approached thoughtfully, with a clear focus on responsible siting and long-term land use impacts—especially when productive farmland is involved. **We urge policymakers, developers, and communities to prioritize solar siting on rooftops, industrial lands, and other areas not well suited for farming.** With smart planning, it is possible to advance clean energy goals while preserving Michigan's high-quality agricultural soils for future food production. Organizations like the American Farmland Trust have outlined principles for "smart solar" development that align energy generation with land stewardship and food security—an approach we strongly support. **One critical concern relates to food safety. When solar panels and systems are eventually removed, small fragments of plastic and metal may remain in the soil. For crops like potatoes, which grow underground, this poses a unique and serious risk. Tuber vegetables can readily engulf foreign objects, creating contamination hazards that impact not just growers, but also processors and consumers. Ensuring clean, safe soil is critical for maintaining the integrity of Michigan's food supply.** Additionally, we are deeply concerned about the use of federal subsidies by energy companies to secure land contracts. These subsidies allow companies to offer prices that are up to ten times higher than fair market value, using taxpayer dollars to artificially inflate land prices. This practice creates an uneven playing field, making it nearly impossible for farmers—particularly beginning and next-generation farmers—to compete for farmland. It also risks long-term harm to Michigan's agricultural economy and land access. PGMI supports a balanced approach to renewable energy development—one that respects private property rights, protects farmland, ensures food safety, and uses public funds responsibly. PGMI urges policymakers, local governments, and energy developers to work collaboratively with the agricultural community to ensure that renewable energy solutions are implemented in ways that protect farmland, promote food safety, and sustain our rural economies for generations to come." — Potato Growers of Michigan, Inc." (92)

Contaminates for soil and waterways

July 28, 2025 - PV Magazine wrote an article about how **solar panels are breaking by the thousands all over the world** and they are breaking for no reason other than they are too thin. Thousands are breaking. The Barren County project includes over 204,000 panels, so it will be millions of glass squares that can break damaging our soils, waterways, our way of life and injuring people and animals.

This creates a very dangerous situation for Barren County. As noted in previous research, this is very much a residential and agricultural community which means people, crops, gardens and livestock are in the project area. It is also in an area with a lot of flooding and underground water systems. Based on the unique and delicate ecosystem in this area, this project should be denied for the potential threats and econonic hardships it will create. For example, if panels break and glass shards are washed to an Amish community, there goes their food supply for now, their food supply for winter and their ability to see vegetables for income. This is a tremendous economic hardship.

Chemicals and heavy metals inside of solar panels (not a complete list)

- Lead
- Zinc
- Silicon
- Ethylene Vinyl Acetate
- Cadmium
- Silver
- Gallium
- Phosphorus
- Copper
- Cadmium Telluride

Lead: The Siting Board was provided a copy of the installation manuel from Canadian Solar with the solar panel make and model that Wood Duck has said they are going to use. Now, I'm sure Wood Duck will change the model since the fact LEAD is in the panels and that has been exposed to the community. What is the mitigation plan that Wood Duck has to check for lead and when identified, how will the soil be removed and replaced and in what time frame?

I ask the siting board to do a thorough review of the model of the panels and have an independent scientist/engineer study what chemicals are encapsulated in the panels and what happens when the break, leak, leach, catch fire and are disposed of which requires transporting th panels out-of-state as Kentucky does not have a landfill to accept them.

An interesing quote from the Journal of Hazardous Materials:

"Given an average panel lifetime of 25 years, a dramatic increase of exhausted PV modules will turn into PV waste by 2025. However, PV panels may suffer ***from incompetent installation, degradation of anti-reflective coating (which is Zinc Oxide), glass***

***breakage*, microcracks in interconnectors and other damages even befor reaching their warranty lifetime,** and those cannot be repaired will participate in PV waste stream ahead of the normal lifetime. In fact, the amount of PV waste is increasing rapidly in recent years, whereas, the majority of end-of-life modules are currently dumpted in landfills because of little economic incentive to collect and recycle them." Page 3*

We live in Tornado Alley and can expect storms and hail. Yet, there are many reasons the systems fail. How can the community reasonably expect Wood Duck to be there to inspect for issues and respond immediately to protect our community. We can't.

We do not feel it will be safe for the residential and farming community and ask the PSC/Siting board to deny this project. Not feeling safe is a health concern and a reduction in daily quality of life.

The average amount of lead in a panel is 12-15 grams. This project will have 204,545 panels, so over 3,068,175 grams of lead. Other research says a 60-cell panel contains 10 grams of lead. (Journal of Hazardous Materials, p. 3). Either one is a significant amount of exposure to lead and a potential health threat to all who live in our community.

"The lead taken by plants deposited in roots, stems and leaves, and demonstrated a noticeable difference compared to plants gorwn in natural soil, indicating a bioaccumulation potential of **lead in food chains**." (Journal of Hazardous Materials, page 5)

I have attached several articles relating to lead from the Journal of Hazardous Materials, Applied Geochemistry, World Journal of Biolgoy Pharmacy and Health Sciences, Environmental International, and Science of the Total Environment. These relate to various heavy metals and contimanants and I have highlighted sections of interest. I hope that you will review them and consider the **science and not the propaganda** from the solar industry.

Cadmium Telluride: is a stable crystalline compound formed from cadmium and tellurium. It is mainly used as the semiconducting material in cadmium telluride photovoltaics and an infrared optical windown. It is usally sandwiched between cadium sulfide to form a p-n junction solar PV cell.

Cadmium Telluride is used to make thin film solar cells. They are among the lowest-costs types of solar cell and has dominated some markets. It can be alloyed with mercury and zinc for infrared detection. It has passed some tests in the European market, tests which America does not have, and with the non regulation of solar panels, it is unknown where the panels may be made. The ones mentioned by Wood Duck are made by Canadian Solar which uses child labor in

China. Recently research has shown China has been purchasing solar panels from other third world countries.

WIKIPEDIA states: "According to the classification provided by companies to the European Chemicals Agency (ECHA) in REACH registration, it is still **harmful to acquatic life** with long lasting effects. Additionally, the classification provided by companies to ECHA notifications classifies it **as very toxic to acquatic life with long lasting effects, very toxic to acquatic life, harmful if inhaled or swallowed and is harmful in contact with skin."**

A Google search and AI reveals the following: Cadmium telluride (CdTe) is a semiconductor material, primarily known for its use in thin-film solar cells. It is a compound formed from the elements cadmium and tellurium, and its properties make it suitable for converting sunlight into electricity with high efficiency. While CdTe solar cells offer advantages in terms of manufacturing speed and lower energy requirements compared to silicon, they also present environmental concerns **due to the toxicity of cadmium.**

Here's a more detailed look at cadmium telluride: Key Properties and Applications:

- **Semiconductor:** CdTe has a direct bandgap of about 1.5 eV, which is ideal for solar energy conversion. This means it can efficiently absorb a large portion of the solar spectrum.

  Thin-film Solar Cells: CdTe is a key material in thin-film solar technology, offering advantages like high efficiency, low manufacturing energy requirements, and a shorter energy payback time.

  High Optical Absorption: CdTe has a high optical absorption coefficient, allowing for the use of thinner layers in solar cells, which reduces material costs and manufacturing complexity.

  High Temperature Stability: CdTe solar cells tend to maintain their efficiency at higher temperatures, unlike some other solar cell technologies.

  Low-Light Performance: CdTe cells can also perform well in low-light conditions, which is beneficial in various geographical locations and weather conditions.

  Infrared Optical Window: CdTe is also used in infrared optical windows due to its specific optical properties.

Environmental Considerations:

Toxicity of Cadmium: Cadmium, a component of CdTe, is a **toxic heavy metal**, and its release into the environment can pose risks **to human health and ecosystems.**

Leaching Potential: Studies have shown that CdTe can leach cadmium into the environment under certain conditions, particularly in landfill scenarios, which applies in the event of a leak or leaching or a natural disaster.

Recycling Efforts: Due to the toxicity of cadmium, recycling CdTe solar panels is crucial to minimize environmental impact. But there are few places to recycle and it is costly.

Cadmium telluride. We ask the siting board to consider the broad overview and the fact this is a heavy metal and can be damaging to our environment and our economic viability.

There are also several publications about the carcinogenic affects of Cadmium. I have listed just two.

Cadmium and Its Epigenetic Effects

Authors: B. Wang[1], Y. Li[2], C. Shao[3], Y. Tan[4] and L. Cai[5] **Source:** Current Medicinal Chemistry, Volume 19, Issue 16, Jun 2012, p. 2611 - 2620

Cadmium (Cd) is a toxic, nonessential transition metal and contributes a health risk to humans, including various cancers and cardiovascular diseases; however, underlying molecular mechanisms remain largely unknown. Cells transmit information to the next generation via two distinct ways: genetic and epigenetic. Chemical modifications to DNA or histone that alters the structure of chromatin without change of DNA nucleotide sequence are known as epigenetics. These heritable epigenetic changes include DNA methylation, post-translational modifications of histone tails (acetylation, methylation, phosphorylation, etc.), and higher order packaging of DNA around nucleosomes. Apart from DNA methyltransferases, histone modification enzymes such as histone acetyltransferase, histone deacetylase, and methyltransferase, and microRNAs (miRNAs) all involve in these epigenetic changes. Recent studies indicate that Cd is able to induce various epigenetic changes in plant and mammalian cells in vitro and in vivo. Since aberrant epigenetics plays a critical role in the development of various cancers and chronic diseases, Cd may cause the above-mentioned pathogenic risks via epigenetic mechanisms. Here we review the in vitro and in vivo evidence of epigenetic effects of Cd. The available findings indicate that epigenetics occurred in association with Cd induction of malignant transformation of cells and pathological proliferation of tissues, suggesting that epigenetic effects may play a role in Cd toxic, particularly carcinogenic effects. The future of environmental epigenomic research on Cd should include the role of epigenetics in determining long-term and late-onset health effects following Cd exposure. © Bentham Science Publishers

Gene Expression and Transcriptome Profiling of Changes in a Cancer Cell Line Post-Exposure to Cadmium Telluride Quantum Dots: Possible Implications in Oncogenesis by Mohammed S. Aldughaim, Mashael R. Al-Anazi, and others. Cite

Abstract

Cadmium telluride quantum dots (CdTe-QDs) are acquiring great interest in terms of their applications in biomedical sciences. Despite earlier sporadic studies on possible oncogenic roles and anticancer properties of CdTe-QDs, there is limited information regarding the oncogenic potential of CdTe-QDs in cancer progression. Here, we investigated the oncogenic effects of CdTe-QDs on the gene expression profiles of Chang cancer cells. Chang cancer cells were treated with 2 different doses of CdTe-QDs (10 and 25 µg/ml) at different time intervals (6, 12, and 24 h). Functional annotations helped identify the gene expression profile in terms of its biological process, canonical pathways, and gene interaction networks activated. It was found that the gene expression profiles varied in a time and dose-dependent manner. Validation of transcriptional changes of several genes through quantitative PCR showed that several genes upregulated by CdTe-QD exposure were somewhat linked with oncogenesis. CdTe-QD-triggered functional pathways that appear to associate with gene expression, cell proliferation, migration, adhesion, cell-cycle progression, signal transduction, and metabolism. Overall, CdTe-QD exposure led to changes in the gene expression profiles of the Chang cancer cells, highlighting that this nanoparticle can further drive oncogenesis and cancer progression, a finding that indicates the merit of immediate *in vivo* investigation.

"The fact that cadmium can be washed out of solar modules by rainwater is increasingly a concern...We estimate there are 100,000 pounds of cadmium contained in 1.8 million panels...leaching from broken panels damaged during natural events-hail storms, tornadoes, hurricanes, earthquakes, etc. – and at decommissioning is a big concern."

Cadmium is water soluble and "can be almost completely washed out over a period of several months by rainwater."

"There is real-world precedent for this concern. A tornado in 2015 broke 200,000 solar modules at southern California solar farm Desert Sunlight. Any modules that were broken into small bits of glass had to be swept from the ground, so rocks and dirt got mixed in that would not work in recycling plans that are designed to take modules." (Source: If solar panels are so clean, why do they produce so much toxic waste by Michael Shellenberger, Forbes, May 23, 2018)

Gallium: particularly in gallium arsenide (GaAs) solar cells, is relatively stable and resistant to leaching under normal conditions. However, under specific conditions like those found in landfill scenarios or during recycling processes, gallium can be mobilized and potentially leach out.

CIGS Solar Cells: Copper indium gallium selenide (CIGS) thin-film solar cells also contain gallium. Recycling these cells requires careful management to recover valuable metals like indium and gallium.

Simulated Acidic Conditions: Research has shown that the leaching of gallium and other metals from thin-film solar panels increases with higher acid concentrations and longer contact times with the acid.

Metal Recovery: Effective recycling of solar panels is important for recovering valuable metals like gallium and indium, which are considered critical resources.

Environmental Concerns: Improper disposal of solar panels can lead to the release **of heavy metals into the environment, potentially causing soil and water contamination**. We acknowledge that it isn't just the improper disposal, but it is the leaking and leaching of the chemicals that can happen any time there is breakage.

A breakage is a race against time to get them removed from the properties to ensure the chemicals do not leach into the soil and the waterways. With 2,300 acres of solar panels, residents do not believe the company can guarantee that our community will be protected.

Silicon solar panels can leak into underground water. Some components within solar panels, like those in perovskite solar cells can contain toxic materials that could leach into the environment if the panels are damaged.

Toxic Materials in Solar Panels:

Perovskite Solar Cells: Some types of solar panels, like perovskite solar cells, contain **lead**, which can be harmful if it leaches into the environment.

Other Toxic Materials: Other materials, like **cadmium telluride and copper indium selenide**, can also be found in solar panels and pose environmental risks if they leak according to American Experiment.

3. Preventing Leaks and Protecting Underground Water:

- **Regular Inspections:** Conduct regular inspections to identify and address any potential leaks or damage early on.
- **Choose Reliable Materials:** Select solar panels and mounting hardware made from durable, weather-resistant materials.
- **Proper Sealing:** Ensure all mounting hardware is properly sealed to prevent water intrusion.
- **Responsible Disposal:** When solar panels reach the end of their lifespan, ensure they are disposed of properly to prevent the release of any hazardous materials.

Copper leaching from solar panels is a process where copper components within the panels, like wiring or contacts, release copper ions into the surrounding environment, often due to corrosion or breakdown of protective layers. While copper is generally considered a relatively safe material, excessive leaching can potentially lead to environmental concerns, particularly in the context of end-of-life solar panel disposal.

How Copper Leaching Occurs in Solar Panels:

- **Corrosion:** Solar panels are exposed to various environmental factors like moisture, temperature fluctuations, and pollutants. Over time, these can cause corrosion of the copper components, leading to leaching.
- **Material Degradation:** The materials used in solar panels, such as encapsulants and backsheets, can degrade over time, exposing the copper to the elements and increasing the risk of leaching.
- **End-of-Life Issues:** When solar panels reach the end of their lifespan, they may be disposed of in landfills or other locations. If not properly managed, the leaching of copper from these panels can become a concern.
- **Environmental Impact:** While copper is generally considered a less toxic heavy metal than others like lead or cadmium, **excessive leaching can still contribute to soil and water contamination in certain situations, according to a study on ScienceDirect.com**.

Zinc is a metal used in the production of solar panels. It offers a corrosion-resistant coating and is also used in the creation of components like zinc oxide nanorods. Zinc is a protective coating and is applied as a coating to steel components in solar panels, such as mounting frames and support structures, through a process called galvanization. It helps protect steel from rust and corrosion caused by exposure to the elements, extending the lifespan of the solar panel system.

Zinc Oxide in Solar Panels is a semiconductor material with properties that make it suitable for use in solar cells. It is used as an anti-reflective coating on every solar panel, improving light trapping and reducing reflection losses which enhances light absorption.

Zinc oxide nanoparticles (ZnO NPs) in water can be toxic to crustaceans, potentially impacting their survival, reproduction, and development. Studies have shown that ZnO NPs can accumulate in crustaceans, cause mortality, and affect their behavior and physiology. Different crustacean species exhibit varying sensitivities to ZnO NPs.

- **Toxicity to Crustaceans:** ZnO NPs have been found to be toxic to various crustacean species, including cladocerans (like Ceriodaphnia cornuta and Moina micrura) and copepods (like Tigriopus fulvus and Corophium insidiosum).
- **Bioaccumulation:** ZnO NPs can accumulate in the bodies of crustaceans, potentially leading to adverse effects.
- **Mortality:** Studies have shown that ZnO NPs can cause mortality in crustaceans, with varying LC50 values depending on the species and NP size.
- **Impacts on Reproduction and Development:** ZnO NPs can negatively impact crustacean reproduction, reducing fecundity and affecting hatching rates.

- **Varying Sensitivity:** Different crustacean species have varying sensitivities to ZnO NPs, with some being more tolerant than others.
- **Mechanism of Toxicity:** The toxicity of ZnO NPs to crustaceans is often attributed to the release of zinc ions (Zn2+), which can cause oxidative stress and other cellular damage.
- **Environmental Concerns:** The widespread use of ZnO NPs in various products raises concerns about their potential impact on aquatic ecosystems, particularly crustacean populations. The siting board must consider this fact and the devastation this could cause on Mammoth Cave and the economic impact.

Nanoparticles: An Experimental Study of Zinc Nanoparticles Toxicity on Marine Crustaceans.

General Overview on the Health Implications in Humans by Luigi Vimercati and others, National Institute of Health

Abstract The presence of products containing nanoparticles or nanofibers is rapidly growing. Nanotechnology involves a wide spectrum of industrial fields. There is a lack of information regarding the toxicity of these nanoparticles in aqueous media. The potential acute toxicity of ZnO NPs using two marine crustacean species: the copepod *Tigriopus fulvus* and the amphypod *Corophium insidiosum* was evaluated. Acute tests were conducted on adults of *T. Fulvus* nauplii and *C. insidiosum*. Both test species were exposed for 96 h to 5 increasing concentrations of ZnO NPs and $ZnSO_4H_2O$, and the endpoint was mortality. Statistical analysis revealed that the mean LC50 values of both ZnO NPs and $ZnSO_4H_2O$ (ZnO NPs: $F = 59.42$; $P < 0.0015$; $ZnSO_4H_2O$: $F = 25.57$; $P < 0.0015$) were significantly lower for *Tigriopus fulvus* than for *Corophium insidiosum*. This result confirms that the toxic effect could be mainly attributed to the Zn ions, confirming that the dissolution processes play a crucial role in the toxicity of the ZnO NPs.
Keywords: nanoparticles, Zinc oxide nanoparticles (ZnO NPs), toxicity, marine crustaceans, health risks, workers, consumers, general population

Are Solar Panels Hazardous Waste?

Yes, they contain metals, like lead and cadmium, zinc, zinc oxide and others which are harmful to human health and the environment at high levels.

Heavy metals like lead and cadmium may be leachable at such concentrations that waste panels would fail the toxicity characteristic leaching procedure (TCLP), a test required under RCRA to determine if materials are hazardous waste. (source epa.gov -updated May 2, 2025)

Does Zinc rust? Rust is a phenomenon that occurs as a result of the oxidation process, which is when a metal like steel comes into direct contact with moisture (even moisture in the air) for long periods of time. Because Zinc acts as a barrier between that moisture and the metal itself, it essentially stops the underlying metal from rusting by sacrificing itself. Zinc is more corrosive and prone to rust than the types of materials it is commonly used to protect. Because of that, the Zinc coating will rust far faster than the iron or steel." (Illinois, Pulley and Gear.com, 10-4-2022)

"If you have an item that is zinc plated that is also permanently outdoors, it could be exposed to lengthy periods of rain or intense humidity. Both of these things will cause rust to form faster than they would in a dryer environment." (Illinois, Pulley and Gear.com)

Zinc Oxide is found in paint, rubber, soaps, batteries, electrical equipment. Zinc plating is a technique used to protect other types of metal from rusting.

Zinc oxide (ZnO) is sometimes applied to the exterior of solar panels. It's used in coatings to protect the panels from environmental damage and improve their performance by reducing light reflection and enhancing light absorption. Zinc oxide nanoparticles can be incorporated into protective coatings, helping to extend the lifespan and reduce maintenance costs of solar panels, according to a materials science website.

- **Protective Coating:** Zinc oxide, especially in nanoparticle form, can act as a barrier against UV radiation, moisture, and other environmental factors that can degrade solar panels over time.
- **Improved Efficiency:** By reducing light reflection and increasing light absorption, zinc oxide coatings can boost the overall efficiency of solar panels.
- **Antireflective Properties:** Zinc oxide nanorods, in particular, can act as effective antireflection coatings, helping to trap more light within the solar cell and improving its performance.
- **Durable and Stable:** Zinc oxide-based coatings can enhance the durability and long-term stability of solar panels, potentially reducing the need for frequent replacements.
- **Other Applications:** Zinc oxide can also be used in other parts of solar cells, such as the electron transport layer in organic solar cells.

Zinc Oxide: deadly to crustaceans in the water. Toxic to people and animals.

We must remember that panels will break, they will leak and leach. The threat to the underground waterways, Mammoth Cave, other farmers will harm the economic viability of our agricultural community.

We cannot allow the panels to be installed and then, say, "Oops, they failed the test."

Contaminates for soil and waterways

Metal racking system frames, metal wire and metal posts.

The Wood Duck Solar Project must install wire fences around the solar fields and the substation and according to their decommission plan, it will be over 30 miles of fence and over 28,000 steel piles. Each of the 204,525 solar panels will be on metal frames. All of these are rust buckets.

Wood Duck proposes a combination of "game fence" and chainlink fence, both of which are metal, both of which will rust. There must also be steel posts for the chainlink fence and either metal or wood posts for the game fence. Gates will also be at each location and they should be hot dipped and top line of industrial chainlink.

Regardless, we request that if this project is approved that the siting board require the top grade chainlink and game/woven wire. Some brands rust in 5 years, some will rust in 20 years. We want the top grade, made in the U.S.A., galvanized steel posts hot dipped gates, top grade industrial chainlink.

Galvanized steel will rust. An article printed April 25, 2025 in HLC Metal Parts, titled "Does galvanized steel rust? Zinc is the main chemical for galvanizing steel which helps to protect the steel. It states the air pollution and acid rain accelerate zinc corrosion. "Moisture-rich environments, especially those with high humanity or frequent acid rain, can cause the zinc to corrode more rapidly. Acid rain contains sulfuric or nitric acids that react with zinc wearing away the protective barrier faster than in dry climates."

This article goes so far as to recommend cleaning to maintain galvanized steel. "Dirt, dust, bird droppings, and other debris can trap moisture against the surface, accelerating corrosion. Use mild soap and water for routine cleaning. Rinse thoroughly to remove soap and residues..." If it is tough dirt, a plastic bristled brush and oil such as WD40, olive oil or vegetable oil is recommended for cleaning.

"Galvanized surfaces should be inspected on a regular schedule to spot, scratches, dents, or chips in the zinc coating. Rust stains that may indicate coating failure, white rust (zinc oxide) which appears in high-humidity environments...."

"Galvanized steel that comes into contact with cooper, brass or untreated steel can experience galvanic corrosion, especially in wet environments. Standing water accelerates corrosion-even on galvanized steel." Airborne pollutants or chemicals can accelerate corrosion.

Acid rain in the Mammoth Cave area was recently documented in an article in the Kentucky Lantern on August 1, 2024. Some of this research goes back to the Clean Air Act of 1960 with several states under consent decrees to improve the air quality around the national parks.

The Journal of Hazardous Materials, Volume 426, March 2022 included an article title, "Co-exposurers of acid rain and ZnO nanoparticles accelerated decomposition of aquatic leaf litter."

"The pattern of acid rain...may affect the dissolution activity of dull heavy metals in the aquatic environment and further complicate the ongoing challenge of ecosystem stability and increase risks. This is a very complicated study, but it clearly connects **acid rain and zinc oxide to have adverse effects on aquatic organisms.**

"However, nZnO have been demonstrated to exert adverse effects on a series of aquatic organisms, including microalgae, daphnia, zebrafish and mematode. More importantly, even nanogram quantieis of nZNO per liter would pose a potenital threat to the structure and function of acquatic fungi and eventually damage freshwater functioning."

Now, this study did not evaluate the Kentucky Cave Shrimp. But, we can conclude that the introduction of zinc, zinc oxide and nanoparticles will be deadly to life in the cave, while also continamating the waterways within the project area and beyond to Green River.

The Department of Defense held a Corrosion Conference in 2011 and presented a paper on "Investigation of Corrosion-Resistant Materials for Security Fencing." They studied fuse-bonded PVC, powder-coated galvanized steel, stainless steel, aluminized steel, and other materials in Hawaii, North Carolina and Maine. They seemed to have the best results with fuse-bonded PVC coated galvanized fencing fabrics and anodized aluminum when considering the various sites and making adjustments for coastal and tropic regions. In Barren County, we would need to consider the amount of rain, humidity and acid rain as documented in the Mammoth Cave area.

In Sustainability, there is an article titled, "Environmental Impact of PV Power Systems," by Mladen Bosnjakovic and others, published in 2023. They "studied the potential fate and transport of leached metal contents from photovoltaic systems and estimated the risk to the environment and human health via dermal exposure and ingestion for subgroups of children and adults. Results showed that children were most at risk from **lead**. Children and adults are more at danger from exposure to metals like **cadmium, lead, indium, molybdenum and tellurium** throughout the skin and soil ingestion. In every case, **lead poses a serious cancer risk** while other metals pose an acceptable non-cancer risk through groundwater exposure.

The main materials used in solar cells, including **lead, tin, cadmium, silicon and copper**, are hazardous to human health if released into the environment." P 4.

Environmental International printed an article titled, "The photovoltaic industry on the path to a sustainable future, environmental and occupational health issues" in January 2014 stated, "It's use of potentially toxic substances and manufacturing processes presenting health and safety problems may jeopardize its benefits. "

"In fact, environmental, public and occupational health concerns can be raised in a definitely young and vigorous industry, but which seems more focused on competitiveness and benefits from substantial subsidies for both manufacturers and consumers.

Likewise, other states are starting to sound the alarm about the **damages to the land.**

"Washington State: Solar panels will damage farm soils" Published 9:30 am Thursday, January 25, 2024 By DON JENKINS Capital Press

"The Federal Bureau of Land Management is updating its plan for developing solar energy on Western public lands. The Washington State Department of Agriculture says solar installations **will damage soils**, disputing a claim by an energy company that 1,000 acres of prime farmland in Klickitat County could revert to agriculture in 25 years and be as productive as before.

Agriculture department policy adviser Kelly McLain said Jan. 24 in an email to the Energy Facility Site Evaluation Council that the proposed Carriger solar project near Goldendale **would compact and shade ground, depriving it of sunlight and organic material. The soil may need decades to recover after the solar panels and posts are gone,** she stated. **"Even with decommissioning, WSDA does not expect the ground to meet pre-project agricultural viability.**"

Read more at: https://capitalpress.com/2024/01/25/washington-state-solar-panels-will-damage-farm-soils/

PV Cables: Rubber conduit wire coatings

This project involves thousands of feet of cables and wires. The cables should be UV resistant, weatherproof, flexible and able to withstand high temperatures generated by sunlight and the electrical currents passing through them, insulated and have a low smoke zero halogen.

They are supposed to have LSZH insulation and sheathing materials to lessen the emissions of toxic gasses and smoke in the event of a fire.

PV cables typically use copper conductors for their superior conductivity, flexibility and durability, though aluminum can be used as a more cost-effective option. Some are covered in durable polymers like polyvinyl chloride (PVC), cross-linked polyethylene (SLPE) or halogen free flame-resistant materials.

We must require that Wood Duck has selected cables made from high-quality materials designed for outdoor use, resisting UV radiation, moisture, heat and weathering. Copper conductors with high conductivity and corrosion resistance, along with insulation and sheathing materials for enhanced durability and safety.

Wires must be inspected regularly for signs of wear, damage and deterioration. Wood Duck has not provided any schedules to ensure the public this will be done.

It is also unknown if all wires will be buried or if wires will stretch above ground between the rows. All must be inspected for damage from rodents who can eat the plastic coatings and discarded in a manner to pollute the underground water systems.

In December 2024, Kuka Cable printed an article titled, "Environmental Challenges of PV Cables" in which they discuss that traditional PV cables often use plastic sheaths and insulation materials which have raised environmental concerns. Many use polyvinyl chloride (PVC) as an insulation material and the production and incineration of PVC can release harmful substances such as hydrogen chloride. These substances not only pollute the environment, but also pose potential health risks.

The article addresses the recyclability and biodegradability of the PV cables. Traditional cable materials, primarily plastics and metals are often complex to recycle and costly to process, especially the copper and aluminum.

"Over time, PV cables may experience aging and wear, particularly under extreme weather conditions. Damage to the cable sheath can lead to the leakage of harmful substances of electrical failures. "

In conclusion, As PV power technology becomes more widespread, PV cables, as a core component must address a range of environment issues. The choice of materials, optimization of the production process, and effective disposal management are all critical to reducing the environmental impact of PV cables. To achieve the vision of green energy, the PV cable industry must continuously improve environmental standards, promote the use of more eco-friendly materials and production technologies, and strengthen recycling and waste management. Only through collaborative efforts across the industry can we ensure that PV cables contribute to clean energy utilization without causing additional environmental burden."

Please specify that **all** wire must be removed at the end of the project and recycled, if possible. Also, please stipulate that all wire must be the most eco-friendly as possible and that cost comparisons be provided, as well as an engineer to ensure Barren County gets only the best.

Contaminates for soil and waterways

Also, please provide a contingency response plan by which Wood Duck/Geenex is going to inspect the wire for breakage on a regular basis and provide documentation to local government officials.

As you consider the many chemicals in the panels and the elements used in the construction, it is important to consider the end result. It is highly unlikely that Wood Duck will be around to decommission the land. Barren County's decommission plan does not require a bond or insurance security, so if Wood Duck LLC dissolves, local farmers will be left with fields of solar panels, posts and wire.

Current formulas in the decommissioning plan allows Wood Duck to take a credit for what may be salvageable. This is just an exercise since Barren County does not require a bond or insurance.

It is ridiculous for the state to consider allowing a solar company to calculate credits toward expenditures. Low demand for scrap and the high cost of employing workers to disassemble the aluminum frames and other components will make it difficult to recycle. It is not economical to recycle and it won't be recycled unless it is mandated. The cost to recycle is putting the responsibility on the solar companies and they are at risk for financial failures. Many solar companies go bankrupt each year. The result of bankruptcies is that the cost of managing or recycling **PV waste** will be paid by the landowners or government. In the event of company bankruptcies, PV module producers would no longer contribute to the **recycling cost** of their products leaving landowners or governments to decide how to deal with the cleanup" (Source, Michael Shellenberger, Forbes, May 2018)

Toxins accumulate on the solar panels

Research at the University of Kentucky confirms the composition of material buildup on the solar modules indicate the presence of pollen, ground soil and potentially fly ash on a solar farm in Harrodsburg, KY. "Over time, soiling and volatile organic compound (VOC) materials deposited and formed a thin film cementation on the surface of the solar panels. Base on the surrounding conditions various compounds from the power plant, dust, pollen, fibers, etc. are expected to be in the soiling materials, as well as general air impurities, sulfates, nitrates, organic carbon, elemental carbon, crustal compound found in the central KY region. (Source: Case Study Report: Solar PV Panel Performance and Soiling Analyses of E.W. Brown Solar Facility, University of Kentucky. 2023).

It is well-documented that dust, pollen, mold, leaves, bird droppings, etc. can accumulate on panels reducing the efficiency and increasing the possibility of breakage and a fire. The farmers in the area will produce dust with their equipment and the floating of pesticides can also land on the solar panels.

Contaminates for soil and waterways

These contaminates must be washed off with water and chemicals creating more danger to local water supplies, underground waterways and the quality of life for residents and livestock. Wood Duck/Geenex has not provided any maintenance provisions or inspections for the panels and how they will ensure these issues do not affect local residents.

What is the contaminated soil remediation plan? Do we have one? Will it transfer to new owners?

In my opinion, the transition to green energy has many negative side effects. They require the sacrifice of vast natural areas and pose a serious-long disruption to nearby ecosystems, reducing biodiversity, contributing to climate change, and reducing water quality and availabiilty. Green energy projects may severly dimish the right to a healthy environment and the enjoyment of other human rights by the communities living by the the proximities of the affected area. Communities are deprived of the natural resources, such as fish and freshwater, on which they depend to feed their families.

There are many discussions on the topic to criminalize ecocide which is the extensive damage, destruction, or loss of ecosystmes, resulting in severe harm to the environment. It's essentially the mass destruction of nature, often on an industrial scale and is being considered as a potential international crime.

Does a solar development fall within this definition? Most definitely in the delicate and karst ecosystem of Mammoth Cave.

The concept of "sacrifice zones" by US based environmental justice activists describes places which are disproportionately impacted by environmental contamination and industrial exploitation, often due to socio-economic or political marginalization. This term is now being used to critique the systemic negative impacts associated with large-scale renewable energy projects.

Therefore, based on the contaminants in the panels, batteries and surrounding barriers, it is much preferred that this project is cancelled. The developer has failed to address issues of concern with the community and has eroded public trust. Their flippant regards toward Mammoth Cave should be enough to run them out of our county and state.

Sincerely yours,

Paula L. Pedigo

Attachments: Toxins and health
Mammoth Cave Letter

Articles:

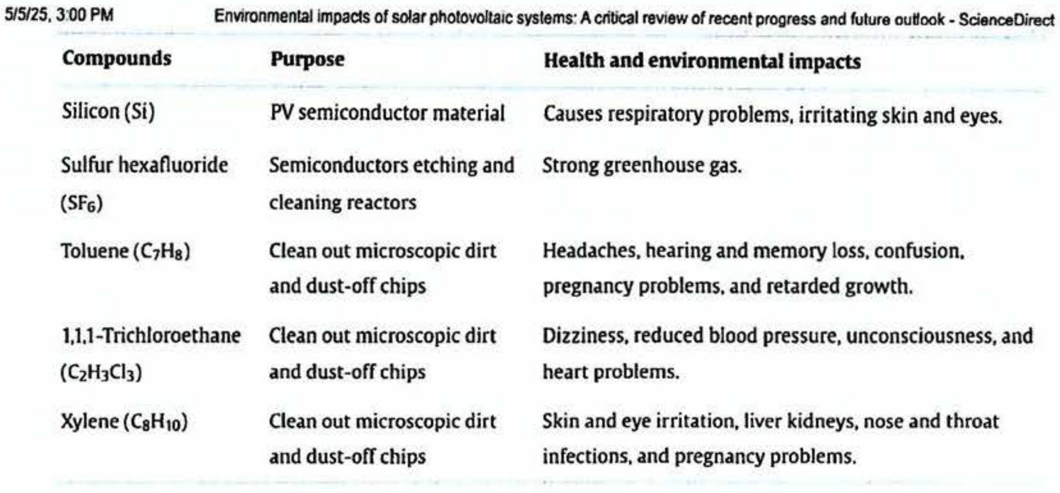
- "Potential lead toxicity and leakage issues on lead halide perovskite photovoltaics," Journal of Hazardous Materials.
- "Release of metal pollutants from corroded and degrade thin-film solar panels extracted by acids and buried in soils," Applied Geochemistry.
- "Co-exposures of acid rain and ZnO nanoparticles accelerate decomposition of aquatic leaf matter,"Journal of Hazardous Materials.
- "A review of life cycle environmental impacts of emerging solar cells," Science of the Total Environment.
- "The photovoltaic industry on the path to a sustainable future- Environmental and occupational health issues," Environmental International.
- "Assessing the environmental health and safety risks of solar energy production," World Journal of Biolgoy Pharmacy and Health Sciences.
- "CEA recommendations for mitigating glass breakage." PV Magazine, July 28, 2025
- "A review on life cycle environmental impacts of emerging solar cells." Science of the Total Environment. September 7, 2023.

Advocates for Farm Preservation – Questions or for a letter to sign: Paula [redacted]

Table 5. Health and environmental impacts of the chemical compounds involved in PV cells' manufacturing (Aman et al., 2015).

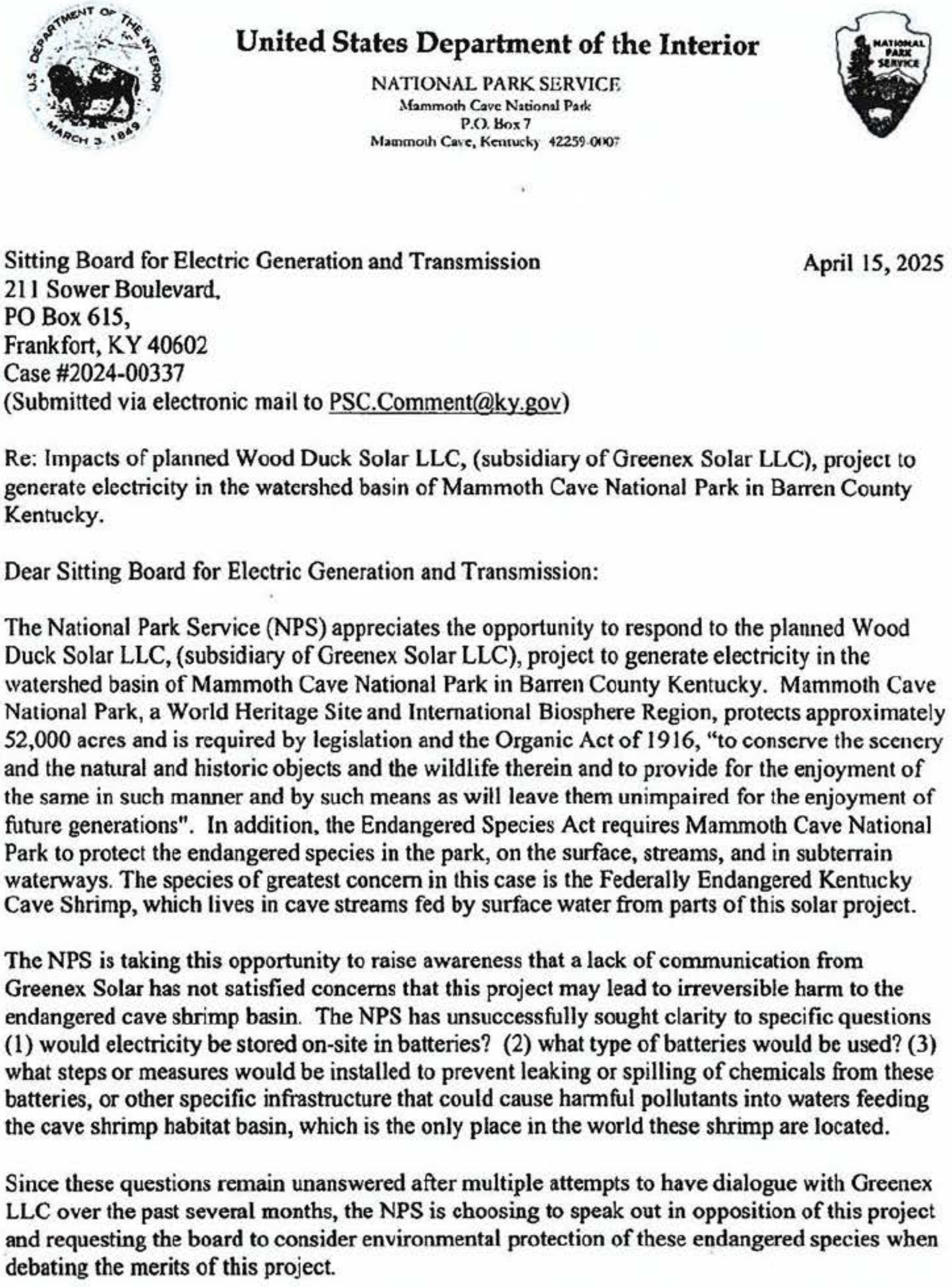
Compounds	**Purpose**	**Health and environmental impacts**
Acetone (C_3H_6O)	Cleaning out microscopic dirt and dust-off chips.	Eyes and nose irritation, throat infection, kidney and liver problems, nerve damage, birth defects and sexual problems including lower ability to reproduce males.
Ammonia (NH_3)	Production of antireflective coatings	Skin and eyes irritation, throat and lungs infections, mouth and stomach burns.
Arsenic (As)	Production of Gallium arsenide (GaAs) solar PV cells	Toxic and carcinogens, heart and liver problems, lung cancer, throat infection, nausea, vomiting, reduced blood cells, dark and red spot on skin, hands and feet etching.
Cadmium (Cd)	Manufacturing cadmium telluride (CdTe) solar cells	Toxic and carcinogenic, kidney, prostate and respiratory system infections, diarrhea, and lung cancer.
Hexavalent Chromium (Cr-VI)	Coating material in solar panel, screws and solar chassis board.	Carcinogenic
Hydrochloric acid (HCl)	Production of electrical grade silicon, clean and etch semiconductors	Skin irritation, eyes, nose, mouth and throat infections, food digestion, and respiratory depression.
Hydrogen (H_2)	Manufacturing amorphous-Si solar cells.	Flammable and highly explosive.
Iso-propanol (C_3H_8O)	Cleaning out microscopic dirt and dust-off chips.	Vomiting, Eyes irritation, depression, dermatitis, nausea, unconsciousness, respiratory failure, death or coma.
Lead (Pb)	Wiring and welding photovoltaic electrical components	Carcinogenic, brain, kidneys and nervous system damage, weakness in bones, anemia, and miscarriage.
Nitric acid (HNO_3)	Cleaning and removing dopants from wafers and reactors	Chemical burns.
Polybrominated biphenyls (PBBs)	Circuit boards and solar panel inverters	Toxic, carcinogenic and cause endocrine disrupters.
Polybrominated diphenylethers (PBDEs)	Circuit boards and solar panel inverters	Toxic, carcinogenic and cause endocrine disrupters.

Contaminates for soil and waterways



Compounds	Purpose	Health and environmental impacts
Silicon (Si)	PV semiconductor material	Causes respiratory problems, irritating skin and eyes.
Sulfur hexafluoride (SF_6)	Semiconductors etching and cleaning reactors	Strong greenhouse gas.
Toluene (C_7H_8)	Clean out microscopic dirt and dust-off chips	Headaches, hearing and memory loss, confusion, pregnancy problems, and retarded growth.
1,1,1-Trichloroethane ($C_2H_3Cl_3$)	Clean out microscopic dirt and dust-off chips	Dizziness, reduced blood pressure, unconsciousness, and heart problems.
Xylene (C_8H_{10})	Clean out microscopic dirt and dust-off chips	Skin and eye irritation, liver kidneys, nose and throat infections, and pregnancy problems.

Contaminates for soil and waterways



United States Department of the Interior

NATIONAL PARK SERVICE
Mammoth Cave National Park
P.O. Box 7
Mammoth Cave, Kentucky 42259-0007

Sitting Board for Electric Generation and Transmission
211 Sower Boulevard,
PO Box 615,
Frankfort, KY 40602
Case #2024-00337
(Submitted via electronic mail to PSC.Comment@ky.gov)

April 15, 2025

Re: Impacts of planned Wood Duck Solar LLC, (subsidiary of Greenex Solar LLC), project to generate electricity in the watershed basin of Mammoth Cave National Park in Barren County Kentucky.

Dear Sitting Board for Electric Generation and Transmission:

The National Park Service (NPS) appreciates the opportunity to respond to the planned Wood Duck Solar LLC, (subsidiary of Greenex Solar LLC), project to generate electricity in the watershed basin of Mammoth Cave National Park in Barren County Kentucky. Mammoth Cave National Park, a World Heritage Site and International Biosphere Region, protects approximately 52,000 acres and is required by legislation and the Organic Act of 1916, "to conserve the scenery and the natural and historic objects and the wildlife therein and to provide for the enjoyment of the same in such manner and by such means as will leave them unimpaired for the enjoyment of future generations". In addition, the Endangered Species Act requires Mammoth Cave National Park to protect the endangered species in the park, on the surface, streams, and in subterrain waterways. The species of greatest concern in this case is the Federally Endangered Kentucky Cave Shrimp, which lives in cave streams fed by surface water from parts of this solar project.

The NPS is taking this opportunity to raise awareness that a lack of communication from Greenex Solar has not satisfied concerns that this project may lead to irreversible harm to the endangered cave shrimp basin. The NPS has unsuccessfully sought clarity to specific questions (1) would electricity be stored on-site in batteries? (2) what type of batteries would be used? (3) what steps or measures would be installed to prevent leaking or spilling of chemicals from these batteries, or other specific infrastructure that could cause harmful pollutants into waters feeding the cave shrimp habitat basin, which is the only place in the world these shrimp are located.

Since these questions remain unanswered after multiple attempts to have dialogue with Greenex LLC over the past several months, the NPS is choosing to speak out in opposition of this project and requesting the board to consider environmental protection of these endangered species when debating the merits of this project.

Contaminates for soil and waterways

We look forward to working with the Board to ensure clean water in our national park for the safety of protection of endangered species. If you have questions, please contact NPS Mammoth Cave NP, Program Lead for Science and Resources Management, Marcus H. Key

[redacted]

Sincerely,

Barclay C. Trimble

Barclay C. Trimble
Superintendent

ScienceDirect

Journal of Hazardous Materials
Volume 426, 15 March 2022, 128141

Co-exposures of acid rain and ZnO nanoparticles accelerate decomposition of aquatic leaf litter

Jingjing Du [a] [b] [c], Wenrui Qv [a], Yulong Niu [a], Shuaikang Yuan [a], Lingyan Zhang [a], Huilian Yang [a], Yuyan Zhang [a]

Show more

Outline | Share Cite

https://doi.org/10.1016/j.jhazmat.2021.128141
Get rights and content

Full text access

Highlights

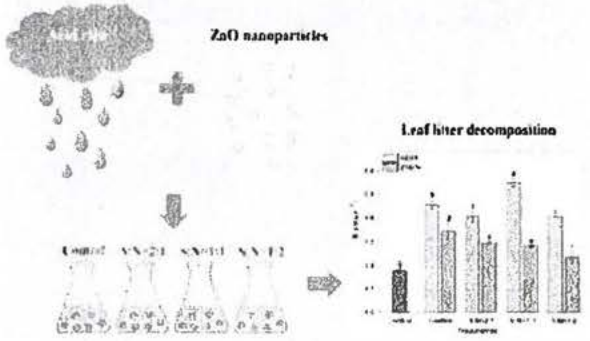
- Co-exposures of acid rain and ZnO nanoparticles accelerated leaf decomposition.
- The ratio of S: N influences the dissolution of ZnO nanoparticles.
- Aquatic fungi had adaptive ability to the combined effect.
- Microbial extracellular enzymes were stimulated by the combined effect.
- Co-exposures enhanced the fungal community diversity.

Abstract

Mammoth Cave area has documented acid rain

The pattern of acid rain is dependent on the ratio of SO_4^{2-} and NO_3^-, which change may affect the dissolution activity of dull heavy metals in the aquatic environment and further complicate the ongoing challenge of ecosystem stability and increase risks. In this study, we assessed the combined effects of acid rain (SO_4^{2-}: NO_3^- was 2:1, 1:1, and 1:2) and ZnO nanoparticles (30 ng L^{-1}) on plant litter decomposition through a microcosm experiment. The highest dissolution of ZnO nanoparticles was achieved when the SO_4^{2-}: NO_3^- ratio was 1:2, and there were no significant differences among other treatments. The fungal biomass showed significant decreases under acute exposures but tended to be adaptive during chronic exposures. The co-exposure significantly stimulated the activities of leucine-aminopeptidase, glycine-aminopeptidase, polyphenol oxidase, and cellobiohydrolase. Besides, the fungal diversity and the relative abundance of some functional genera (e.g. *Anguillospora*) were enhanced when the SO_4^{2-}: NO_3^- ratio was 1:2 and 2:1. In conclusion, the decomposition rate of plant litter was increased by 123–204% by co-exposures. Collectively, the findings underline the importance of considering environmental context to assess nanoparticle toxicity.

Graphical abstract



Previous
Next

Keywords

ZnO nanoparticles; Acid rain; SO_4^{2-}: NO_3^- ratio; Plant litter decomposition; Stream ecosystem

1. Introduction

Plant litter decomposition represents a major flux of fixed carbon (C) and nutrients in forest stream ecosystems (Wallace and Eggert, 1997). One of the most important aspects of evaluating stream function is quantifying leaf litter mass loss rates (Gessner and Chauvet, 2002). It has been demonstrated that the rate of litter decomposition in streams is controlled by biotic (i.e., litter quality, decomposing organisms, etc.) and abiotic variables (i.e., temperature, light, external contaminants, etc.) (Boyero et al., 2016). Among the microbial driving factors in this process, aquatic fungi, specifically aquatic hyphomycetes, are regarded as the primary decomposers (Gessner et al., 2007). For instance, previous studies have shown that the plant litter decomposition rate is often related to the maximum fungal biomass and sporulation rate (Gessner and Chauvet, 1994, Chauvet, 1997). Fungi, particularly aquatic hyphomycetes, can transform refractory plant materials into labile and digestible organic matters for higher trophic levels in aquatic food webs due to their excellent activities of extracellular enzymes (Schweizer and Barlocher, 1983, Arsuffi and Suberkropp, 1988, Dighton et al., 2005). Furthermore, the diversity of the fungal community has been demonstrated to influence the dynamics of plant litter decomposition (Pascoal et al., 2010). Therefore, fungal biomass, enzymatic activity, and community structure are often used as biotic indicators to assess the stream ecosystem functioning.

Acid rain (pH < 5.6) is formed because of sulfur dioxide and nitrogen oxide emissions from industrial and energy-production activities and has been recognized as an increasingly severe ecological problem in China over the last three decades (Xu and Hao, 1990). According to the data of Statistical Gazette (2019), almost 5.0% of the entire area of China still suffers from acid rain though acid deposition has been alleviated due to governmental policies and regulations over the years. Besides, another notable trend is detected in several regions, such as Beijing (Pu et al., 2017), Henan (Zhang et al., 2017), Xi'an (Wang et al., 2019), Sichuan (Li et al., 2019), and Shanghai (Meng et al., 2019), that the ratio of sulfur (S) and nitrogen (N) in emissions decreases, suggesting that the deposition pattern evolves from a sulfuric acid pattern to a mixed pattern, simultaneously controlled by sulfuric acid and nitric acid.

The influence of mixed acid rain on terrestrial ecosystem function has been the focus of ecologists since the last decade. For example, Lv et al. (2014) reported that the mixed acid rain could directly suppress litter decomposition, reduce microbial biomass and enzymatic activities, and indirectly slow down soil C, N, phosphorus (P), and S mineralization in both coniferous and broad-leaved forests. Liu et al. (2018) found that the growth rate of Chinese fir sapling decreased as foliar and root properties were affected by the increasing ratio of nitric acid in acid rain. A deposition pattern change may further challenge stream ecosystem stability because of the close connection between forests and streams. Our latest study showed that the litter decomposition under a mixed acid rain pattern was significantly inhibited with the decreases of fungal biomass, enzyme activity, and relative abundance of fungal hub genera such as *Tetracladium* and *Anguillospora* (Du et al., 2020a). When this important ecological process is simultaneously exposed to acid rain and other environmental stressors such as metallic nanoparticles, whether the mixed acid rain can change the ionic strength of stream water and affect the dissolution of these dull metals and therefore lead to combined effects on plant litter decomposition should be addressed.

The massive global proliferation and release of synthetic chemicals have evolved as a major agent of global change (Bernhardt et al., 2017), particularly engineered nanoparticles, which harm human health and ecosystem balance and have received considerable attention (Elsaesser and Howard, 2012). ZnO nanoparticles (nZnO) are widely used in food, pharmaceuticals, sunscreens, cosmetics, coating, and rubber and have become a part of daily life (Klaine et al., 2008). However, nZnO have been demonstrated to exert adverse effects on a series of aquatic organisms, including microalgae (Cai et al., 2016), daphnia (Bacchetta et al., 2017), zebrafish (Kim et al., 2017), and nematode (Ma et al., 2011). More importantly, even nanogram quantities of nZnO per liter would pose a potential threat to the structure and function of aquatic fungi and eventually damage freshwater functioning (Du et al., 2020b).

Gessner and Tlili (2016) underline the importance of understanding the effects of environmental context when assessing the potential threat of nanoparticles to ecosystems because environmental conditions can alter the fate of nanoparticles and therefore their toxicity. For instance, Luo et al. (2020) found that elevated CO_2 could mitigate the harmful effect of CeO_2 and Cr_2O_3 nanoparticles on soil bacterial communities. In addition, Pradhan et al. (2016) demonstrated that co-exposure of humic acid and CuO nanoparticles could alleviate the deleterious effects of nanoparticles on microbial decomposers and plant litter decomposition in streams. Against this background, the combined effects of mixed acid rain (pH 5.0) and nZnO ($30 ng L^{-1}$) on plant litter decomposition were assessed with a well-established microcosm assay in the present study. Three acid deposition patterns with different ratios of S and N (2:1, 1:1, and 1:2) in nowadays and the future China were applied (Wang et al., 2019, Zhang et al., 2018). The dissolution activity of ZnO increased with the increasing acidity of solutions (Huang et al., 2019). In addition, changes in the ionic strength of solutions could affect the dissolution activity of ZnO (Bian et al., 2011). So, the first hypothesis was that the dissolution activity of ZnO would be promoted by the acid rain and influenced by the ratio of S and N. Our previous study demonstrated that both acid rain and ZnO showed significant inhibitions on the fungal biomass and microbial enzyme activities after 45-day exposures (Du et al., 2020a, Du et al., 2020b). Based on these outcomes, we predicted that the fungal biomass and microbial enzyme activities would be decreased under co-exposures because the individual effects were both adverse. As a result, the plant litter decomposition would be further affected by the combined effects.

2. Materials and methods

Acid Rain increases rust - zinc oxide - metal

2.1. Leaf litter

The litter, representing common litter inputs to the stream in the study area, was from a dominant riparian species (*Populus nigra* L.) across China plains. In November 2017, we collected recently abscised leaves from a forest in the Yanwa River (34°56′24.73″N, 112°25′56.15″E, Jiyuan, China). The collected leaf materials were leached in deionized water overnight to remove the surface dust and periphyton and were cut into disks with a diameter of 12 mm (avoiding the basal midrib). Then the leaf disks were dried at 40°C for 72h to constant weight and were divided into each microcosm with a weight of 0.5±0.03g. Each litter bag (15× 15cm) with fine meshes (0.5mm, to prevent the entrance of invertebrates) was filled with a group of leaf disks and immersed in the Tiannv stream (34°56′24.73″N, 112°25′56.15″E, belonging to Yanwa River catchment, 1–3m in width, 0.5–1m in depth, 134.5m in altitude) for 15-day microbial colonization.

2.2. Metallic nanomaterials

Nanomaterials (nZnO, CAS. 1314–13-2, 10–30nm) were purchased from J&K Scientific. (Beijing, China) and used as the model metallic nanomaterials (Ma et al., 2012). The stock solution of nZnO at $0.18 g L^{-1}$ was prepared in deionized water (18MΩ·cm) and sonicated for 30mins in an ultrasonic bath at 40kHz before being diluted to the desired concentrations for the following experiment. The morphology and actual size of nZnO in the stock solution was characterized by the field emission scanning electron microscopy, which was provide in the Supporting Information as Fig. S1.

2.3. Experimental design

As shown in Table 1, three kinds of acid rain (S: N=2:1, S: N=1:1, and S: N=1:2) coupled with nZnO (the nominal concentration was $30 ng L^{-1}$) and $ZnSO_4$ (the concentration of Zn^{2+} was $30 ng L^{-1}$) were designed, respectively. Moreover, the simulated unpolluted rain coupled with the corresponding concentration of nZnO and $ZnSO_4$ were used as positive controls (Control-nZnO and Control-$ZnSO_4$). The simulated unpolluted rain and acid rain were simulated and prepared according to Wang et al. (2010) that were composed by the ions shown in Table S1. The pH value of unpolluted rain was finally buffered to 5.6 by adding the stock solution of H_2SO_4 and HNO_3 with a volume ratio of 2:1. The pH value of acid rain was buffered to 5.0 by adding the stock solutions of three kinds of acid rain (S: N=2:1, S: N=1:1, and S: N=1:2), which were prepared by mixing $0.1 mol L^{-1}$ H_2SO_4 and $0.1 mol L^{-1}$ HNO_3 at volume ratios of 2:1, 1:1, and 1:2, respectively. The microcosms without acid rain, nZnO, or $ZnSO_4$ were used as negative controls. A total of nine treatments (Table 1), each with three replicates, were acclimated within a chamber where the temperature was controlled at 20±1.5°C under shaking (150rpm) with natural light: dark regime of 12: 12h.

Table 1. Treatments designed in the microcosm experiment.

Treatments	Abbreviation	pH
Control	Control	5.6
Control-nZnO	CnZ	5.6
S:N=2:1-nZnO	AnZ1	5.0
S:N=1:1-nZnO	AnZ2	5.0
S:N=1:2-nZnO	AnZ3	5.0

Treatments	**Abbreviation**	**pH**
Control-$ZnSO_4$	CZ	5.6
S:N=2:1-$ZnSO_4$	AZ1	5.0
S:N=1:1-$ZnSO_4$	AZ2	5.0
S:N=1:2-$ZnSO_4$	AZ3	5.0

In the experiment, artificial reconstituted freshwater (ARFW, Table S2) was used as stream water to avoid the influence of humic acid or other complex components in natural stream water. Microcosms consisted of a 150-mL sterile glass flask with 80-mL autoclaved ARFW (121 °C, 20 min, pH 7.6) and a group of leaf disks after microbial colonization. The experiment was run for 45 days, with replacements of ARFW, simulated rainwater, nZnO, or $ZnSO_4$ weekly. A set of 27 flasks (three replicates of each treatment) were prepared to determine the remaining leaf mass and enzyme activity at different time intervals of 0, 5, 10, 15, 30, and 45 days. The fungal biomass was measured on day 5, 15, and 45. The fungal diversity and community composition were measured by sampling at the end of the experiment.

2.3.1. Zn concentration

The Zn concentration in microcosms without leaf disks was monitored after 0-, 1-, 3-, and 7-day exposure to avoid the influence of leaf and microbial absorption. Briefly, the ionic Zn and nZnO in 3-mL water samples were separated by ultrafiltration at 7500 g^{-1} for 40 mins (Bacchetta et al., 2017). The concentration of ionic Zn in the filtrate was determined by atomic absorption spectroscopy (ZEEnit 700 P, Analytik Jena AJ, Germany) with the graphite furnace method.

2.3.2. Litter decomposition

Time-course changes of leaf litter dry mass were expressed as % mass loss relative to the original dry mass. After the experiment was terminated, the remaining litter disks in each microcosm were gently rinsed with deionized water to remove the surface chemicals, oven-dried at 40 °C for 72 h to constant mass, and weighed to estimate the final dry mass. The decomposition rate (k, mon^{-1}) of leaf litter was calculated with the loss rate of litter mass over the decomposition time (Olson, 1963):

$$\frac{M_t}{M_0} = exp^{-kt}$$

where M_0 is the original dry mass of leaf litter; M_t is the remaining dry mass of leaf litter at time *t*; *k* is the decomposition rate of leaf litter; *t* is the decomposition time (month).

2.3.3. Fungal biomass

Fungal biomass associated with litter disks was estimated by ergosterol extraction and quantification with high-performance liquid chromatography (HPLC) because ergosterol is one of the main sterol substances in fungal cell membranes and can be used as the fungal biomass proxy (Gessner, 2005). A subset of eight-leaf disks from each microcosm was randomly selected to extract ergosterol: heated in 0.8% KOH-methanol, purified by the solid-phase extraction cartridges (SPE81201, Mediwax, China), and subsequently eluted with isopropanol. Ergosterol content was determined with HPLC (Thermo Ultimate 3000 DGLC equipped with a Merck LiChrospher 100 RP-18 column set at 33 °C). The UV detector was set at 282 nm, and the flow rate of 100% methanol was set at 1.4 mL min^{-1}. A conversion factor of 5.5 mg ergosterol per gram of fungal (dry mass) was used to consider the fungal biomass on litter disks (Gessner and Chauvet, 1993).

2.3.4. Extracellular enzyme activity

The microbial enzymatic potential was estimated from measurements of acid phosphatase (AP, EC 3.1.3.2), β-glucosidase (BG, EC 3.2.1.21), glycine-aminopeptidase (GAP, EC 3.4.11), leucine-aminopeptidase (LAP, EC 3.4.11.1), N-acetylglucosaminidase (NAG, EC 3.2.1.52), cellobiohydrolase (CBH, EC 3.2.1.91), polyphenol oxidase (PPO, EC 1.10.3.1), phenol oxidase (POD, EC 1.14.18.1), and aryl-sulfatase (ARS, EC 3.1.6.1) activities using the colorimetric method described in The Allison Lab (2001). Briefly, a subset of ten-leaf disks from each microcosm was incubated with 10 mL of sodium acetate buffer (50 mM, pH 7.6) and ultrasonic oscillated with ice at 40 kHz for 2 mins. Afterward, the crude enzyme was obtained by centrifugation at 4 °C for 5 mins and incubated with the specific substrate analog for each enzyme at the previously determined saturating concentration. After the incubation, the activities of each enzyme were measured with a microplate reader (Thermo scientific multiskan FC, USA). The unit of each enzyme activity was defined as the amount of enzyme that releases 1 μmol of production per hour under per gram of leaf disks.

2.3.5. Fungal community

Fungal communities associated with litter disks were identified from leaf samples on days 0 and 45 according to the procedure described in Du et al. (2017). Total DNA extraction was performed for three-leaf disks from each sample using the FastDNA® SPIN kit for soil (Mpbio, U.S.A.) following the manufacturer's protocols (https://media.mpbio.com/productattachment/LS082019-EN-FastDNA-SPIN-Kit-for-Soil-116560200-Manual.pdf). Extracted DNA was quantified and amplified by PCR targeting the ITS2 hypervariable region of the fungal genomic rDNA via the primer pair ITS4/ITS3F (White et al., 1990). The PCR analysis was performed in the following sequence: initial denaturation at 95 °C for 3 min, followed by 35 cycles of denaturation at 95 °C for 30 s, annealing at 55 °C for 30 s and extension at 72 °C for 45 s, and a final extension at 72 °C for 10 min. The PCR mixtures contained 5 × *TransStart* FastPfu buffer 4 μL, 2.5 mM dNTPs 2 μL, forward primer (5 μM) 0.8 μL, reverse primer (5 μM) 0.8 μL, *TransStart* FastPfu DNA Polymerase 0.4 μL, template DNA 10 ng and finally ddH_2O up to 20 μL. Then, purified amplicons were pooled in equimolar and paired-end sequencing was conducted for them (2 × 300 bp) on a MiSeq (Illumina, San Diego, USA) platform following the standard protocols by Majorbio Bio-Pharm Technology Co., Ltd. (Shanghai, China). The raw read data have been submitted to the NCBI Sequence Read Archive database, and the assigned accession number was SRP307705. Sequences were run against the Unite fungal ITS database (version 8.0) with a confidence threshold of 70% for the identification of fungal taxa. Sequences were clustered at the operational taxonomic unit (OTU) level based on 97% identity using the UPARSE OTU clustering (version 7.0), and chimeric OTUs were detected with the UCHIME method (Edgar et al., 2011). The standard 97% identity eliminates many potential sequencing errors and is considered sufficient to estimate community richness and evenness (Patin et al., 2013).

2.4. Data analysis

Regression lines of ln-transformed values of leaf dry mass against time were performed and the significant differences in decomposition rate along time were measured by analysis of covariance (ANCOVA) according to Pradhan et al. (2011). The differences in fungal biomass on days 5, 15, and 45 among treatments were tested with a significance level of $P < 0.05$ using a one-way analysis of variance (ANOVA) with the least significant difference test. A two-way ANOVA was used to test the individual and interactive effects of acid rain and Zn type on extracellular enzyme activities. To evaluate how microbial enzyme activities varied among treatments, a principle component analysis (PCA) was performed. The relationships between the ordination axes and individual enzymatic traits were tested using the Pearson correlation analysis. The direct and indirect effects of fungal biomass and extracellular enzyme activities on decomposition rate were analyzed using structural equation modeling (SEM) in AMOS 25.0 (Amos Development Co., Greene, Maine, USA). A more specific interpretation of the multivariate analysis of fungal genera was detected by non-metric multidimensional scaling (NMDS) using the Vegan package based on Bray-Curtis distances of OTUs at a genus level. We also constructed and visualized the network analysis using NetworkX (version 1.11, https://networkx.github.io/) to reveal the connection between aquatic fungi and treatments to identify the hub genera.

3. Results

3.1. Changes in Zn^{2+} concentration

In ARFW, the concentration of Zn^{2+} was significantly influenced by exposure time, Zn type, and the ratio of S: N in acid rain (Table 2). The Zn^{2+} concentration increased with exposure time in microcosms with nZnO or $ZnSO_4$ under the acid rain pattern. Specifically, the concentration of Zn^{2+} tended to be stable in the CnZ treatment after day 1, while the gradual release of Zn^{2+} was still observed after 3 days in nZnO microcosms with the acid rain, especially when the S: N ratio was 2:1 (Table 2, $P < 0.05$). Under the same S: N ratio, the concentration of Zn^{2+} in microcosm with $ZnSO_4$ was almost twice as much as that in microcosms with nZnO at the same time point (Table 2, $P < 0.05$). Besides, nZnO achieved the highest dissolution in acid rain when the S: N ratio was 1:2, and there were no significant differences among other treatments (Table 2, $P > 0.05$).

Table 2. The concentration of ionic Zn varied with treatment and exposure time in the artificial reconstituted fresh water.

	Positive control		**S:N = 2:1**		**S:N = 1:1**		**S:N = 1:2**	
Time (days)	**nZnO (ng L^{-1})**	**$ZnSO_4$ (ng L^{-1})**	**nZnO (ng L^{-1})**	**$ZnSO_4$ (ng L^{-1})**	**nZnO (ng L^{-1})**	**$ZnSO_4$ (ng L^{-1})**	**nZnO (ng L^{-1})**	**$ZnSO_4$ (ng L^{-1})**
0	14.16 ± 0.74Bd	27.60 ± 0.37Ca	13.07 ± 0.58Dd	25.74 ± 0.46Bb	13.45 ± 1.07Bd	24.76 ± 0.64Cb	15.75 ± 0.87 BCE	25.34 ± 0.42Cb
1	17.89 ± 2.34Ac	28.00 ± 0.36BCa	14.20 ± 0.46 Cd	26.14 ± 0.46Bb	13.82 ± 0.34Bd	25.16 ± 0.64BCb	16.37 ± 0.69 BCE	26.56 ± 1.34BCab
3	19.04 ± 0.56 CE	28.74 ± 0.56ABa	15.38 ± 0.11Be	27.79 ± 0.94Aab	15.89 ± 1.33Ae	25.90 ± 0.74ABc	17.78 ± 0.84 CE	27.22 ± 0.22ABb
7	19.79 ± 0.02 CE	29.00 ± 0.35Aa	17.22 ± 0.56Af	28.18 ± 0.69Ab	16.59 ± 0.42Af	26.32 ± 0.26Ac	18.80 ± 0.23Ae	27.98 ± 0.17Ab

Note: Values are given as mean ± SD, n = 3. Different uppercase letters denote significant differences between exposure times ($P < 0.05$), and different lowercase letters denote significant differences between treatments ($P < 0.05$).

3.2. Litter decomposition

Litter decomposition of poplar leaf was significantly promoted by treatments (Fig. 1a, $P < 0.001$). Generally, promoting effects in treatments of CnZ and CZ were stronger than those in treatments with acid rain (Fig. 1a, $P < 0.05$). On day 45, the litter decayed faster in the microcosms under co-exposure of acid rain and nZnO (mass loss of 45–54%) than in Control (mass loss of 20%) (Fig. 1a, $P < 0.05$). As a result, the decomposition rate was increased by 123–204% compared to the Control (Fig. 1b, $P < 0.05$). Moreover, the microcosms under the combined effect of $ZnSO_4$ and acid rain had higher litter mass loss (31–34%) than Control except in the AZ3 treatment on day 45 (Fig. 1a, $P < 0.05$). Under the same S: N ratio, the decomposition rate of the litter was increased by 36–93% in microcosms with nZnO than in those with $ZnSO_4$ (Fig. 1b, $P < 0.05$). The highest decomposition rate for microcosms with nZnO was detected when the S: N ratio was 1:1 (Fig. 1b, $P < 0.05$).

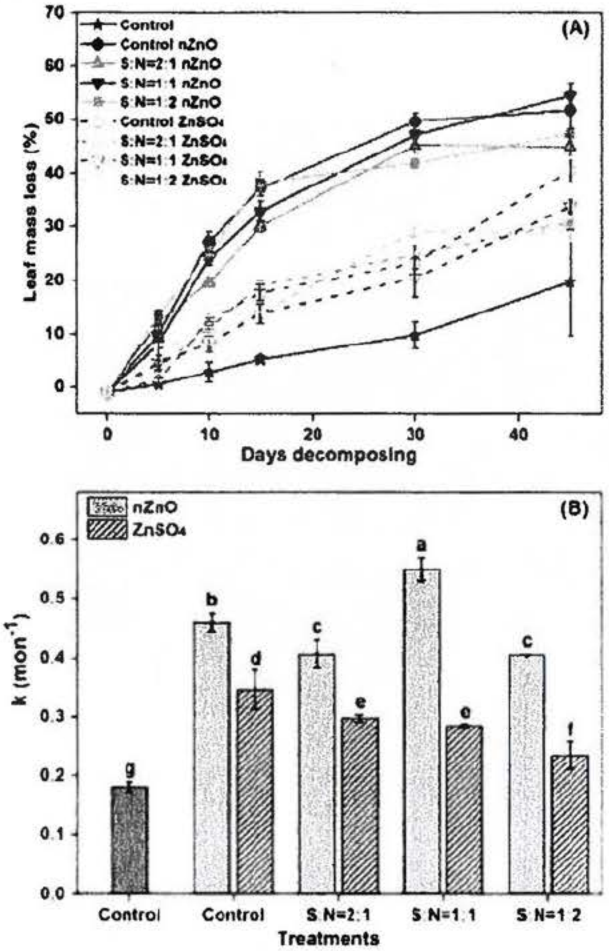


Fig. 1. Changes in leaf mass loss (A) and decomposition rate (B) after 45 days of exposure (mean ± standard deviation, n = 3). Different letter on top of the bar denotes significant differences ($P < 0.05$) among the treatments.

3.3. Fungal biomass

On day 5, the fungal biomass in microcosms under the combined effect of acid rain and nZnO was reduced by 24–50% than in Control except in the AnZ3 treatment (Fig. 2, $P < 0.05$). The fungal biomass of microcosm with acid rain and $ZnSO_4$ was reduced by 25–49% (Fig. 2, $P < 0.05$). The combined effects of acid rain and nZnO seemed to be alleviated over time in treatments of AnZ2 and AnZ3. In the AnZ3 treatment, fungal biomass was increased by 22% and 51% on day 15 and 45 than in Control, respectively (Fig. 2, $P < 0.05$). After 15 days of exposure, fungal biomass was significantly higher in microcosms with nZnO than in those with $ZnSO_4$ when the S: N ratio was 1:1 and 1:2 (Fig. 2, $P < 0.05$).

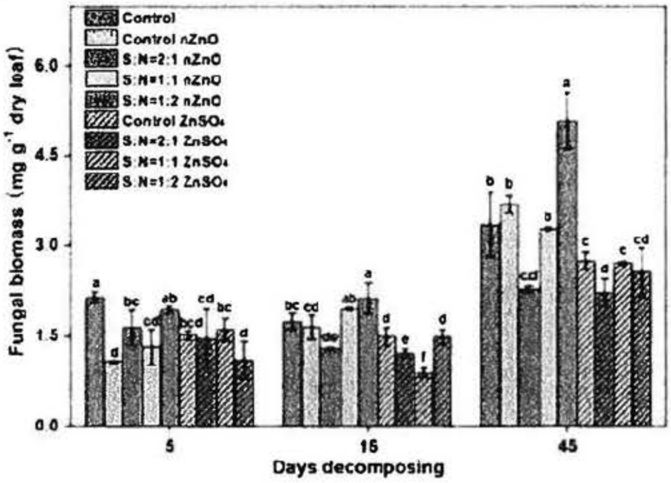


Fig. 2. Changes in fungal biomass during exposure (mean ± SD, n = 3).

3.4. Microbial enzymatic activity

A significant interactive effect of acid rain and Zn type could be detected on microbial enzyme activities (Table S2, $P < 0.001$). The results of PCA showed that the first axis (PC1) explained that 69.39% of the variation and was positively related to the activities of AP, LAP, GAP, PPO, BG, POD, NAG, and CBH, indicating that PC1 denoted microbial metabolic properties relating to the cycling of C, N, and P (Fig. 3). The second axis (PC2) explained that 11.17% of the variation and was positively related to ARS activity, suggesting that PC2 denoted the microbial metabolic property relating to the cycling of S. Generally, throughout the decomposition process except on day 10, the combined effects of acid rain and nZnO tended to increase the microbial enzyme activities compared to the Control, whereas the combined effects of acid rain and $ZnSO_4$ inhibited the enzyme activities (Fig. 3). To be specific, ARS activity on day 5 was increased by 101–219% under co-exposures of acid rain and nZnO but decreased by 57–72% under co-exposures of acid rain and $ZnSO_4$ (Fig. S2i, $P < 0.05$). Under the same S: N ratio, the activity of extracellular enzymes was significantly higher in microcosms with nZnO than in those with $ZnSO_4$ (Fig. S2i, $P < 0.05$). Particularly, the activity of AP in the AnZ3 treatment was 20–80% higher than that in AZ3 treatment except on day 45 (Fig. S2a, $P < 0.05$). Besides, the activities of BG and CBH in the AnZ2 treatment were increased by 19–94% and 59–85%, respectively, than that in the AZ2 treatment (Fig. S2b and S2h, $P < 0.05$). For microcosms with nZnO, the highest activity of the microbial enzymes, such as AP, GAP, NAG, and CBH, was observed when the S: N ratio was 1:1, and the lowest activity was detected when the S: N ratio was 1:2, on day 10 (Fig. S2).

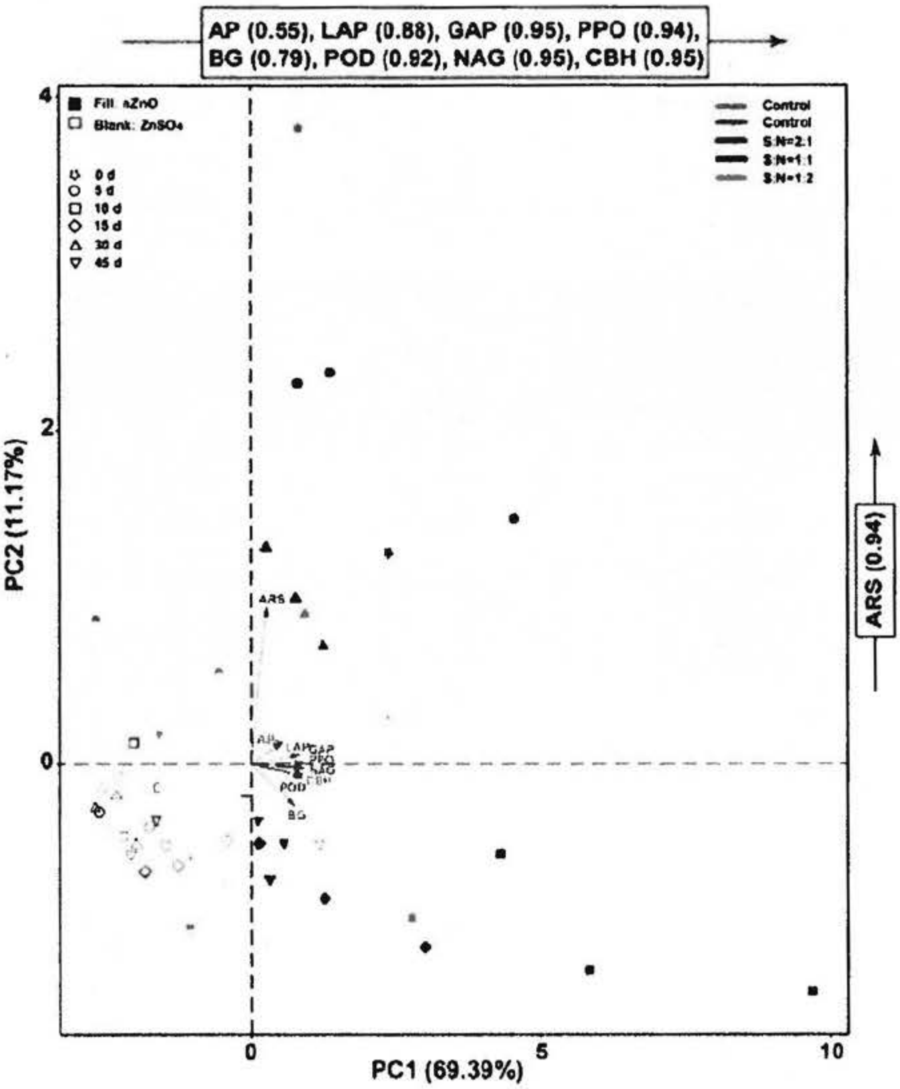


Fig. 3. Principal component analysis of the interactive effects of acid deposition type × Zn type × exposure time on enzyme activities. The gray symbol with half-sided blank represents the Control (without ZnO nanoparticles or $ZnSO_4$).

3.5. Associations between fungal biomass, extracellular enzyme activities, and decomposition rate

The final model explained 75% of the variation in decomposition rate (Fig. 4). The decomposition rate was not directly affected by the fungal biomass (Fig. 4, $P > 0.05$). The activities of LAP, GAP, PPO, and CBH displayed a positive correlation with decomposition rate, while BG, POD, and ARS displayed a negative correlation with decomposition rate (Fig. 4, $P < 0.001$). Standardized total effects obtained by the SEM indicated that decomposition rate was mainly driven by POD, followed by LAP, GAP, and CBH (Table S4).

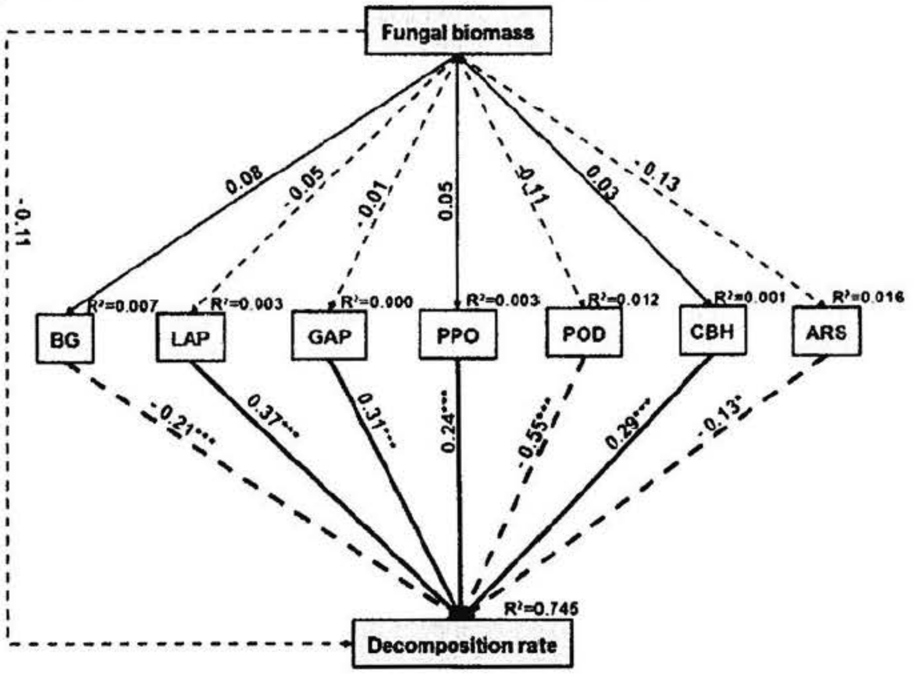


Fig. 4. Structural equation model (SEM) showing the direct and indirect effects of fungal biomass and extracellular enzymes on decomposition rate. Continuous and dashed arrows indicate positive and negative relationships, respectively. Numbers adjacent to arrows are the standardized path coefficients (equivalent to correlation coefficients). Asterisks denote significant effects (*, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$). R^2 values associated with response variables indicate the variance accounted for by the mode. Non-significant paths are removed in the final model.

3.6. Fungal community structure

With the 18 S rDNA sequencing, more than 33,092 read data with a length of 161 bp were obtained from each sample. The number of OTUs at 97% sequence identity ranged from 59 to 189 (Table 3). Species richness indices showed that the number of OTUs was increased in microcosm with acid rain and nZnO but decreased in those with acid rain and $ZnSO_4$ compared to Control (Table 3). The diversity indices also indicated that the treatments with nZnO increased the fungal diversity compared with the treatments with $ZnSO_4$ under the same S: N ratio (Table 3). For microcosms with nZnO, higher diversity indices such as Chao 1 and ACE were observed in treatments of AnZ2 and AnZ3 (Table 3).

Table 3. Fungal community richness and diversity indices after 45 days of exposure.

Samples	Sequence	OTUs	Chao	ACE	Simpson	Shannon	Coverage
Initial	55404	72	53.33	71.28	0.90	0.30	0.99

Samples	Sequence	OTUs	Chao	ACE	Simpson	Shannon	Coverage
Control	55371	136	80.89	86.98	0.36	1.61	0.99
Control-nZnO	68152	158	183.07	180.25	0.22	2.17	0.99
S:N = 2:1-nZnO	33092	135	157.00	171.43	0.12	2.65	0.99
S:N = 1:1- nZnO	71854	173	208.05	211.23	0.13	2.65	0.99
S:N = 1:2-nZnO	69546	189	208.56	216.50	0.22	2.17	0.99
Control-$ZnSO_4$	38265	59	92.00	145.53	0.23	1.79	0.99
S:N = 2:1- $ZnSO_4$	56241	85	114.55	115.44	0.20	2.02	0.99
S:N = 1:1- $ZnSO_4$	51399	99	108.56	110.42	0.40	1.61	0.99
S:N = 1:2-$ZnSO_4$	66540	129	150.75	163.62	0.33	1.78	0.99

The unclassified Ascomycota was initially determined as the dominant fungal genus (Fig. 5). The NMDS plot separates the fungal community from initial litter and exposed litter under different treatments (Fig. S3). In Control, unclassified fungi (28%), *Anguillospora* (28%), *Tetracladium* (23%), and unclassified Ascomycota (18%) were detected as the dominant fungal genera (Fig. 5). The proportion of *Anguillospora* (24–48%), *Setophaeosphaeria* (8–23%), and Ciliophora (2–24%) was increased in microcosms with acid rain and nZnO (except for the AnZ2 treatment) than in Control. In contrast, the proportion of unclassified Ascomycota and *Tetracladium* was reduced to 2–8% and 0, respectively (Fig. 5). Therefore, *Setophaeosphaeria* and *Ciliophora* were also the dominant genera after co-exposure of acid rain and nZnO in addition to *Anguillospora*.

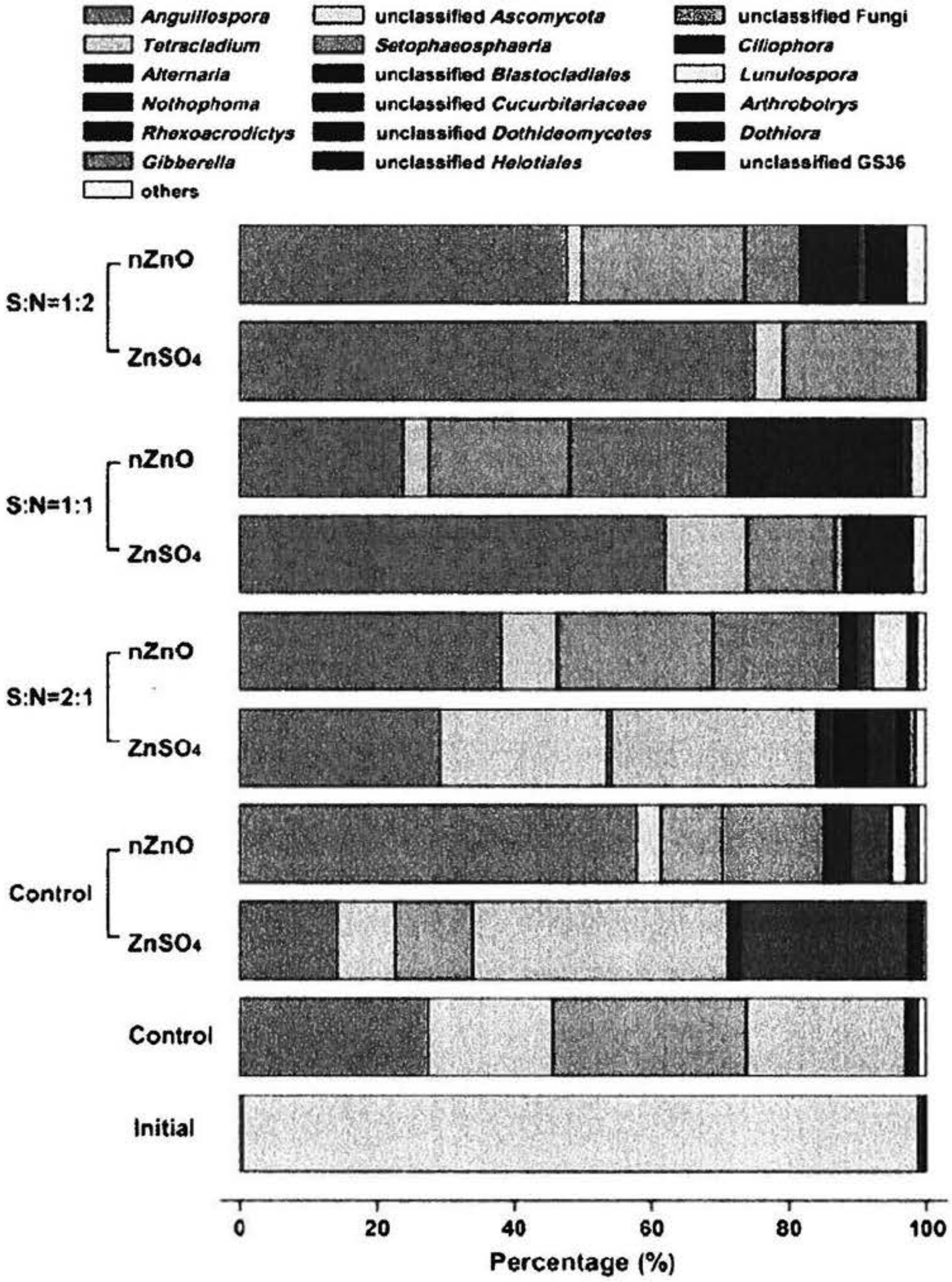


Fig. 5. Structure of the fungal community associated with poplar leaf litter after 45 days of exposure.

Network analysis was conducted to explore the hub genera in different treatments. The network topological parameters showed that *Anguillospora*, unclassified Ascomycota, and unclassified Fungi had a higher weighted degree and betweenness centrality, which were associated with each treatment (Table S5), indicating that the three fungal genera play an important role in the litter decomposition. Besides, co-occurrence network analyses indicated that a marked variation in hub genera was observed between different treatments (Fig. 6). For example, *Ciliophora* was observed to be the hub genera in all treatments except CnZ and AZ3 samples. *Setophaeosphaeria* was the hub genus in treatments with nZnO. *Tetracladium* was the hub genus in treatments with $ZnSO_4$ except the S: N ratio was 1:2.

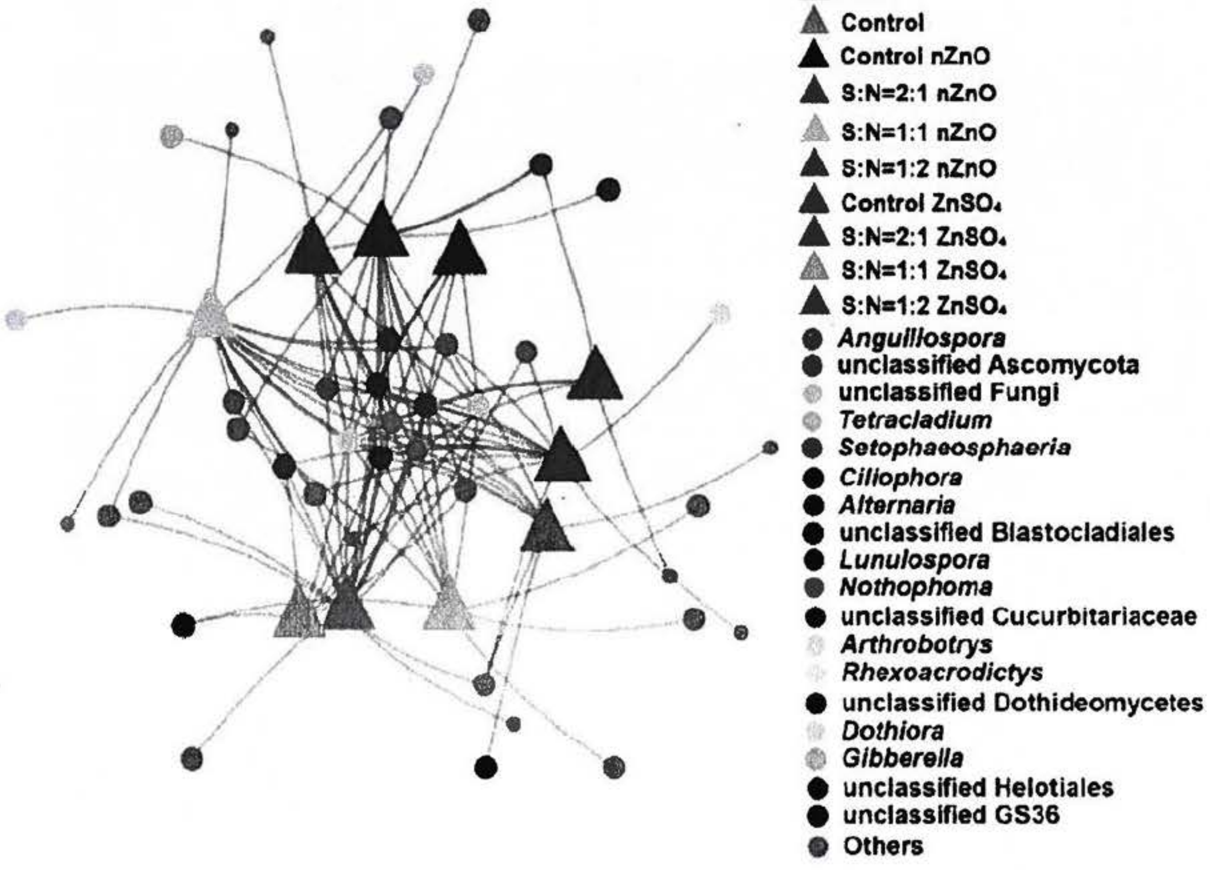


Fig. 6. Co-occurrence networks of fungal communities at the genus level after 45 days of exposure.

4. Discussion

To date, many studies have explored the individual effect of environmental factors, such as driving factors of climate change and emerging contaminants, on plant litter decomposition and its microbial communities (Tlili, 2021, Amani et al., 2019), which have greatly enhanced our understanding of stream ecology. However, the frequent interaction of multiple environmental stressors results in nonadditive and complex outcomes which cannot be predicted based on the individual effects (Folt et al., 1999, Du et al., 2021a, Du et al., 2021b). In this sense, there are still many large research gaps, some of which have been addressed in this study, namely, the combined effects of acid rain and nZnO on leaf litter decomposition, microbial activity, and fungal community structure. In this study, the co-exposures of acid rain and nZnO accelerated the microbial decomposition of poplar leaves though the ecological process would be inhibited by any one of the factors alone (Du et al., 2020a, Du et al., 2020b).

4.1. The effect of acid rain on the dissolution of nZnO

It is generally believed that the acidity of solutions influences the dissolution of nZnO, and high acidity is beneficial to the dissolution of Zn^{2+} (Huang et al., 2019). However, we found that the concentration of Zn^{2+} in the CnZ treatment was significantly higher than in microcosms of acid rain (Table 2, $P < 0.05$) though the pH of the former was lower than the latter. Besides, it was found that the concentration of Zn^{2+} for microcosms with acid rain and nZnO in the AnZ3 treatment was significantly higher than that in the other two treatments (Table 2, $P < 0.05$). These results were inconsistent with the first hypothesis, suggesting that the dissolution of nZnO is related to the ratio of S: N instead of the pH of acid rain. Thus, we speculated that decreasing the ratio of SO_4^{2-} to NO_3^- will significantly affect the dissolution of metal ions of metallic nanoparticles, which may further influence the activity of decomposers and even the ecosystem structure and functioning of streams.

4.2. Changes in aquatic fungal biomass under co-exposures of acid rain and nZnO

In this study, the fungal biomass showed significant decreases under acute exposures of acid rain and nZnO, but chronic exposures caused negligible even promoting effects except for the AnZ1 treatment, which was inconsistent with the second hypothesis, as aquatic fungi become adaptive to the combined effects along with the exposure time. The complex organelle structure and advanced reproduction modes of aquatic fungi make them more sensitive to environmental stressors, leading to transient decreases in fungal biomass (Zubrod et al., 2015). However, the fungal biomass gradually increased with the prolongation of the exposure time under multiple stressors (especially the AnZ3 treatment), indicating that fungal adaptation was achieved by a 45-day co-exposure of acid rain and nZnO. Besides, the adaptation time might be influenced by the ratio of S: N in acid rain, and higher N concentration contributes to rapid adaptation. In addition, the combined effect of acid rain and $ZnSO_4$ significantly reduced the fungal biomass, indicating that aquatic fungi showed more sensitivity to $ZnSO_4$ after the intervention of acid sedimentation. This outcome may be related to the higher initial concentration of Zn^{2+} that reaches the inhibition threshold for aquatic fungi.

4.3. Changes in microbial extracellular enzymes under co-exposures of acid rain and nZnO

Previous studies have shown that acid rain decreases microbial enzymatic activity (Du et al., 2020a), and nZnO at environmental concentrations have negligible even negative effects on microbial enzymatic activity (Du et al., 2020b). Based on these outcomes, we speculated that microbial enzyme activity would be inhibited by the combined effect of acid rain and nZnO. Unexpectedly, we found that except in AnZ3 treatment, the activity of most extracellular enzymes was significantly increased in the coupling treatments of acid rain and nZnO, especially that in AP, BG, and NAG activities, which increased at each time point (Fig. S2, $P < 0.05$). This result reflects the natural complexity of underpinning ecosystems, that is, the interaction of multiple stress factors can exert opposing effects via antagonism (Jackson et al., 2016). The combined effects of acid rain and $ZnSO_4$ on microbial enzymatic activities could be overlooked in this experiment. A similar outcome was also observed in treatments of CZ and CnZ, respectively (Fig. S2). Therefore, the contradiction could be explained by the different dissolution of nZnO and $ZnSO_4$ in microcosms. Although Zn^{2+} is a vital micronutrient for protein synthesis and energy production as well as a catalytically active cofactor for some extracellular hydrolytic enzymes (Hänsch and Mendel, 2009, Serero et al., 2001, Snaith and Levvy, 1968, Maidment et al., 1999), Zn is still recognized as a typical heavy metal when the environmental concentration is above a certain level (Pu et al., 2014, Medeiros et al., 2010). In this experiment, the concentration of Zn^{2+} in microcosms with $ZnSO_4$ was higher than 24 ng L^{-1}, almost twice as much as that in microcosms with nZnO under the same S: N ratio (Table 2, $P < 0.05$). Besides, nZnO achieved the highest dissolution activity (18.80 ng L^{-1}) in the AnZ3 treatment (Table 2, $P < 0.05$). These results suggest that the threshold of Zn^{2+} concentration inhibiting microbial enzymatic activity may be between 18 and 20 ng L^{-1}. Therefore, the variations in combined effects of acid rain and nZnO on microbial metabolic activity result from differences in dissolution of Zn^{2+}.

4.4. Changes in fungal community structure under co-exposure of acid rain and nZnO

It was reported that heavy metals could result in the loss of fungal diversity in freshwater ecosystems by reducing the sensitive species (Niyogi et al., 2009, Sridhar et al., 2000). Our previous studies affirmed that nZnO at 30 ng L^{-1} increased the fungal diversity (Du et al., 2020b). Once again, this finding was confirmed by the CnZ treatment in the present study. Moreover, either the co-exposure of acid rain and nZnO or $ZnSO_4$ enhanced the fungal diversity though acid rain had negative effect on it (Du et al., 2020a). The promoting effects rely on the Zn^{2+} in microcosms. Medeiros et al. (2010) suggested that whether metallic contaminants affect fungal diversity depends on the concentration of metals in aquatic environments. Our study supports this finding, as Zn^{2+} at such a concentration may drive the evolution of fungal communities by playing a role of selective agents (Hoostal et al., 2008). Furthermore, we found that the promoting effect of nZnO seems to be much stronger than that of $ZnSO_4$ (Table 3) under co-exposures, which might be related to the speed and level of Zn^{2+} being released to microcosms. In other words, nZnO dissolved to Zn^{2+} in a slower and lower way, which could work as a selective agent to gradually promote the fungal evolution. Besides, the coupling treatments increased the relative abundance of some functional fungal genera in the fungal community. For instance, *Anguillospora* was reported to play a major role in plant litter decomposition when exposed to heavy metal pollution (Medeiros et al., 2010, Pascoal et al., 2005), and its abundance was improved by the combined effect of acid rain and nZnO, and therefore the decomposition of leaf litter was accelerated.

4.5. The driving factors of plant litter decomposition under co-exposures of acid rain and nZnO

It is widely accepted that microbial decomposition is mainly attributed to the action of aquatic fungi (Canhoto et al., 2016) because of its predominance in biomass production (Baldy et al., 1995, Baldy et al., 2002). The SEM analysis indicates that the decomposition rate is uncorrelated with the fungal biomass, which seems to be inconsistent with our previous understanding about the advantage of fungal biomass in plant litter decomposition under unpolluted conditions (Gessner and Chauvet, 1994). However, the importance of fungal biomass is weakened when simultaneously exposed to acid rain and nZnO. Nanoplastic exposures also lead to a similar outcome (Du et al., 2021a, Du et al., 2021b). These results suggest that changes in fungal biomass contribute little to illustrating the process of plant litter decomposition under environmental stressors.

As the functional microbes, the decomposers produce extracellular enzymes (CBH and POD) to break down plant fibers and other enzymes (LAP, GAP, and AP) to play essential roles in the microbial acquisition of nitrogen and phosphorus (Sinsabaugh et al., 2002a). The significant increases in activities of LAP, GAP, PPO, and CBH provided a favorable condition for microbial decomposition and contributed to a high decomposition rate. Extracellular enzyme activities of microbial decomposers correlate with the decomposition rate under co-exposures, which is confirmed by the SEM analysis. It indicates that these enzymes are driving factors of plant litter decomposition under co-exposures of acid rain and nZnO. The results highlight the importance of microbial enzyme activity as a biotic marker to estimate decomposition rates of plant litter even under pollution conditions in the freshwater ecosystem.

The co-exposures of acid rain and nZnO accelerated the microbial decomposition of plant litter though the ecological process would be inhibited by any one of the factors alone (Du et al., 2020a, Du et al., 2020b). This finding might be attributed to the enhancement of fungal community diversity because Duarte et al. (2008) demonstrated that the high fungal diversity might mitigate the impact of anthropogenic stress on microbial decomposition of leaves in streams. Besides, the important role of *Anguillospora* in plant litter decomposition is implied by the co-occurrence network analyses. These observations underscore the importance of fungal community structure in plant litter decomposition and even ecological functioning in streams (Bai et al., 2018).

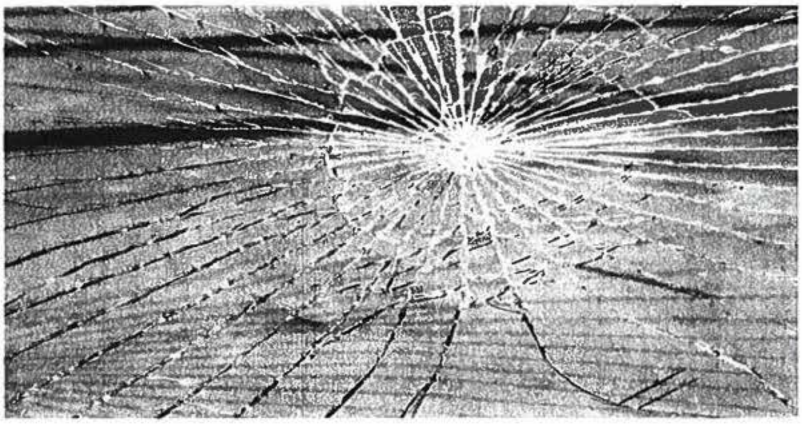
5. Conclusion

In this study, the plant litter decomposition was accelerated under co-exposures of acid rain and nZnO, which could not be predicted based on the individual effects of acid rain or nZnO. The much higher decomposition rate under the combined effects could be attributed to the increases in microbial enzyme activities, fungal community diversity, and the hub genera. Changes in the three factors were related to the dissolution of nZnO, which was influenced by the ratio of S: N in acid rain. Therefore, the mechanism of metallic nanoparticles dissolution should be further explored under the changing aquatic environment. Besides, our observations highlight the importance of

CEA recommendations for mitigating glass breakage

Solar modules are getting bigger, thinner, and more powerful. But from Texas to Thailand, the same problem is appearing: broken glass. Not from hail or mishandling, but from cracks that spider from frame edges, splinter near clamps, and web across modules. In cases seen by Jörg Althaus, director of engineering and quality assurance at Clean Energy Associates (CEA), it starts with a few panels – then dozens, hundreds, even thousands.

July 28, 2025 PV MAGAZINE



From pv magazine 6/25

Clean Energy Associates has investigated glass breakages at utility-scale solar sites across three continents. It has found that there isn't a single root cause, but a perfect storm: thinner glass combined with design shortcuts, evolving materials, and field realities that stress modules beyond what was simulated in the lab.

For years, the industry relied on single-glass modules made with sturdy, fully tempered 3.2 mm glass. But the push toward bifacial modules, combined with the appeal of lower material costs and slimmer profiles, led many manufacturers to adopt 2.0 mm double-glass designs using heat-strengthened but not fully tempered glass on both sides.

Two sheets of 2 mm glass should match the strength of one thicker pane, on paper. In practice, modules are now more fragile. These thinner sheets don't just flex, they bend and bow like diving boards when subjected to wind loads and tracker movement. They're more sensitive to where and how they're clamped. Push too hard, too close to the edge, and the stress builds invisibly. The larger the module format gets, the more pronounced these issues become. More surface area means more deflection, more vibration, and more potential for tiny weaknesses to transform into full-on fractures.

In the field

The same red flags keep appearing when CEA inspects sites with widespread breakage. Cracks tend to start near clamp points, at corners or edges where the frame exerts pressure on unsupported spans.

Modules often show no sign of external impact, just a sudden, sharp fracture that runs across the glass. Some modules arrive pre-stressed. We've seen glass curvature baked in before the panel even leaves the crate, likely introduced during lamination or framing. Large modules vibrate in the wind. On long trackers with flexible purlins, we've measured subtle but persistent shaking that amplifies structural fatigue over time.

ass
nards

In one case, glass fragments literally popped off a module during routine maintenance weeks after the initial fracture. The cause? A combination of internal tension and poor edge grinding, with no outside force to blame.

Lab report

CEA has recreated these breakages in controlled testing and confirmed that even modules certified to pass industry module testing standard IEC 61215 can fail under real-world stress.

Dynamic mechanical load (DML) testing, which simulates wind gusts and movement, has revealed failures that static load tests do not catch. When mounted on field-realistic setups including the underlaying purlins, some modules slipped from their clamps during testing or cracked after repeated flexing due to substructure deflection.

Fractography points to clamp zones as the stress epicenter, especially when clamp spacing is tight or torque settings are off. The back glass measured as thin as 1.9 mm in some samples, still within spec but barely. Marginal tolerances leave little room for site-specific quirks.

Certification gap

The current standards were designed for yesterday's modules. While dynamic testing was added to IEC 61215 in 2021, it's still not widely applied. When it is, it often doesn't replicate real-life mounting configurations that projects use in the field.

CEA has seen cases where clamp positions in lab tests differ from the field, leading to stress concentrations in completely different areas.

Substructure flexibility, especially in long-span, tracker-mounted systems, introduces torsion that certification tests don't account for. Torque settings during installation also vary significantly in the field and can create unaccounted-for stress at clamp zones.

As a result, modules that pass IEC 61215 tests may still fail in actual deployment, not because they're defective, but because the certification regime doesn't fully reflect the mechanical realities of today's solar systems.

Even when everything else looks right, hidden defects can tip the balance. In several investigations, we've found tiny air bubbles or foreign particles embedded in the glass. These micro-enclosures are invisible at a glance but can act like time bombs – stress concentrators that weaken the glass just enough to let a fracture propagate.

Time Bombs

For toughened or heat-strengthened glass, surface stress is normal. However, we've seen variation in this surface stress, which indicates that not all glass is manufactured the same way. Heat strengthening processes may also vary. Without serial traceability for the glass itself, tracking these issues back to a specific batch, line, or shift is nearly impossible. That makes systemic prevention harder than it should be.

Stress cocktail

The takeaway is that glass breakage isn't caused by one thing, it's caused by five or six things happening at once: a slightly bent module, slightly over-torqued clamps, slightly under-supported spans, slightly thinner glass, slightly flexible racking.

Each of these might be survivable in isolation, but when combined with added temperature, wind and hail stress, it can be too much for the glass to withstand.

This isn't a mystery anymore. The next step is applying that knowledge across the industry. Addressing these risks requires a coordinated effort from designers and manufacturers to EPCs and asset owners.

CEA recommends:

- Make testing more realistic. Use project-specific mounting configurations. Include dynamic loading. Measure deflection and torque tolerances in context. Some flaws in testing may require standards to be updated. For example, torsional stress is not included currently and may be solved by added procedures not yet standardized.

- Clamp smarter. Harmonize clamp design and spacing with the actual glass and frame properties of modern modules.
- Push for better traceability. Glass deserves the same scrutiny as cells and wafers, including batch tracking and process transparency.
- Watch for micro-defects. Whether it's edge finishing, inclusions, or stress from lamination, these should be screened systematically. Include glass edge trimming and grinding as well as framing inspections in your quality assurance programs, as small impurities in frame parts can be the death of glass edges.
- Treat mounting as part of the design. It's not just about the module, it's about the system it lives in.

The promise of double-glass modules is real. Better longevity, better moisture protection, higher energy yields. But those benefits won't materialize if we keep underestimating the mechanical realities of large, thin-glass panels mounted on flexible structures.

Solar is scaling up fast and the systems deployed today will be out there for 30 years or more. Let's make sure the glass can last that long.

About the author

Jörg Althaus is director of engineering and quality assurance services at Clean Energy Associates (CEA). An electrical engineer by training, Althaus has spent over 20 years overseeing inspections of solar equipment in deserts, typhoon zones, and factory lines across four continents. His current work focuses on identifying systemic risks in modern PV module design – especially those that hide in plain sight until the glass shatters.

WJBPHS
World Journal of Biology Pharmacy and Health Sciences
eISSN: 2582-5542
Cross Ref DOI: 10.30574/wjbphs
Journal homepage: https://wjbphs.com/

(REVIEW ARTICLE)

Assessing the environmental health and safety risks of solar energy production

Alex Olanrewaju Adekanmbi [1], Nwakamma Ninduwezuor-Ehiobu [2,*], Uchenna Izuka [3], Ayodeji Abatan [4], Emmanuel Chigozie Ani [5] and Alexander Obaigbena [6]

[1] *Independent Researcher, California, USA.*
[2] *FieldCore, part of GE Vernova, Canada.*
[3] *YMCA GTA, Canada.*
[4] *Saltwire Network, Halifax, Canada.*
[5] *Department of Electrical Engineering, The University of Nebraska-Lincoln, USA.*
[6] *Darey.io, United Kingdom.*

World Journal of Biology Pharmacy and Health Sciences, 2024, 17(02), 225–231

Publication history: Received on 08 January 2024; revised on 15 February 2024; accepted on 17 February 2024

Article DOI: https://doi.org/10.30574/wjbphs.2024.17.2.0080

Abstract

Solar energy production has gained significant traction as a promising alternative to fossil fuels, yet its widespread adoption raises questions regarding its environmental health and safety (EHS) risks. This review presents an overview of the current state of research in assessing these risks associated with solar energy production. Firstly, it examines the environmental impacts of solar energy, including the life cycle assessment of photovoltaic (PV) panels and solar thermal systems. Key considerations include the energy and resources required for manufacturing, transportation, installation, operation, and end-of-life disposal or recycling of solar panels. Furthermore, the potential for land use change, habitat disruption, and biodiversity loss due to large-scale solar installations is addressed. Secondly, the review discusses the safety risks associated with solar energy production, focusing on occupational health and safety hazards for workers involved in manufacturing, installation, maintenance, and decommissioning of solar energy systems. It examines exposure to hazardous materials such as lead, cadmium, and silicon during the manufacturing process, as well as the risks of falls, electrical hazards, and other workplace accidents during installation and maintenance activities. Moreover, the review highlights emerging technologies and best practices aimed at mitigating EHS risks in solar energy production. These include advancements in PV panel recycling technologies, improvements in manufacturing processes to reduce environmental impacts, and enhanced safety protocols and training for workers in the solar energy industry. While solar energy offers numerous environmental and economic benefits as a renewable energy source, it is essential to comprehensively assess and manage its EHS risks throughout the life cycle of solar energy systems. This review underscores the importance of ongoing research, innovation, and regulatory oversight to ensure the sustainable and safe deployment of solar energy technologies in the transition towards a low-carbon future.

Keywords: Health; Environment; Solar; Energy; Safety; Review

1. Introduction

Solar energy production has gained significant attention as a sustainable and renewable energy source. The process involves harnessing sunlight to generate electricity through various technologies such as photovoltaic systems and solar thermal collectors (Mugagga & Chamdimba, 2019). The importance of assessing environmental health and safety (EHS) risks associated with solar energy production cannot be overstated. Solar energy technologies have the potential to bring about positive environmental impacts, but they also pose certain risks that need to be carefully evaluated (Ramírez-Márquez et al., 2019). Therefore, it is crucial to comprehensively assess the EHS risks to ensure the

---

* Corresponding author: Nwakamma Ninduwezuor-Ehiobu.

sustainable and safe deployment of solar energy technologies. This introduction outlines the purpose of assessing EHS risks in solar energy production and provides an overview of the significance of this assessment.

Assessing EHS risks in solar energy production is essential to identify and mitigate potential adverse effects on the environment, human health, and safety. The rapid growth of solar energy technologies, including photovoltaic systems and solar thermal collectors, necessitates a thorough understanding of their environmental and health implications (Alinda et al., 2021). Environmental considerations encompass aspects such as land use, water consumption, and the potential for pollution during the manufacturing, operation, and disposal of solar energy systems (Cao et al., 2023). Furthermore, the safety of workers involved in the production, installation, and maintenance of solar energy technologies must be carefully evaluated to prevent occupational hazards and accidents. Therefore, the assessment of EHS risks serves as a proactive measure to address potential environmental and health concerns associated with solar energy production.

The purpose of this outline is to provide a comprehensive framework for evaluating the EHS risks of solar energy production. By synthesizing the existing literature on solar energy technologies and their environmental and health implications, this outline aims to facilitate a systematic and evidence-based approach to EHS risk assessment in the context of solar energy production. The diverse range of solar energy technologies, including photovoltaic systems, solar thermal collectors, and solar-powered water purification systems, necessitates a multifaceted assessment that considers various environmental and health factors. Additionally, the outline will address the challenges and opportunities associated with solar energy production, providing insights into sustainable practices and risk mitigation strategies.

In conclusion, the assessment of EHS risks in solar energy production is crucial for ensuring the sustainable and safe deployment of solar energy technologies. This introduction highlights the significance of evaluating environmental and health implications associated with solar energy production and emphasizes the need for a comprehensive framework to assess EHS risks. By synthesizing the existing literature, the outline aims to provide a structured approach to evaluating the environmental, health, and safety aspects of solar energy technologies, thereby contributing to informed decision-making and sustainable practices in the solar energy sector.

2. Environmental Impacts of Solar Energy Production

Solar energy production, particularly the life cycle assessment (LCA) of photovoltaic (PV) panels, encompasses several phases with distinct environmental impacts. The manufacturing phase of PV panels involves significant environmental impacts, including energy consumption and emissions (Galimshina et al., 2023). Additionally, the production of PV cells, such as perovskite PV cells, contributes to environmental impacts due to the higher environmental impacts from unit electricity generated (Celik et al., 2016; Held & Ilg, 2011). Furthermore, the operation and maintenance phase of PV panels, including the adoption of rooftop solar panels, has been shown to contribute to environmental impact savings from a societal-level perspective (Grant & Hicks, 2020). Moreover, the end-of-life disposal or recycling of PV panels is crucial, with studies indicating that the recovery of materials from solar modules results in lower environmental impacts compared to other end-of-life scenarios (Lunardi et al., 2018; Boussaa et al., 2020; Aryan et al., 2018).

In conclusion, the life cycle assessment of solar energy production, including PV panels, involves various phases with distinct environmental impacts, emphasizing the importance of considering the environmental implications from the manufacturing phase to end-of-life disposal or recycling of solar panels.

3. Safety Risks in Solar Energy Production

Occupational health and safety hazards in solar energy production encompass various stages, from manufacturing to installation, maintenance, and decommissioning. In manufacturing facilities, workers face exposure to hazardous materials such as lead and cadmium, necessitating stringent safety protocols (Ndejjo et al., 2015; Ibekwe et al., 2024). Similarly, during installation and maintenance, the risks of falls, working at heights, and electrical hazards are prevalent, along with other workplace accidents (Wright & Norval, 2021; Odeleye et al., 2018). Furthermore, decommissioning and disposal pose risks associated with dismantling solar systems and the proper disposal or recycling of materials (Schulte et al., 2013; Etukudoh et al., 2024).

The rapid growth of solar energy production, as well as other renewable energy sources, has led to an increased focus on identifying and eliminating hazards to workers, emphasizing the importance of occupational safety and health in these industries (Schulte et al., 2016; Ukoba et al., 2018). Legislation needs to recognize solar ultraviolet radiation cumulative GHG emissions from PV are likely to arise from improvements in module efficiency, increased lifetime, less silicon mass per module and lower use of electricity for the production process [65]. It is also important to note that solar PV technology is a fast-improving technology and frequent LCA studies are being published in order to keep the pace with the advancements.

4.1.5. *Noise and visual impacts*

Solar modules do not suffer with the noise problem. Solar energy is a static source of power generation with no rotating parts. Also, there will be some employment benefits during the construction phase and especially for large schemes during the operational phase. Solar panels contain no moving parts and thus produce no noise. Wind turbines, by contrast, require noisy gearboxes and blades. However fossil fuel based plants and renewable source of energy (including wind and hydro) have noise problems [21,60,107,108]. The noise problem from power plants makes it unsuitable for placement nearer to the population. Proper sites are marked for their placements. Solar technology is changing is very fast. Options for reduction of energy demand must always be considered along with the assessment of PV application. Instead of roof-topped panels, special bricks with integrated special PV modules are also made. Fig. 11 shows such type of construction giving esthetic look [60,109].

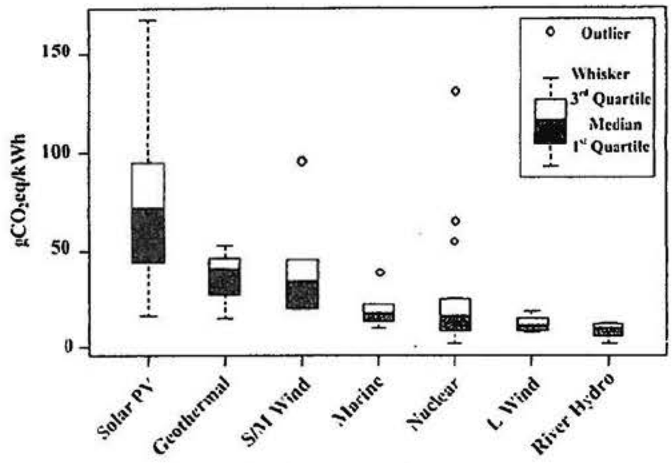


Fig. 10. Carbon Footprints for renewable electricity [64].

Visual intrusion is highly dependent on the type of the scheme and the surroundings of the PV systems. It is obvious that, if a PV system is applied near an area of natural beauty, the visual impact would be significantly high. In case of modules integrated into the facade of buildings, there may be positive esthetic impact on modern buildings in comparison to historic buildings or buildings with cultural value.

4.2. *Negative impacts of solar energy*

Solar energy is considered as a 'Green Source' of energy. However there are some Safety, Health and Environmental issues, which should be addressed before the wide spread application of solar technology. Solar panels are based on nanotechnology, which is considered as a 'clean tech' technology [114]. To see the impact of solar panel, its life could be split into three stages, manufacturing, operation (generation), decommissioning. It is true that photovoltaic solar panels do not pollute the air during power generation however

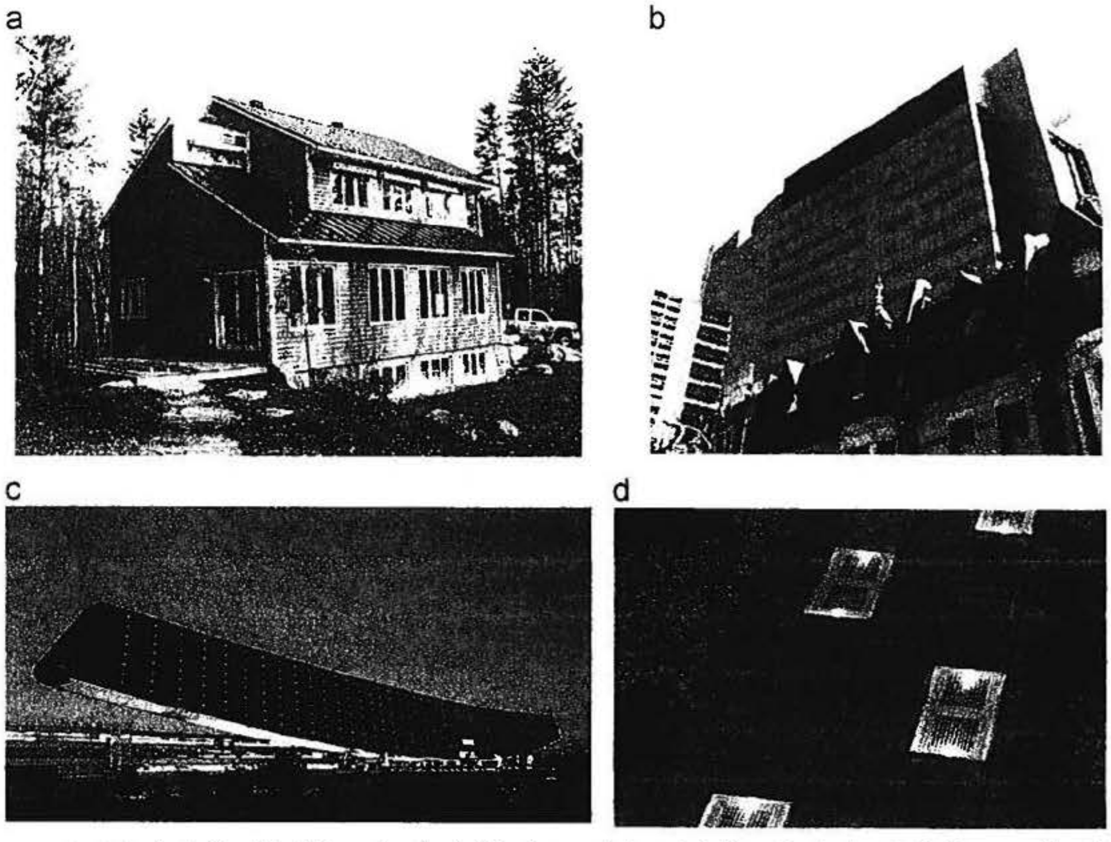


Fig. 11. Solar energy constructed outlook; (a) residential house based on building integrated photovoltaic/thermal technology [110]; (b) Integrated combined solar thermal and electric generation building [111] at John Molson School of Business, Concordia University. (c) The Solar Ark [112, 113], a sign board in Japan under Sanyo Electric Co., Ltd. (d) Solar Brick LED Lights.

manufacturing process of them involves many toxic materials, which is highly harmful from SHE perspective. There are some concerns after the completion of expected life of panel and in their recycling process. These issues will be discussed in this section [115].

4.2.1. *Cost of land*

Large-scale solar farms need a big space for their installation. Approximately 1 m^2 of land produces 200 W of electricity, depending on the location, efficiency and other environmental conditions [6,116,117]. This problem becomes prominent for those countries which have already high population density like Singapore, having an area of 697 sq.km [66], with population density above 7680/sq.km. Finding cheap land in such countries is quite difficult. Also high cost of land will also affect the per unit electricity cost. Land use could be minimized by increasing the solar panels efficiency or to mount the cells on a rooftop [6]. With current efficiency of solar panel, the top roof area of houses in USA will only fulfill the 1/10th of total US energy requirement [6].

4.2.2. *Toxic chemical content in solar panel manufacturing*

Different chemicals are used in manufacturing of solar panels, particularly during extraction of solar cell. For example, cadmium (Cd) is used in cadmium telluride based thin film solar cells as a semiconductor material to convert solar energy into electrical energy which is highly toxic element. National Institute of Occupational Safety & Health (NIOSH) considers cadmium dust and vapors as carcinogens (causing ~~cancer).~~ Similarly many hazardous chemicals are used as solvents to clean dust and dirt from the solar panels. European Union has initially banned Cd, Pb, Hg and other toxic compounds as per the regulations of the Restriction of Hazardous Substances Directive (RoHS) [118–122]. However the European Union decision highly affected the production of solar panel based on cadmium telluride (CdTe). In November 2010, EU law exempted the solar panel from a ban in order to facilitate the solar manufacturing industry and also to attain the set targets for renewable energy generation [123]. These toxic materials have special concerns, particularly for local habitats. In recent years, September 2011, accidents due to dumping of hazardous chemicals into the water supply has led to local protest and finally resulted the shutdown of the company [124]. PV panels are threat to the environmental contamination if improperly disposed of upon decommissioning due to the use of toxic materials in their composition [76]. On the other hand, the accidental release of heat transfer fluids (water and oil) from parabolic trough and central receiver systems could form a health hazard. The hazard could be substantial in some central tower systems, which use liquid sodium or molten salts as a heat-transfer medium. Indeed a fatal accident has occurred in a system using liquid sodium. These dangers could be avoided by moving to volumetric systems that use air as a heat-transfer medium. Central tower systems have the potential to concentrate light to intensities that could damage eyesight. Under normal operating conditions this should not pose any danger to operators, but failure of the tracking systems could result in straying beams that might pose an occupational safety risk at site [60]. The partial list of toxic materials used in solar industry, their use and impact on human health, safety and environments are presented in Table 11.

inca

4.2.3. *Ecological impacts*

Solar energy facilities have direct impacts on local habitats and nearby surroundings. The construction of solar farms on large scale needs clearing of land which adversely affects the native

Table 11
Safety, Health and Environmental (SHE) impact from the toxic compounds [78,80,125–127].

Toxic Compounds	Purpose	Safety, health and environmental impact
Ammonia (NH_3)	To produce anti-reflective coatings for solar PV modules.	Skin irritation, eyes irritation, throat problem, lungs problems, mouth and stomach burns.
Arsenic (As)	Used in GaAs solar PV cells, resulted from the decomposition of GaAs	Heart beat problems, throat infection, lung cancer, nausea, vomiting, reduced blood cells, skin darkening, red spot on skin, liver problem, etching in hands and feet.
Silicon (Si)	Used as a PV semiconductor material	Crystalline Si causes respiratory problems, irritating skin and eyes, lung and mucus problems
Lead (Pb)	To wire, solder photovoltaic electrical components.	Damages nervous system, weakness in bones, can also cause anaemia,high level exposure resulting in miscarriage for pregnant woman, damages the brain and kidneys, highly carcinogen element.
Nitric acid (HNO_3)	To clean wafers and reactors, remove dopants.	Potential cause for chemical burns.
Sulfur hexafluoride (SF6)	Used to etch semiconductors and clean reactors in PV manufacturing.	The most powerful greenhouse gas known.
Cadmium (Cd)	Cd is used in cadmium telluride based solar cells as a semiconductor to convert solar energy into electricity.	Cd dust and vapours are highly toxic and considered as carcinogens. Also effectthe respiratory system, kidneys and blood cells and can cause prostate, diarrhoea, chest tighten and lung cancer.
Hydrogen (H_2)	Used in manufacturing amorphous-Si solar cells.	Highly explosive.
Hexavalent Chromium (Cr-VI)	Used in screw, solar chassis board and as a coating material in solar panel to absorb solar radiation.	Cr is a carcinogenic element, means causes cancer.
Polybrominated biphenyls (PBBs) and brominated diphenylethers (PBDEs)	Used in circuit boards and solar panel inverters	Recognized as toxic and carcinogenic and are described as endocrine disrupters.
Acetone	These solvents are used to clean microscopic dirt and dust off of chips.	Eyes andnose irritation, throat infection, kidney and liverproblem, nerve damage, birth defects, sexual problems including lowered ability to reproduce males.
Iso-propanol	To clean microscopic dust and dirt from solar chips.	Vomiting, Eyes irritation, depression, dermatitis, nausea, unconsciousness, respiratory failure, death or coma.
Toulene		Headaches, hearing loss, confusion, memory loss, pregnancy problems, retarded growth.
Xylene		Skin irritation, eye irritation, nose infection, throat and breathing problems, pregnancy problems, liver and kidneys infection.
1,1,1-Trichloroethane		Dizziness and loss of mind, reduced blood pressure, unconsciousness, stop heart beating.
Hydrochloric acid (HCl)	To produce electrical grade silicon, clean and etch semiconductors	Skin problem, eyes and nose infection, respiratory problem, food digestion, mouth and throat infection, respiratory depression.

Environment International 73 (2014) 224–234

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

The photovoltaic industry on the path to a sustainable future — Environmental and occupational health issues

Bouchra Bakhiyi [a], France Labrèche [a,b], Joseph Zayed [a,b,*]

[a] *Department of Environmental and Occupational Health, School of Public Health, University of Montreal, Montreal, Quebec, Canada*
[b] *Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST), Montreal, Quebec, Canada*

ARTICLE INFO

Article history:
Received 31 January 2014
Accepted 30 July 2014
Available online 27 August 2014

Keywords:
Photovoltaic systems
Sustainability
Life cycle analysis
Occupational health

ABSTRACT

As it supplies solar power, a priori considered harmless for the environment and human health compared with fossil fuels, the photovoltaic (PV) industry seems to contribute optimally to reduce greenhouse gas emissions and, overall, to sustainable development. However, considering the forecast for rapid growth, its use of potentially toxic substances and manufacturing processes presenting health and safety problems may jeopardize its benefits. This paper aims to establish a profile of the PV industry in order to determine current and emerging environmental and health concerns. A review of PV system life cycle assessments, in light of the current state of the industry and its developmental prospects, reveals information deficits concerning some sensitive life cycle indicators and environmental impacts, together with incomplete information on toxicological data and studies of workers' exposure to different chemical and physical hazards. Although solar panel installation is generally considered relatively safe, the occupational health concerns related to the growing number of hazardous materials handled in the PV industry warrants an all-inclusive occupational health and safety approach in order to achieve an optimal equilibrium with sustainability. To prevent eco-health problems from offsetting the benefits currently offered by the PV industry, manufacturers should cooperate actively with workers, researchers and government agencies toward improved and more transparent research, the adoption of specific and stricter regulations, the implementation of preventive risk management of occupational health and safety and, lastly, greater responsibilization toward PV systems from their design until their end of life.

Contents

1. Introduction

Like many industries based on renewable resources, that of solar energy seems to be a compromise between concerns related to fossil fuel supply (price and market instability) and the growing menace of climate change.

The photovoltaic (PV) industry sets itself apart through its achievements on technological and economical levels. The industry uses PV semi-conductor cells alone, as consumer products (solar powered watches, calculators, toys, etc.) or assembled and encapsulated in solar modules. We will hereafter focus on PV systems based on solar modules with a 20–30-year lifetime, commonly referred to as solar panels. Solar cells benefitted from intensive research and development efforts leading to three cell generations:

- ➢ the first, in mono or multicrystalline silicon as wafers, ingots or ribbons;

---

* Corresponding author at: Department of Environmental and Occupational Health, School of Public Health, University of Montreal, P.O. Box 6128, Main Station, Montreal, Quebec H3C 3J7, Canada. Tel.: +1 514 343 5912; fax: +1 514 343 2200.
E-mail address: joseph.zayed@umontreal.ca (J. Zayed).

http://dx.doi.org/10.1016/j.envint.2014.07.023
0160-4120/

- the second, in thin films composed mainly of amorphous silicon, cadmium telluride (CdTe), copper indium selenide (CIS) or copper indium gallium selenide (CIGS);
- the third generation, that uses new materials beside silicon and produces multi-junction panels mainly consisting of indium gallium phosphide, gallium arsenide or indium gallium arsenide and germanium (InGaP/GaAs/InGaAsGe) cells and systems coupled with lenses to produce concentrated photovoltaics (CPV) systems.

In 2012, silicon-based cells dominated the global market with 86% of total production while thin films cells, including second and third generations, shared the remainder with CdTe technology at the top (Fraunhofer ISE, 2013).

In order to amplify the power generation capacity, solar panels are connected to form a PV system for residential, commercial, industrial or rural applications around which gravitates a basic component complex (inverters to convert direct current to alternating current, wiring, circuit breakers and a mounting structure, mainly in aluminum and steel for roof-top laminate panels) and additional accessories which vary according to the type of system (i.e., solar batteries for stand-alone systems, diesel generator or wind turbine for hybrid systems, import/export meter for on-grid systems, mirrors and trackers for concentrated PV). The combination of basic components and accessories constitute the "balance of system" (EPIA/Greenpeace, 2011).

The world's cumulative PV capacity varied from 1.4 GW installed electrical power in 2000 to over 102 GW in 2012, with more than 70 GW for Europe, 8.3 for China, 7.77 for the United States and 6.9 for Japan. The global cumulative PV capacity could reach between 290 GW and more 420 GW in 2017 (EPIA, 2013). Between the end of 2007 and 2012, PV solar energy production experienced a 60% growth compared to 25% for wind energy and 3.3% for hydroelectricity (REN, 2013).

PV industry offers attractive economic prospects: PV module prices, thanks to constant technological improvements in Europe and the United States, went down from an average US$5.5/Watt-peak (Wp)[1] at the end of 2001 (Solarbuzz, 2012) to less than US$1/Wp in December 2013 (PvXchange, 2013). The sector generated some 1.36 million jobs in the world in 2009–2012 (REN, 2013) while the expected number of workers would be around 2 million in 2030 and 6 million in 2050 (Grossmann et al., 2012). Employment in the PV industry concerns various jobs involved in each step of the PV system life cycle. Most jobs associated with the PV industry are not new occupations. The major occupational activities deal with (CanMetEnergy, 2012; Hamilton, 2011; ILO, 2011):

- research and development (e.g. physicists, chemists, materials scientists);
- industrial solar modules engineering and manufacturing (e.g. semi-conductor process engineers, mechanical and manufacturing engineers, high-tech technicians, glaziers, coating and painting machine setters and operators, maintenance technicians) and BOS manufacturing (e.g. high-tech technicians, metal workers, assemblers, coaters and testers);
- solar power plant construction (e.g. civil engineers, general construction laborers, heavy equipment operators, welder, structural iron and steel workers);
- solar plant operation, care and maintenance (e.g. electrical engineers, power plant operators, electricians, plumbers);
- PV waste recycling workers (dismantling and processing).

Several PV waste recycling plants are now established in European countries such as France and Germany, in the United States of America, in Taiwan and in China. Some recycling plants specialize in thin films and others in crystalline silicon, and some manufacturers also recycle their PV waste (Bilimoria and Defrenne, 2013; ENF, 2014).

In 2012, the top 5 countries in terms of industrial and installation PV work forces employment were China (300,000 workers), United States (119,000), Germany (100,000), Japan (47,000), Belgium (20,500) and France (18,000) (IEA/PVPS, 2013a). In the same year, five of the 10 main manufacturers of PV modules (in terms of production/sales/shipment) were Chinese, producing 8249 megawatt-peak (MWp) versus 2 United States manufacturers with 2811 MWp and one Canadian company with 1543 MWp (EurObserv'ER, 2013).

At face value, the PV industry seems to adhere optimally to the concept of sustainable development. Bakhiyi and Zayed (2011) showed that the PV industry can be considered as a barometer of human and sustainable development in a given country according to its main principles (economic efficiency, health and safety, quality of life, precaution/prevention, subsidiarity/delegation, equity and social solidarity, environmental protection, preservation of biodiversity and respect of ecosystems).

From this perspective, the PV industry uses an unlimited solar resource and provides energy that is both "clean", i.e. considered harmless to the environment and human health compared with fossil fuels, and increasingly accessible, while creating jobs. In addition, due to low maintenance costs, PV energy could help improve standards of living in developing countries with a high solar irradiation by increasing access to electricity (ILO, 2012), and in fact, solar energy investment increased by 72% in developing countries during 2012 (Frankfurt School-UNEP Centre/BNEF, 2013).

However, upon examination of its life cycle, from production to the end of life of the PV systems, the PV industry's adherence to the concept of sustainable development may not be as strong as it appears. In fact, environmental, public and occupational health concerns can be raised, in a definitely young and vigorous industry, but which seems more focused on competitiveness (Taylor, 2010) and benefits from substantial subsidies for both manufacturers and consumers (Platzer, 2012). Moreover, PV panel waste is now considered potentially dangerous, akin to e-waste, and is, since August 2012, subject to the European Directive WEEE (Waste Electrical and Electronic Equipment) (European Union, 2012). In the United States of America, a regulation that adds PV modules to the e-waste category has been proposed by the Department of Toxic Substances Control of California and is still under discussion (CDTSC, 2013). In addition, an extended producer liability in terms of PV waste management will be applicable to European Union PV panels on February 2014 (Bilimoria and Defrenne, 2013).

The occupational safety and health concerns related to the growing hazardous materials handling in workplaces in general and PV industry in particular, encourage to an all-inclusive approach in order to achieve an optimal alignment of key targets: occupational safety and health, sustainability and the novel concept of "green chemistry". It requires above all a broad and clear overview of work-related potential hazards, the only way to achieve sustainable workplace practices objective (Schulte et al., 2013) and should not be only seen as an effective way to minimize occupational hazard issues but also as a great engine for green jobs creation and innovation (ILO, 2013).

This review plans to profile the PV industry in order to determine current and emerging environmental and health concerns. More specifically, it involves identifying and exposing certain information gaps in terms of potential eco-health impacts associated with the PV industry by examining PV system life cycle assessments (LCA) conducted to date and relevant occupational health and safety data.

2. Results and discussion

2.1. Gaps in PV system life cycle assessments

The manufacturing of PV systems requires high-tech procedures consuming primary energy, mainly fossil fuel, and involves a variety of materials, most of which are potentially toxic or hazardous (NRC, 2010). This combination may contribute to the emission of deleterious

---

[1] The *Watt-peak* (Wp) indicates the power of a solar panel under standard test conditions (1.000 W/m^2 of sunshine, panel temperature of 25 °C, "AM 1.5" visible spectrum).

environmental
& health

substances for which potential environmental and health risks are evaluated using a LCA, which takes into account the nature and intensity of inflow (energy/raw material) and outflow (pollutant emissions in environmental compartments) during the production, use, decommissioning and end of life phases of PV systems according to the "cradle-to-grave" concept (Fthenakis et al., 2011; Jungbluth et al., 2008).

In practice, within ISO standards 14040 and 14044, the choice of parameters considered in a PV system LCA (such as the generation and type of PV system, the life cycle phases, the inflow/outflow inventories and the impact analysis methods) is quite flexible.

These impact analysis methods differ through their approach, which can be:

> One-dimensional, evaluating a group of performance and environmental indicators such as the Energy Payback Time (EPBT), which is the time required to "pay off" the energy debt, the carbon footprint (greenhouse gas emission) or the Cumulative Energy Demand (Fthenakis and Kim, 2011).

> Multi-dimensional, evaluating damages and the cause/effect relationships between outflow, environmental impact mechanisms (climate changes, acidification, eutrophication, marine ecotoxicity, etc.) and other impact categories such as risks for human health, ecosystem diversity and accessibility of resources (Laleman et al., 2011).

The results from numerous PV system LCAs published to date generally agree on a favorable EPBT as well as relatively modest eco-health impacts compared with fossil fuels. The average EPBTs calculated for PV systems range from 5 years for solar silicon systems installed in Central Europe (Laleman et al., 2011) to a minimum of 0.5 year for CdTe systems installed in the Southwest United States (Fthenakis, 2012). PV systems perform advantageously in terms of greenhouse gas (GHG) emissions, with median estimate ranging from 18.0 to 72.4 g Carbon dioxide per kilowatt-hour (CO_2eq/kWh) for multicrystalline silicone technology to 15.5–66.0 g CO_2eq/kWh for CdTe PV technology and 20.5–95.0 g CO_2eq/kWh for CIGS PV technology (Bekkelund, 2013), compared to fossil fuels such as coal (519 to 1200 g CO_2eq/kWh) or oil (800 to 1280 g CO_2eq/kWh) (Dones et al., 2003; Weisser, 2007).

However, the published LCAs do not give a clear and complete picture of their potential environmental and health impacts, considering recent developments such as: the expanding market for PV components and PV systems installation capacity, particularly in emerging economies such as China, India and Malaysia – the different type of systems such as off-grid PV systems (e.g., stand-alone and hybrid systems) – the large surface area installations such as very large scale photovoltaics (VLS PV) in desert lands – the bold architecture designs such as large scale building integrated photovoltaics (BIPV) – the technological developments (e.g., nanotechnology applications).

Considering only environmental impacts, information deficits concern sensitive life cycle indicators such as GHG emissions, and also potential ecotoxicity of chemicals related to PV systems life cycle, including basic and accessory balance of system (BOS) components.

The major information gaps can be divided according to the PV systems life cycle phase, i.e. production phase (Table 1), operational phase (Table 2) and end-of-life (Table 3), all generations and types of PV systems included. Although relatively distant, the end-of-life stage warrants serious reflection since PV waste is nowadays considered e-waste. On a global basis, e-waste management is still facing challenges in terms of proper collection, safe disposal and improved rate of recycling in both developed and developing countries (Kiddee et al., 2012; Lundgren, 2012; Reck and Graedel, 2012). Moreover, data gaps in PV panels waste management concern not only the end-of-life phase, but also manufacturing waste such as broken and/or defective panels and production process waste.

Table 4 presents additional information gaps concerning second and third generation PV technologies, alone or after they are building integrated. Finally, Table 5 focuses on information gaps concerning the stand-alone PV systems (generally using lead–acid batteries) and the hybrid systems (generally using both lead–acid batteries and diesel generators).

In addition, LCAs of other BOS components, such as inverters, mounting structures and cabling, are still poorly documented (Fthenakis et al., 2011; Jungbluth et al., 2012), apart from inverters electronics compounds and aluminum frame (for framed modules), which are associated with a substantial level of toxicity risk that contribute significantly to the global PV system environmental and health impacts (Alsema and Wild-Scholten, 2004; Jungbluth et al., 2012).

Given the various developments expected of the PV industry around the world and the concern for environmental and health sustainability, these information gaps would require steady attention from the scientific community in order to get a LCA as complete as possible, considering all the PV systems specifics. The continuous search toward less potential toxic risk and sustainability has produced a complementary method to LCA, based on a "hazard screening approach", and called "chemical alternatives assessments (CAA)". CAA focuses more on toxicological aspects, in particular CIS and CIGS manufacturing that use some potential toxic raw materials (such as cadmium sulfide) and processes (such as indium or zinc based-deposition). The objective of that "green engineering" approach is to select, as far as possible, the less hazardous raw materials in order to increase both efficiency and sustainability (Eisenberg et al., 2013).

2.2. Gaps in occupational health and safety

toxic

Although most of these jobs are not new occupations, some emerging technological procedures during solar modules manufacturing and some job features involve new work conditions and consequently potential new risks for workers' health and safety. Thus, the World Health Organization considers the occupational health and safety issue an essential component of sustainable development (WHO, 2007). Risks associated with the PV industry are likely to occur at each step of the PV system life cycle, and concern both health and safety.

A wide range of potential toxic chemicals are used, generated or manipulated in the PV industry, routinely or accidentally. Potential exposure can occur through dust, smoke and/or vapor inhalation but also through ingestion and eye contact (EPRI, 2003; Fthenakis, 2013; Fthenakis and Moskowitz, 2000). Table 6 presents the main potentially toxic chemicals associated with PV industry according to their toxic potential (carcinogenic and/or non-carcinogenic), principal usage and the PV industry process concerned, as potential source exposure.

Exposure varies according to PV module generation, although some exposures are common to all PV systems, such as adjuvants or cleaning agents. PV modules recycling can also imply potential workers exposure to several carcinogenic substances such as arsenic, bromine-containing flame retardants, cadmium and hexavalent chromium. In addition, health risks related to manufacturing and recycling BOS system components should also be considering due to the presence of various potential hazardous chemicals such as lead, arsenic, strong acid and dioxins. The level of occupational health risk depends on the toxicological profile of chemicals and their environmental concentrations as well as the frequency and duration of exposure. The efficiency of general and local exhaust ventilation systems and the adequacy of protective equipment are also relevant parameters to consider (Fthenakis, 2013; Fthenakis and Moskovitz, 2000).

Occupational health risk associated with PV systems during installation is mainly related to possible presence of asbestos in buildings, classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC, 2012). Occupational exposure to asbestos can potentially occur during PV-building integrated system installation when building components need to be dismantled (OPPBTP, 2011; OSEIA, 2006).

Safety risks can derive from chemical and physical agents. Chemical risks are linked with substances which have asphyxiant,

Table 1
Information gaps in life cycle assessments regarding data on photovoltaic systems production phase.

Expected developments	Source of potential risks	Information gaps	Comments
- Monopoly of solar silicon industry (incl. crystalline & thin-film silicon cells) at least until 2017 with global markets share ~80% (EPIA, 2013).	- Greenhouse gas emissions due to primary energy supply (mainly fossil) & to fluorinated gases (F-gases), e.g. nitrogen trifluoride (NF_3), sulfur hexafluoride (SF_6) & pure fluorine (F_2).	- Current Life Cycle Inventories of PV systems used for the calculation of GWP estimate based mostly on Western European & USA manufacturing data. - F-gases barely quantified if at all during carbon footprint assessment.	- Electricity from mc-Si panels produced in China & installed in Europe causes more greenhouse gas emissions (70% higher vs. electricity from pure European panels) given reliance of Chinese electricity supply on carbon intensive coal power (Jungbluth et al., 2012). - Estimated increase in greenhouse gas effect from 60 to 85% per KW-h with NF_3 (GWP100 ~ 16,600) & from 11 to 100% with SF_6 (GWP100 ~ 22,800) for micromorph PV modules[a] (Arnold et al., 2013; Meulen and Alsema, 2011).
- Compound annual growth rate (CAGR): global increase of 9–22% expected in PV production capacity & maintenance of control of Si PV market by China (EPIA, 2013).	- Potentially toxic chemical used or generated during PV panels and BOS components manufacturing: raw materials (e.g. Al, As, Cd, CdTe, CrVI, Cu, Ga, In, Pb), intermediate products ($SiCl_4$, $SiHCl_3$), etchants (strong acids & bases), additives (e.g. flame retardant PBDE). - Indirect emission of heavy metals from electricity & fossil primary energy; direct emission from PV panel processing (As, Cd, Hg, Ni, etc.) (Fthenakis et al., 2008; Jungbluth et al., 2012). - Waste from PV processing lines.	- Limited data on specific air emission & liquid and/or solid effluents from PV cells & BOS processing (Jungbluth et al., 2012). - Current Life Cycle Inventories of PV systems do not include all European PV projects & all manufacturers' data from market leaders in China or Taiwan (Jungbluth et al., 2012).	- Atmospheric emission of potentially toxic substances & soil contamination around silicon PV manufacturing plants reported in China (Cha, 2008). - Fossil energy-intensive manufacturing of Si PV cells (4900 MJ/m^2 vs. 992–1523 MJ/m^2 for CdTe cells) (Fthenakis and Kim, 2011). - Hazardous waste containing 630 lbs of Cd recently removed from a closed US PV plant (Colthorpe, 2013).

Al: aluminium; As: arsenic; BOS: balance of system; Cd: cadmium; CdTe: cadmium telluride; CrVI: hexavalent chromium; Cu: copper; Hg: mercury; In: indium; Ga: gallium; GWP100: global warming potential on a 100-year time scale; mc-Si: multicrystalline silicon; MJ/m^2: megajoules per square meter; NF_3: nitrogen trifluoride; Ni: nickel; Pb: lead; PBDE: polybrominated diphenyl ethers; Si: silicon; $SiCl_4$: silicon tetrachloride; $SiHCl_3$: trichlolosilane.

[a] A tandem junction of amorphous silicon and microcrystalline silicon.

Table 2
Information gaps in life cycle assessments regarding data on photovoltaic systems operational phase.

Expected developments	Source of potential risks	Information gaps	Comments
- Expansion of large fully building-integrated PV (with building materials) & large scale PV system installation on industrial rooftops (EPIA, 2012; RENI, 2013). - Active support for Very Large Scale-PV/VLS-PV systems projects in desert areas in the Mediterranean region, the Middle East, Northern Africa, Asia and Oceania. (Boudghene Stambouli et al., 2013; Komoto et al., 2013).	- Solar panels, all generations included.	- Uncertainty regarding potentially toxic emissions in case of fire – in particular Cd from CdTe panels (Dhere and Shiradkar, 2012; Fraunhofer CSP, 2012). - Potential toxic rainwater leaching from broken CdTe panels poorly documented if at all. Limited studies considering only small scale commercial & residential PV applications (Sinha et al., 2012). - Some environmental indicators still overlooked, in particular for large scale PV plants (e.g., water usage, impacts on wildlife and habitats, surface water runoff) (Turney and Fthenakis, 2011).	- Degradation risks related to bad weather (Jordan et al., 2012) & spontaneous "cracks" in panels (Köntges et al., 2011). - Accelerated aging laboratory tests need improvement to accurately reflect PV panel long-term use conditions (Ball et al., 2012). - Fire hazards concerns during PV panels installation & operation (e.g. ground fault, electrical arcing, open circuit) (Dhere and Shiradkar, 2012). - Ongoing monitoring program on VLS-PV in desert areas (BLM, 2012) & research on potential environmental impacts, e.g. IEA Photovoltaic Power Systems Programme Task 8 (IEA/PVPS, 2013b).

Cd: cadmium; CdTe: cadmium telluride; VLS-PV: very large scale photovoltaic.

Batteries risk

Table 3

Information gaps in life cycle assessments regarding data on photovoltaic systems end-of-life phase.

Expected developments	Source of potential risks	Information gaps	Comments
- Increase in PV panel waste: from 3 million tons in 2035 to 9.5 million tons in 2050, of which ~1.5 million for CdTe technology (Monier and Hestin, 2011).	- PV systems, including BOS, waste (batteries & diesel generators discussed in Table 5).	- Toxic potential of PV panel waste in case of landfilling and/or incineration not clarified, although possible leaching of metals (e.g., Ag, Cd, Co, CrVI & Pb) & PBDE and possible contamination of food chain through bioamplification and bioaccumulation reported (Kiddee et al., 2013; Monier and Hestin, 2011). - Poor documentation of environmental impacts of PV panels dismantling, transport to recycling site & electricity demand for processing (Jungbluth et al., 2012). - No available estimates on quantity of PV waste in developing countries, while expansion increase expected (IEA/PVPS, 2013b; Ispy Publishing, 2013). - Limited data on BOS, incl. end-of-life (Fthenakis et al., 2011; Jungbluth et al., 2012).	- PV panels waste managing still not efficient in developed countries, in terms of waste collection, industry-led end-of-life program & recycling processes (Bilimoria and Defrenne, 2013; Klugmann-Radziemska, 2013; Montgomery, 2013). - E-waste recycling & landfilling considered as a serious threat in developing countries given lack of control and reported landfill leachate & soil contamination in the vicinity of recycling sites (Daso et al., 2013; Lundgren, 2012; Otsuka et al., 2012; Pramila et al., 2012; Zhang et al., 2012).

Ag: silver; Al: aluminum; BOS: balance of system; Cd: cadmium; CdTe: cadmium telluride; Co: cobalt; CrVI: hexavalent chromium; GW: gigawatt; incl.: including; Pb: lead; PBDE: polybrominated diphenyl ethers; PV: photovoltaic.

Table 4

Information gaps in life cycle assessments regarding second and third generations of photovoltaic systems.

Expected developments	Source of potential risks	Information gaps	Comments
- Global market stabilization of second-generation thin films technology (a-Si, CdTe, CIS, CIGS) & global growth of CPV & HCPV until 2017 (EPIA, 2013; Kurtz, 2012).	- Raw materials for thin film cells manufacturing & mounting hardware. - Fossil primary energy necessary for production.	- Toxic potential of Te, CdTe, Ga, Ge & In still under study.	- CdTe compounds considered of low ecotoxicity in scarce literature (Kaczmar, 2011). - Environmental impacts of CdTe PV systems on slanted roofs estimated much higher according to multi-dimensional method of LCA, due to larger surface area & greater consumption of primary, mainly fossil, energy & raw materials with documented ecotoxicity (e.g. Al, Cu, plastics & steel) (Jungbluth et al., 2008).
- Special development for nanoparticles photovoltaic technology (semiconductor nanostructures) due to competitive performances and production costs (Kamat, 2013; Razykov et al., 2011). - Growing market of organic photovoltaics (OPV) until 2017 (EPIA, 2013) leading to an increased use of nanotechnology (Stratakis and Kymakis, 2013; Zimmermann et al., 2012).	- Engineered nanomaterials (e.g. CdTe or InP quantum wells; silver nanowires or gold nanoparticles for OPV).	- Toxic potential still under study. - Potential environmental risk of nanomaterials to upper-food chain organisms still not clarified (Parks et al., 2013).	- Toxic potential estimated high according to few experimental studies, probably owing to their critical size, release of potential toxic compounds & ability to generate reactive oxygen species (Liu et al., 2007; Suresh et al., 2013). - Higher heavy metal emissions during production phase of quantum dot solar cells (Hatice and Theis, 2010).

a-Si: amorphous silicon; Al: aluminium; Cd: cadmium; CdTe: cadmium telluride; CIS: copper indium selenide; CIGS: copper indium gallium selenide; CPV: concentrated photovoltaic; Cu: copper; HCPV: high concentration photovoltaics; In: indium; InP: indium phosphide; Ga: gallium; Ge: germanium; GW: gigawatts; LCA: life cycle assessment; OPV: organic photovoltaics; Te: tellurium.

Battery

Table 5
Information gaps in life cycle assessments regarding off-grid PV systems (stand-alone and hybrid PV systems).

Expected developments	Source of potential risks	Information gaps	Comments
- Increase of global off-grid applications from 21 GW of cumulative installed PV capacity in 2020 to 463 GW in 2050 (IEA, 2010). - Increase of stand-alone system market in developed & developing countries, taking advantage of financial incentives & supports (IEA/PVPS, 2013a; Lena, 2013). - PV diesel hybrid plants planned in developing countries (ILO, 2012; Ispy Publishing, 2013; Lena, 2013).	- Solar battery (mainly lead–acid & to a lesser extent Ni–Cd & Li) & diesel generator (alternative energy source).	- Very few stand-alone and hybrid PV systems LCA, especially in developing countries. - Incomplete life-cycle inventories for batteries manufacturing and no available LCA for recycling (Sullivan and Gaines, 2012). - Few information available on life cycle greenhouse gases (GHS) emissions of diesel generators (Yumoto, 2011)	- Well documented environmental impacts of production of batteries in terms of GHG, metal depletion and fossil fuel depletion (McManus, 2012). - GHG conservative estimate of 787 g CO_2eq/kWh according to a rare PV diesel hybrid system LCA (Yumoto, 2011). - Battery waste collecting and recycling sector both disorganized and potentially hazardous in developing countries. - High blood lead level also reported among children living nearby battery recycling sites (Gottesfeld and Pokhrel, 2011; Pramila et al., 2012).

Cd: cadmium; GHG: greenhouse gases; GW: gigawatts; KW: kilowatt; LCA: life cycle assessment; Li: lithium; Ni–Cd: nickel–cadmium; Pb: lead; PV: photovoltaic.

lung disease

death

irritating, corrosive, flammable or even explosive properties. Table 7 synthesizes the main hazardous substances associated with PV modules manufacturing according to the principal process concerned and their toxic effect.

Installation, care & maintenance and dismantling of PV systems present safety risks from physical agents essentially associated with accidents and injuries. Main physical risks related to PV systems installation, their major sources and some aggravating factors are presented in Table 8. The major risks are falls from heights, ergonomic risks and injuries related to the handling of unwieldy and solar panels and their sharp edges and electric shock hazards. Electrical risks are complex, involving both direct current circuit (DC), associated with the PV panels and their wiring complex, and alternating current circuit (AC), associated with inverters and their cabling for public power grid, solar batteries and/or diesel generator connection. Potential DC-related risks cause more concern because of the possibility of persisting electric arc that could eventually start a fire (MCS, 2012).

Despite the expected increase in the number of workers, occupational health and safety aspects in the PV industry have not been thoroughly examined and certain deficiencies should be addressed:

- ➢ the toxic effects of several chemicals, in particular telluride, cadmium telluride, gallium and germanium, are still under study, although the acute toxicity of CdTe is considered less than cadmium itself (Zayed and Phillipe, 2009);
- ➢ the PV industry interest toward engineered nanomaterials could raise additional occupational safety and health concerns despite their anticipated technological and economical contribution to "green and sustainable growth" (OECD, 2012). Indeed, the toxicology of these nanomaterials is still not fully understood, and some animal studies show pulmonary toxicity (Bonner et al., 2013). More knowledge needs to be assembled on nanomaterials' workplace health and safety, particularly in terms of exposure and risk assessment (NIOSH, 2012; Savolainen et al., 2013).
- ➢ very little quantitative and qualitative studies have been published on risk assessment of potential chemical exposures, although occupational health issues during manufacturing and recycling processes have been raised (Bradbrook et al., 2013; Mulloy et al., 2013). A recent study conducted in American facilities handling indium materials show that indium air concentrations can exceed the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) of 0.1 mg/m^3, in particular during some resurfacing indium tin oxide sputter target process. In one facility, indium air concentration (IAC) has increased in personal air samples from below the detection limit in 2008 to 0.049 mg/m^3 and 0.061 mg/m^3 in two maintenance technicians in 2010. Even not exceeding indium NIOSH REL, the IAC has shown an important increase. This study has put the emphasis not only on continuous engineering control and respiratory protection assessment but also possible reconsideration of NIOSH REL for indium (Hines et al., 2013). Moreover, indium phosphide is classified as probably carcinogenic to humans (Group 2A) by IARC (IARC, 2006) and occupational exposure to indium compounds is associated with lung diseases from pulmonary alveolar proteinosis to emphysema and eventually death (Cummings et al., 2012);
- ➢ the occupational injuries of PV workers have also been the subject of very few publications, although the safety aspect of solar panel installation has been highlighted (MCS, 2012; Mulloy et al., 2013). Although many chemicals used in the PV industry are regulated by US EPA's Risk Management Program (which requires hazard assessment, a prevention plan and an emergency response program), the industry is considered relatively safe during the production phase (Fthenakis et al., 2006). However, fatal explosions have been reported in some PV plants (Chen et al., 2006). The installation phase can also be problematic and fatal falls were reported in California (CDPH, 2012) and in France (OPPBTP, 2011). Moreover,

Table 6
Main toxic potential substances associated to PV industry considering their toxic potential (carcinogenic and/or non-carcinogenic), principal usage and some PV industry processes concerned as potential exposure sources.

Chemical substance[a]	Carcinogenic potential: IARC[b] classification and principal target organs	Non-carcinogenic potential: some target organs and/or tissues	Principal usages	Examples of PV industrial processes as potential exposure sources
Aluminium	Group 1[c] for occupational exposures during aluminium production: *Lung, urinary bladder*	Lung (Krewski et al., 2007)	Metallization contact Raw material for mounting frame	x-Si and a-Si manufacturing and recycling Mounting frame manufacturing and recycling
Arsenic and gallium arsenide	Group 1[c]: *Lung, Skin, Urinary Bladder*	Skin, blood, nerves (ATSDR, 2007a)	Raw material	GaAs panels and lead–acid manufacturing and recycling
Arsine		Blood, kidney (CDC, 2013)	Dopant	PV cells manufacturing
Asbestos	Group 1[c]: *Mesothelium, lung, larynx, ovary*	Lung (WHO, 1998)	Building and construction materials (roof-top, façade, pipes)	Tear-off building components before installation of partially or fully PV-building integrated system
Cadmium	Group 1[c]: *Lung*	Lung, bones, kidney (ATSDR, 2012)	Raw material	Zinc, copper and lead smelting; CdTe, CIS/CIGS panels manufacturing and recycling
Carbon tetrachloride	Group 2B[d] *Kidney, liver, breast* (*Cancers in experimental animals*)	Central nervous system, liver, lung (EPA, 2010)	Etching agent	x-Si panels manufacturing
Copper		Lung, kidney, liver (ATSDR, 2004)	Raw material; Component for PV cells electrical contact; Thin film deposition agent	CdTe and CIS/CIGS panels manufacturing and recycling
Crystalline Silica	Group 1[c] *Lung*	Lung (Sellamuthu et al., 2011)	Raw material	Silica sand mining, x-Si and a-Si manufacturing and recycling (silica dust exposure)
Hexavalent chromium (Chrome VI)	Group 1[c] *Lung*	Lung, skin (Assem and Zhu, 2007)	Raw material for chrome plated components (screw, frame, coating)	PV panels manufacturing and recycling
Hydrofluoric acid		Skin, eyes, lung (ATSDR, 2003)	Cleaning and etching agent	x-Si panels manufacturing
Indium phosphide	Group 2A[e] *Lung* (*Cancer in experimental animals*)	Adverse effects in experimental animals (Lung; reproductive system) (ECHA, 2010)	Raw material	GaAs multi-layer PV cell manufacturing and recycling
Lead	Group 2A[e] *Stomach*	Blood, kidney, central nervous system, digestive tract (ATSDR, 2007b)	Raw material (lead–acid batteries, tempered glass for PV panels) Soldering	Lead-batteries and PV panels manufacturing and recycling
Organic solvents	Benzene: Group 1[c] – *Blood* Trichloroethylene: Group 1[c]: *Kidney*	Central nervous system, skin, kidney, liver, blood, eyes (SPP, 2002)	Cleaning and extracting agent	PV panels and BOS components manufacturing and recycling (potential volatile organic compounds exposure)
Polybrominated diphenyl ethers	Group 2B[d] *Liver* (*Cancer in experimental animals*)	Adverse effects in experimental animals: Central nervous system, endocrine system (Buckenmeier et al., 2010)	Flame retardant Component for integrated circuits	PV panels and inverters manufacturing and recycling

BOS: balance of system; CdTe: cadmium telluride; CIS: copper indium selenide; CIGS: copper indium gallium selenide; GaAs: gallium arsenide; a-Si: amorphous silicon; x-Si: crystalline silicon.

[a] Extracted from: Baldwin and Gerami (2011), EPRI (2003), Fthenakis (2013), Jungbluth et al. (2012), Miquel (2009), OSEIA (2006), Popovich et al. (2013), Wild-Scholten and Alsema (2004), and Wild-Scholten et al. (2009).

[b] IARC: International Agency for Research on Cancer (Available on-line at: http://monographs.iarc.fr/ENG/Classification/Table4.pdf).

[c] Group 1: carcinogenic to humans.

[d] Group 2B: possibly carcinogenic to humans.

[e] Groupe 2A: probably carcinogenic to humans.

Table 7
Main hazardous substances associated to PV modules manufacturing considering their principal usage and hazardous properties.

Chemical substance[a]	Principal usage	Hazardous properties[a]				
		A	C	I	F	E
Ammonia	Anti-reflective coating			■		■
Argon gas	Thin film deposition	■				
Boron trifluoride	Dopant		■	■		
Diborane	a-Si dopant			■	■	
Helium gas	Thin film deposition	■				
Hydrochloric acid	x-Si raw material Etching and cleaning		■	■	■	
Hydrofluoric acid	x-Si cleaning and etching		■	■	■	
Hydrogen gas	a-Si deposition				■	■
Hydrogen selenide	CIS sputtering			■	■	
Hydrogen sulfide	CIS sputtering			■	■	■
Methane gas	a-Si and GaAs manufacturing	■			■	■
Nitrogen trifluoride	Silicon wafer plasma etching and a-Si PECVP chamber cleaning	■				
Phosphine gas	Thin film dopant			■	■	■
Phosphorous oxychloride	x-Si dopant			■		
Selenium	CIS/CIGS raw material			■		
Silane gas	Intermediate product during x-Si production – a-Si deposition			■		■
Silicon tetrachloride (tetrachlorosilane)	x-Si and a-Si deposition		■	■		
Strong bases (e.g. soda, potash)	Cleaning		■	■		
Tellurium	CdTe and CIS raw material			■		■
Trichlorosilane	x-Si and a-Si deposition			■	■	

A: asphyxiant; C: corrosive; Ir: irritating; F: flammable; E: explosive; CdTe: cadmium telluride; a-Si: Amorphous silicon; x-Si: crystalline silicon; CIS: copper indium selenide; CIGS: copper indium gallium selenide; GaAs: gallium arsenide; PV: photovoltaic.

[a] Extracted from: Baldwin and Gerami (2011), EPRI (2003), Ferrazza (2013), Fthenakis (2013), Fthenakis et al. (2006), INRS (2013a), Miquel (2009), Ngai (2012), and Pham et al. (2013).

higher injury rates, including falls, have been reported during the construction of LEED-certified (Leadership in Energy and Environmental Design) sustainable buildings compared to conventional buildings, and some of these injuries have been linked to installation of PV systems on roofs and facades (Fortunato et al., 2012).

3. Conclusion

The technological advances of the PV industry stem from efforts to reduce greenhouse gas emissions and comply with current sustainable development principles. However, to achieve its global environmental, health and economic sustainability ambitions, additional joint efforts on the part of manufacturers, workers, scientists and government authorities are essential. The obvious solutions remain:

- active cooperation of all manufacturers worldwide, in order to promote the disclosure of sensitive data to carry out refined LCAs as technological advances are made;
- identification, recognition and assessment of occupational health and safety risks along the PV industry life cycle, as well as their expanded management, including worker and employer training and accreditation, based on a partnership between all stakeholders (mainly manufacturers, workers, occupational health and safety professionals, insurance companies, contractors, emergency responders, governments);
- improvement of research and development adopting a green chemistry approach in order to limit the handling of potentially toxic substances throughout PV systems life cycle;
- identification and assessment of potential environmental and health burdens across all phases of the PV systems life cycles, particularly for the increasing numbers of large and very large scale PV applications;
- lastly, provision of a strategic framework for the recycling sector through sustained research and development to ensure viable and economical recycling techniques and through stricter regulation to extend manufacturers responsibility concerning dismantling and recycling the PV systems components they produce.

While challenges remain significant, the dynamism of the PV industry bodes well for rapid advances. Its supervision, through local and

Table 8
Main physical risks related to PV systems installation, major sources and some example of aggravating factors.

Main physical risk	Some major causes	Examples of aggravating factors
- Fall from heights - Falling objects	- Working at heights, on slopes, from scaffolding; climbing ladders. - Collapsing surfaces under workers' weight (PV panels, roof, structural components, etc.). - Unwieldy equipment (e.g., handles, harnesses).	- Extreme weather (e.g., ice, heavy snow, strong winds). - Slope angles > 15°. - Low-quality/suitability of, or defective equipment. - Low-skilled workers & poor coordination. - Lack of storage for equipment.
- Electric shock - Electrical burns	- Direct current (DC) arcing. - Electrical work on AC and DC circuits (PV panel serial connection, battery and/or power-grid connection).	- Working close to high-voltage grid. - Stripped overhead electric lines. - Low-quality of PV devices & defective shutdown systems. - Improper electrical wiring (e.g., electrical circuit overheating) - Lack of DC circuit experience. - Bad weather (heat & humidity, lightning, etc.).
- Traffic accident	- Heavy truck traffic (loading hoist, telescopic forklifts, etc.).	- Lack of traffic signs & plan in the construction site. - Lack of worker training.
- Ergonomic risks	- Awkward body postures and repetitive movements during PV panels installation (e.g., handling and carrying heavy loads).	- Inappropriate work methods.
- Wounds - Lacerations	- PV panels handling (sharp edges, fragments).	- Lack of protective clothing (e.g., gloves, long-sleeved shirts). - Lack of worker training.
- Thermal burns	- Excessive heat from PV panels.	- Walking on PV panels without protective shoes. - Excessive heat.
- Fire	- DC current arcing. - Overloaded circuit.	- Non-compliance with building standards. - Improper electrical wiring (e.g., electrical circuit overheating).

Adapted from: INRS (2013b), MCS (2012), OPPBTP (2011), OSEIA (2006), and Ridal et al. (2010).

international regulations and shared procedures for limiting potential eco-health risks, is both an imperative and a driving force for the PV industry worldwide.

Acknowledgments

This research was supported by the Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST), Montreal, Quebec, Canada (grant 2011–0051)

References

Alsema EA, Wild-Scholten MJ. Environmental life cycle assessment of advanced silicon solar cell technologies. Proceeding from the nineteenth European Photovoltaic Solar Energy Conference. Paris, France; 2004. [7–11 June].

Arnold T, Harth CM, Mühle J, Manning AJ, Salameh PK, Kim J, et al. Nitrogen trifluoride global emissions estimated from updated atmospheric measurements. Proc Natl Acad Sci U S A 2013;110(6):2029–34.

Assem L, Zhu H. Chromium. Toxicological overview. Version 1. Health Protection Agency; 2007 [Available: http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1194947362170 [accessed 8 December 2013]].

ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile for fluorides, hydrogen fluoride, and fluorine. U.S. Department of Health And Human Services, Public Health Service; 2003 [Available: http://www.atsdr.cdc.gov/ToxProfiles/tp11.pdf [accessed 20 December 2013]].

ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile for copper. U.S. Department of Health And Human Services, Public Health Service; 2004 [Available: http://www.atsdr.cdc.gov/toxprofiles/tp132.pdf [accessed 20 December 2013]].

ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile for arsenic. U.S. Department of Health And Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry; 2007a [Available: http://www.atsdr.cdc.gov/ToxProfiles/tp2.pdf [accessed 20 December 2013]].

ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile for lead. U.S. Department of Health And Human Services, Public Health Service; 2007b [Available: http://www.atsdr.cdc.gov/ToxProfiles/tp13.pdf [accessed 20 December 2013]].

ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile of cadmium. U.S. Department of Health And Human Services, Public Health Service; 2012 [Available: http://www.atsdr.cdc.gov/ToxProfiles/tp5.pdf [accessed 20 December 2013]].

Bakhiyi B, Zayed J. Photovoltaic conversion: outlook at the crossroads between technological challenges and eco-strategic issues. Chap 15. In: Nayeripour M, Kheshti M, editors. Sustainable growth and applications in renewable energy sources. Croatia: InTech; 2011. p. 313–38.

Baldwin D.G., Gerami A., Rubin J.R. Silicon semiconductor manufacturing, In: in 83. Microelectronics and Semiconductors, Williams, Michael E., Editor, Encyclopedia of Occupational Health and Safety, Jeanne Mager Stellman, Editor-in-Chief. International Labor Organization, Geneva; 2011 [Available: http://www.ilo.org/oshenc/part-xiii/microelectronics-and-semiconductors/item/700-silicon-semiconductor-manufacturing [accessed: 19 December 2013]].

Ball G, Zgonena T, Flueckiger C. Photovoltaic module grounding: issues and recommendations. Report commissioned by Solar America Board for Codes and Standards with support from the U.S. Department of Energy; 2012 [Available: http://www.solarabcs.org/about/publications/reports/module-grounding/ [accessed 20 December 2013]].

Bekkelund K. A comparative life cycle assessment of PV solar systems (Master's thesis) Norwegian University of Science and Technology; 2013 [Available: http://www.diva-portal.org/smash/get/diva2:654872/FULLTEXT01.pdf [accessed 18 December 2013]].

Bilimoria S, Defrenne N. The evolution of photovoltaic waste in Europe. Study 1305-01. S&T Consulting and CERES; 2013 [Available: http://www.sandtconsulting.eu/app/download/6093396/The+evolution+of+photovoltaic+waste+in+Europe.pdf [accessed 20 December 2013]].

BLM (Bureau of Land Management). Approved resource management plan, Amendments/record of Decision (ROD) for solar energy development in six southwestern states. Washington, D.C.: United States Department of the Interior; 2012 [Available: http://solareis.anl.gov/documents/docs/Solar_PEIS_ROD.pdf [accessed 19 December 2013]].

Bonner JC, Silva RM, Taylor AJ, Brown JM, Hilderbrand SC, Castranova V, et al. Interlaboratory evaluation of rodent pulmonary responses to engineered nanomaterials: the NIEHS Nano GO Consortium. Environ Health Perspect 2013;121(6):676–82.

Boudghene Stambouli A, Koinuma H, Flazi S, Khiat Z, Kitamura Y. Sustainable development by Sahara Solar Breeder plan: energy from the desert of Algeria, a Green Energy Dream grows in the Sahara. Renew Energy Power Qual J2172-038 X 2013;11.

Bradbrook S, Duckworth M, Ellwood P, Miedzinski M, Ravetz J, Reynolds J. Green jobs and occupational safety and health: foresight on new and emerging risks associated with new technologies by 2020. Report commissioned by the European Agency for Safety and Health at Work; 2013 [Available: https://osha.europa.eu/en/publications/reports/green-jobs-foresight-new-emerging-risks-technologies [accessed 21 December 2013]].

Buckenmeier N, Dereumeaux C, Rouy P, Vigneron M. Polybromodiphenyl ethers, health risk assessment project. France: School of Public Health, Rennes; 2010 [In French] [Available: http://documentation.ehesp.fr/memoires/2010/persan_igs/pbde.pdf [accessed 18 December 2013]].

CanmetENERGY. Sector profile for solar photovoltaics in Canada. Report no. 2012-063 (RP-TEC). Natural Resources Canada, Varennes Research Centre Canmet ENERGIE; 2012 [Available:http://cansia.ca/sites/default/files/policy_and_research/sectorprofile_solarphotovoltaicscanada.pdf [accessed 18 December 2013]].

CDC (Centers for Disease Control, Prevention). Arsine (SA): systemic agent. The emergency response safety and health database. Content source: National Institute for Occupational Safety and Health, Education and Information Division; 2013 [Last updated: 18 June Available: http://www.cdc.gov/niosh/ershdb/EmergencyResponseCard_29750014.html [accessed 20 December 2013]].

CDPH (California Department of Public Health). Preventing worker deaths in the solar industry; 2012 [Last modified: 31 May Available: http://www.cdph.ca.gov/programs/ohb-face/Pages/Solar.aspx [accessed 23 December 2013]].

CDTSC (California Department of Toxic Substances Control). Proposed regulations: proposed standards for the management of hazardous waste solar modules; 2013 [Available: http://www.dtsc.ca.gov/LawsRegsPolicies/Regs/upload/ISOR-080112.pdf [accessed 21 December 2013]].

Cha AE. Solar energy firms leave waste behind in China. Washington, DC: The Washington Post; 2008 [March Available: http://www.washingtonpost.com/wp-dyn/content/article/2008/03/08/AR2008030802595.html?sub=new [accessed 14 December 2013]].

Chen JR, Tsai HY, Chen SK, Pan HR, Hu SC, Shen CC, et al. Analysis of a silane explosion in a photovoltaic fabrication plant. Process Saf Prog 2006;25(3):237–44.

Colthorpe A. US news reports hazardous thin-film waste at abound solar factory. PV Tech News; 2013 [01 November Available: http://www.pv-tech.org/news/us_news_carries_alarmist_reports_on_hazardous_thin_film_waste_at_abound_sol [accessed 18 December 2013]].

Cummings KJ, Nakano M, Omae K, Takeuchi K, Chonan T, Xiao YL, et al. Indium lung disease. Chest 2012;141(6):1512–21.

Daso AP, Fatoki OS, Odendaal JP, Olujimi OO. Polybrominated diphenyl ethers (PBDEs) and 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa. Environ Monit Assess 2013;185:431–9.

Dhere NG, Shiradkar NS. Fire hazard and other safety concerns of photovoltaic systems. J Photon Energy 2012;2(1):022006/1–022006/13.

Dones R, Heck T, Hirschberg S. Greenhouse gas emissions from energy system: comparison and overview. Switzerland: Paul Scherrer Institute Annual Report, Annex IV, Villigen; 2003 [Available: http://gabe.web.psi.ch/pdfs/Annex_IV_Dones_et_al_2003.pdf [accessed 25 November 2013]].

ECHA. Background document to the opinion of the committee for risk assessment on a proposal for harmonized classification and labelling of indium phosphide. EC number: 244-959-5, CAS number: 22398-80-7. European Chemical Agency, Committee for Risk Assessment; 2010 [Available: http://echa.europa.eu/documents/10162/56fcaf7e-ed65-4d3c-9e8f-4fddef879789 [accessed 7 November 2013]].

Eisenberg DA, Yua M, Lama CW, Ogunseitanb OA, Schoenunga JM. Comparative alternative materials assessment to screen toxicity hazards in the life cycle of CIGS thin film photovoltaics. J Hazard Mater 2013;260:534–42.

ENF (ENergy Focus). Solar recycling companies. Available: http://www.enfsolar.com/service/manufacturers-recycling, 2014. [accessed 23 January 2014].

EPA (United States Environmental Protection Agency). Toxicological review of carbon tetrachloride (CAS No. 56-23-5). Support of Summary Information on the Integrated Risk Information System (IRIS); 2010. [Available: http://www.epa.gov/iris/toxreviews/0020tr.pdf [accessed 20 December 2013]].

EPIA (European Photovoltaic Industry Association). Connecting the sun, solar photovoltaics on the road to large-scale grid integration, Report 09/12. Available: http://www.epia.org/fileadmin/user_upload/Publications/Connecting_the_Sun_Full_Report_converted.pdf, 2012. [accessed 20 December 2013].

EPIA (European Photovoltaic Industry Association). Global outlook market for photovoltaics 2013–2017. Report 05/13. Available: http://www.epia.org/fileadmin/user_upload/Publications/GMO_2013_-_Final_PDF.pdf, 2013. [accessed 20 December 2013].

EPIA/Greenpeace (European Photovoltaic Industry Association/Greenpeace). Solar generation 6, solar photovoltaic electricity empowering the world. Amsterdam, The Netherlands: EPIA: Brussels, Belgium and Greenpeace International; 2011 [Available: http://www.greenpeace.org/international/Global/international/publications/climate/2011/Final%20SolarGeneration%20VI%20full%20report%20lr.pdf [accessed 20 December 2013]].

EPRI (Electric Power Research Institute). Potential health and environmental impacts associated with the manufacture and use of photovoltaic cells. Sacramento, CA: Palo Alto, CA, and California Energy Commission; 2003. p. 1000095 [Available: http://www.energy.ca.gov/reports/500-04-053.PDF [accessed 7 November 2013]].

EurObserv'ER. Photovoltaic barometer. J Photovolt 2013;9:55–75. [Available: http://www.energies-renouvelables.org/observ-er/stat_baro/observ/baro-jdp9.pdf. [accessed 7 November 2013]].

European Union. Directive 2012/19/EU of the European parliament and of the council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Off J Eur Union 2012; 197:38–71.

Ferrazza F. Crystalline silicon: manufacture and properties, Chapter IB-1. In: McEvoy A, Markvart T, Castañer L, editors. Solar cells, materials, manufacture and operation. 2nd ed. Great Britain: Elsevier Ltd.; 2013. p. 69–86.

Fortunato B, Hallowell M, Behm M, Dewlaney K. Identification of safety risks for high-performance sustainable construction projects. J Constr Eng Manag 2012;138(4): 499–508.

Frankfurt School-UNEP Centre/BNEF. Global trends in renewable energy investment 2013. United Nation Environment Protection Collaborating Centre for Climate & Sustainable Energy Finance, Frankfurt School of Finance, Management & Bloomberg New Energy Finance; 2013 [Available: http://www.unep.org/pdf/GTR-UNEP-FS-BNEF2.pdf [accessed 19 December 2013]].

Fraunhofer CSP (Fraunhofer Center Fur Silizium-Photovoltaik). Scientific comment of Fraunhofer to life cycle assessment of CdTe photovoltaics (28.12.2012). Available: http://www.csp.fraunhofer.de/aktuelles/details/id/47/, 2012. [accessed 20 December 2013].

Fraunhofer ISE (Fraunhofer Institute for Solar Energy Systems). Photovoltaics report. Available: http://www.ise.fraunhofer.de/en/downloads-englisch/pdf-files-englisch/photovoltaics-report-slides.pdf, 2013. [accessed 20 December 2013].

Fthenakis VM. How long does it take for photovoltaics to produce the energy used? National Society of Professional Engineers Publication; February 2012 [Available: http://www.clca.columbia.edu/236_PE_Magazine_Fthenakis_2_10_12.pdf [accessed 18 December 2013]].

Fthenakis VM. Overview of potential hazards. Chapter IIB-1. In: McEvoy A, Markvart A, Castañer L, editors. Solar Cells, materials, manufacture and operation. 2nd ed. Great Britain: Elsevier Ltd.; 2013. p. 533–45.

Fthenakis VM, Kim HC. Photovoltaics: life-cycle analyses. Sol Energy 2011;85:1609–28.

Fthenakis VM, Moskowitz PD. Photovoltaics: environmental, health and safety issues and perspectives. Prog Photovolt Res Appl 2000;8:27–38.

Fthenakis VM, Kim HC, Colli A, Kirchsteiger C. Evaluation of risks in the life cycle of photovoltaics in a comparative context. Proceeding from the First European Photovoltaic Solar Energy Conference, Dresden, Germany; 2006. [4–8 September Available: http://www.bnl.gov/pv/files/pdf/abs_191.pdf [accessed 2 December 2013]].

Fthenakis VM, Kim HC, Aselma E. Emissions from photovoltaic life cycles. Environ Sci Technol 2008;42(6):2168–74.

Fthenakis VM, Frischknecht R, Raugei M, Kim HC, Alsema E, Held M, et al. Methodology guidelines on life cycle assessment of photovoltaic electricity. International Energy Agency Photovoltaic Power Systems Programme Task 122nd ed. ; 2011 [Available: http://www.australiansolarinstitute.com.au/SiteFiles/australiansolarinstitutecomau/Methodology_Guidelines_on_Life-Cycle_Assessment_of_PV_Elec.pdf [accessed 2 December 2013]].

Gottesfeld P, Pokhrel AK. Review: lead exposure in battery manufacturing and recycling in developing countries and among children in nearby communities. J Occup Environ Hyg 2011;8(9):520–32.

Grossmann W, Steininger KW, Schmid C, Grossmann I. Investment and employment from large-scale photovoltaics up to 2050. Empirica 2012;39:165–89.

Hamilton J. Green jobs: solar power. Report 2. United States Bureau of Labor Statistics; 2011 [Available: http://www.bls.gov/green/solar_power/solar_power.pdf [accessed 18 December 2013]].

Hatice S, Theis TL. An environmental impact assessment of quantum dot photovoltaics (QDPV) from raw material acquisition through use. J Clean Prod 2010;19(1):21–31.

Hines CJ, Roberts JL, Andrews RN, Jackson MV, Deddens JA. Use of and occupational exposure to indium in the United States. J Occup Environ Hyg 2013;10(12):723–33.

IARC (International Agency for Research on Cancer). Indium phosphide. Monogr Eval Carcinog Risks Hum 2006;86:197–224.

IARC (International Agency for Research on Cancer). Asbestos (chrysotile, amosite, crocidolite, tremolite, actinolite, and anthophyllite). Monogr Eval Carcinog Risks Hum 2012;100C:219–309.

IEA (International Energy Agency). Technology roadmaps. Solar photovoltaic energy. Available: http://www.iea.org/publications/freepublications/publication/pv_roadmap.pdf, 2010. [accessed 25 November 2013].

IEA/PVPS (International Energy Agency/Photovoltaic Power System Programme). Trends 2013 in photovoltaic applications, survey report of selected IEA countries between 1992 and 2012. Report T1-23:2013. Available: http://www.iea-pvps.org/index.php?id=1&eID=dam_frontend_push&docID=1733, 2013. [accessed 20 December 2013].

IEA/PVPS (International Energy Agency/Photovoltaic Power System Programme). Annual report 2012. Available: http://iea-pvps.org/index.php?id=6, 2013. [accessed 16 December 2013].

ILO (International Labour Organization). Skills and occupational needs in renewable energy; final report. Available: http://www.ilo.org/wcmsp5/groups/public/-ed_emp/-ifp_skills/documents/publication/wcms_166823.pdf, 2011. [accessed 20 December 2013].

ILO (International Labour Organization). Working towards sustainable development: opportunities for decent work and social inclusion in a green economy. Available: http://www.ilo.org/wcmsp5/groups/public/—dgreports/—dcomm/—publ/documents/publication/wcms_181836.pdf, 2012. [accessed 10 December 2012].

ILO (International Labour Organization). Promoting decent work in the chemical industry: innovative initiatives, issues paper for discussion at the global dialogue forum on initiatives to promote decent and productive work in the chemical industry. Available: http://www.ilo.org/wcmsp5/groups/public/—ed_dialogue/—sector/documents/publication/wcms_226385.pdf, 2013. [accessed 21 December 2013].

INRS (Institut National de la Recherche Scientifique). Toxicological profile information sheets. Available: http://www.inrs.fr/accueil/produits/bdd.html, 2013. [in French], [accessed 21 December 2013].

INRS (Institut National de la Recherche Scientifique). Safe installation, maintenance and deinstallation of solar thermal and photovoltaic panels. Recommendation R. 467. Available: http://www.ameli.fr/employeurs/prevention/recherche-de-recommandations/pdf/R467.pdf, 2013. [in French], [accessed 21 December 2013].

Jordan DC, Wohlgemuth JH John H, Kurtz SR Sarah R. Technology and climate trends in PV module degradation. National Renewable Energy Laboratory Conference Paper: NREL/CP-5200-56485; Twenty-seventh European Photovoltaic Solar Energy Conference and Exhibition Frankfurt, Germany, September 24–28; 2012. [Available: http://www.nrel.gov/docs/fy13osti/56485.pdf [accessed 2 December 2013]].

Jungbluth N, Tuchschmid M, Wild-Scholten M. Life cycle assessment of photovoltaics: update of Ecoinvent Data v2.0. ESU-Service Working paper; 2008. [Available: http://www.esu-services.ch/fileadmin/download/jungbluth-2008-LCA-PV-web.pdf [accessed 8 December 2013]].

Jungbluth N, Stucki M, Flury K, Frischknecht R, Büsser S. Life cycle inventories of photovoltaics. Version: 2012. ESU-services Ltd., Fair Consulting in Sustainability; 2012 [Available: http://www.esu-services.ch/fileadmin/download/publicLCI/jungbluth-2012-LCI-Photovoltaics.pdf [accessed 18 December 2013]].

Kaczmar S. Evaluating the read-across approach on CdTe toxicity for CdTe photovoltaics. Society of Environmental Toxicology and Chemistry (SETAC) North America thirty-second Annual Meeting, Boston, MA; 2011. [13–17 November Available: ftp://ftp.co.imperial.ca.us/icpds/eir/campo-verde-solar/final/evaluating-toxicity.pdf [accessed 20 December 2013]].

Kamat PV. Quantum Dot solar cells. The next big thing in photovoltaics. J Phys Chem Lett 2013;4(6):908–18.

Kiddee P, Naidu R, Wong MH. Electronic waste management approaches: an overview. Waste Manag 2012;33(5):1237–50.

Kiddee M, Naidua R, Wong MH. Metals and polybrominated diphenyl ethers leaching from electronic waste in simulated landfills. J Hazard Mater 2013;252–253:243–9.

Klugmann-Radziemska E. Current trends in recycling of photovoltaic solar cells and modules waste. Chemistry–Didactics–Ecology–Metrology 2013;17(1–2):89–95.

Komoto K, Cunow E, Breyer C, Faiman D, Megherbi K, van der Vleuten P. Very large scale photovoltaic power — state of the art and into the future — summary. International Energy Agency/Photovoltaic Power System Programme Task 8; 2013 [Available: http://iea-pvps.org/index.php?id=35 [accessed 20 December 2013]].

Köntges M, Kajari-Schröder S, Kunzel I, Jahn U. Crack statistic of crystalline silicon photovoltaic modules. Proceedings from the Twenty-sixth European Photovoltaic Solar Energy Conference, Hamburg, Germany; 2011. [5–9 September 4], [EO.3.6].

Krewski D, Yokel RA, Nieboer E, Borchelt D, Cohen J, Harry J, et al. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. J Toxicol Environ Health Part B Crit Rev 2007;10(Suppl. 1):1–269.

Kurtz S. Opportunities and challenges for development of a mature concentrating photovoltaic power industry. National Renewable Energy Laboratory Technical Report: NREL/TP-5200-43208. Prepared under Task No. PVA7.4401; 2012 [Available: http://www.nrel.gov/docs/fy12osti/43208.pdf [accessed 25 February 2013]].

Laleman R, Albrecht J, Dewulf J. Life cycle analysis to estimate the environmental impact of residential photovoltaic systems in regions with a low solar irradiation. Renew Sust Energ Rev 2011;15(1):267–95.

Lena G. Rural electrification with PV hybrid systems, overview and recommendations for further Deployment. Report IEA-PVPS T9-13:2013. International Energy Agency/Photovoltaic Power System Programme Task 9, Subtask 4, CLUB-ER, Thematic Paper; 2013 [Available: http://www.iea-pvps.org/index.php?id=1&eID=dam_frontend_push&docID=1590 [accessed 20 December 2013]].

Liu Y, Chen W, Joly AG, Wang Y, Pope C, Zhang Y, et al. Comparison of water-soluble CdTe nanoparticles synthesized in air and in nitrogen. J Phys Chem 2007;B110:16992–7000.

Lundgren K. The global impact of e-waste: addressing the challenge. International Labour Office, Programme on Safety and Health at Work and the Environment (SafeWork); 2012 [Available: http://www.ilo.org/wcmsp5/groups/public/—ed_dialogue/—sector/documents/publication/wcms_196105.pdf [accessed 20 December 2013]].

McManus MC. Environmental consequences of the use of batteries in low carbon systems: the impact of battery production. Appl Energ 2012;93:288–95.

MCS (Microgeneration Certification Scheme). Guide to the installation of photovoltaic systems. Available: http://www.microgen-database.org.uk/uploads/34/53/34535a6ed1852e96406ec03c4a46fb2c/New_Guide_to_installlation_of_PV_systems-MCS.pdf, 2012. [accessed 22 December 2013].

Meulen R, Aselma E. Life-cycle greenhouse gas effects of introducing nanocrystalline materials in thin-film silicon solar cells. Prog Photovolt Res Appl 2011;19(4):453–63.

Miquel C. Photovoltaic systems: manufacturing and environmental impacts. Villeurbanne, France: Hepsul; 2009 [in French] [Available: http://www.photovoltaique.info/IMG/pdf/PV_Fab_Envt_final_26082009.pdf [accessed 6 December 2013]].

Monier V, Hestin M. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive. Final Report ENV.G.4/FRA/2007/0067. European Commission Studies on Waste Electrical and Electronic Equipment; 2011 [Available: http://ec.europa.eu/environment/waste/weee/studies_weee_en.htm [accessed 6 December 2013]].

Montgomery J. US PV recycling: the solar industry needs a plan now. RenewableEnergyWorld.com; 2013. [25 October Available: http://www.renewableenergyworld.com/rea/news/article/2013/10/us-pv-recycling-the-solar-industry-needs-a-plan-now [accessed 22 December 2013]].

Mulloy KB, Sumner SA, Rose C, Conway GA, Reynolds SJ, Davidson ME, et al. Renewable energy and occupational health and safety research directions: a white paper from the Energy Summit, Denver Colorado, April 11–13, 2011. Am J Ind Med 2013;56:1359–70.

Ngai EY. Photovoltaic specialty materials safety. Proceedings from thirty-eighth IEEE Photovoltaics Specialists Conference, Austin, Texas; 2012. [3–8 June].

NIOSH (National Institute for Occupational Safety and Health). Filling the knowledge gaps for safe nanotechnology in the workplace. A progress report from the NIOSH Nanotechnology Research Center 2004–201; 2012 [Available: http://www.cdc.gov/niosh/docs/2013-101/pdfs/2013-101.pdf [accessed 20 December 2013]].

NRC (National Research Council). Hidden costs of energy: unpriced consequences of energy production and use. Washington, DC, USA: The National Academy Press; 2010. p. 105–6 [506 pp.].

OECD (Organisation for Economic Co-operation and Development). OECD/NNI International symposium on assessing the economic impact of nanotechnology. Background paper 3: the economic contributions of nanotechnology to green and sustainable growth. JT03317980; 2012 [Available: http://www.oecd.org/sti/nano/49932107.pdf [accessed 22 December 2013]].

OPPBTP (Organisme Professionnel de Prévention du Bâtiment et des Travaux Publics). Photovoltaic panels installation, site preparation. Job's practical file. Available: http://www.preventionbtp.fr/Documentation/Publications/Ouvrages/Electricite/Installations-industrielles-ou-tertiaires/Pose-de-panneaux-photovoltaiques-Preparation-d-un-chantier, 2011. [in French], [accessed 10 December 2013].

OSEIA (Oregon Solar Energy Industries Association). Solar construction safety. Solar safety manual. Available: http://www.coshnetwork.org/sites/default/files/OSEIA_Solar_Safety_12-06.pdf, 2006. [accessed 2 December 2013].

Otsuka M, Itai T, Asante KA, Muto M, Tanabe S. Trace element contamination around the E-waste recycling site at Agbogbloshie, Accra City, Ghana. Interdiscip Stud Environ Chem—Environ Pollut Ecotoxicol 2012;6:161–7. [Available: http://www.terrapub.co.jp/onlineproceedings/ec/06/pdf/PR620.pdf [accessed 20 December 2013]].

Parks AN, Portis LM, Schierz PA, Washburn KM, Perron MM, Burgess RM, et al. Bioaccumulation and toxicity of single-walled carbon nanotubes to benthic organisms at the base of the marine food chain. Environ Toxicol Chem 2013;6(32):1270–7.

Pham TT, Stuchlikova TH, Ledinsky M, Hruska K, Le VTH Stuchlik J. Deposition of Si:H thin films on transparent and conductive ZnO at boundary parameters of PECVD if Sn as catalyst element is used. Proceedings first International Symposium on Plasma Chemistry (ISPC 21), Cairns Convention Centre, Queensland, Australia; 2013. [4–9 August Available: http://www.ispc-conference.org/ispcproc/ispc21/ID396.pdf [accessed 20 December 2013]].

Platzer MD. U.S. solar photovoltaic manufacturing: industry trends, global competition, Federal Support. R42509. Washington, DC: Congressional Research Service Report for Congress; 2012 [Available: http://www.fas.org/sgp/crs/misc/R42509.pdf [accessed 5 December 2013]].

Popovich VA, Van Maris MPFHL, Janssen J, Bennett IJ, Richardson IM. Understanding the properties of silicon solar cells aluminium contact layers and its effect on mechanical stability. Mater Sci Appl 2013;4:118–27.

Pramila S, M.H.F, Bhawana P. E-waste — a challenge for tomorrow research. Res J Rec Sci 2012;1(3):86–93.

Publishing Ispy. PV and solar market intelligence report, report 1–2013. Part of ISPY Publishing Industry Survey, Market Intelligence and Forecasts Series; 2013 [Available: http://www.pipelineme.com/media/797151/PV-and-Solar-Market-Intelligence-Report.pdf [accessed 23 December 2013]].

PvXchange. Price index. Available: http://www.pvxchange.com/priceindex/Default.aspx?langTag=en-GB, 2013. [accessed 23 janvier 2014].

Razykov TM, Ferekides CS, Morwl D, Stefanakos E, Ullal HS, Upadhyaya HM. Solar photovoltaic electricity: current status and future prospects. Sol Energy 2011;85:1580–608.

Reck B, Graedel TE. Challenges in metal recycling. 2012;6095(337):690–5.

REN (Renewable Energy Policy Network for the 21st Century). Renewables 2013. Global status report. Available: http://www.ren21.net/Portals/0/documents/Resources/GSR/2013/GSR2013_lowres.pdf, 2013. [accessed 5 December 2013].

RENI (Renewable Insight-Energy Industry). PV power plants 2013, industry guide. Available: http://www.pv-power-plants.com/fileadmin/user_upload/pdf/PVPP13_GW-Screen-DS-LowRes.pdf, 2013. [accessed 20 December 2013].

Ridal J, Garvin S, Chambers F, Travers J. Risk assessment of structural impacts on buildings of solar hot water collectors and photovoltaic tiles and panels. Report commissioned by: Building Standards Division Directorate for the Built Environment. The Scottish Government; 2010 [Available: http://www.scotland.gov.uk/Resource/Doc/217736/0097116.pdf [accessed 20 December 2013]].

Savolainen K, Backman U, Brouwer D, Fadeel B, Fernandes T, Kuhlbusch T, et al. Nanosafety in Europe 2015–2025: towards safe and sustainable nanomaterials and nanotechnology innovations. Finnish Institute of Occupational Health; 2013 [Available: http://www.ttl.fi/en/publications/Electronic_publications/Nanosafety_in_europe_2015-2025/Documents/nanosafety_2015-2025.pdf [accessed 20 December 2013]].

Schulte PA, McKernan LT, Heidel DS, Okun AH, Dotson GS, Lentz TJ, et al. Occupational safety and health, green chemistry, and sustainability: a review of areas of convergence. Environ Health 2013;12:31.

Sellamuthu R, Umbright C, Li S, Kashon M, Joseph P. Mechanisms of crystalline silica-induced pulmonary toxicity revealed by global gene expression profiling. Inhal Toxicol 2011;23(14):927–37.

Sinha P, Balas YR, Krueger ZL, Wade A. Fate and transport evaluation of potential leaching risks from cadmium telluride photovoltaics. Environ Toxicol Chem 2012;7(31):1670–5.

Solarbuzz. Modules pricing. Retail price summary. March 2012 Update Available: http://www.solarbuzz.com/facts-and-figures/retail-price-environment/module-prices, 2012. [accessed 22 December 2013].

SPP (Service de Pathologie Professionnelle). Basic data on the toxicity of principal industrial solvent. Preparatory document for the 2002 September seminar. Paris: France: Hôpital Cochin, Department of Pathology; 2002. [in French], [Available: http://www.uvmt.org/Multimedia/solvants.pdf [accessed 20 December 2013]].

Stratakis E, Kymakis E. Nanoparticle-based plasmonic organic photovoltaic devices. Mater Today 2013;4(16):133–46.

Sullivan JL, Gaines L. Status of life cycle inventories for batteries. Energ Convers Manag 2012;58:134–48.

Suresh AK, Pelletier DA, Doktycz MJ. Relating nanomaterial properties and microbial toxicity. Nanosc 2013;5:463–74.

Taylor AD. On the job with solar PV. Environ Health Perspect 2010;118(1):A19.

Turney D, Fthenakis VM. Environmental impacts from the installation and operation of large-scale solar power plants. Renew Sust Energ Rev 2011;15(6):3261–70.

Weisser D. A guide to life-cycle greenhouse gas (GHG) emissions from electric supply technologies. Energy 2007;32(9):1543–59.

WHO (World Health Organization). Chrysotile asbestos. Environmental health criteria 203. Available: http://whqlibdoc.who.int/publications/1998/9241572035_eng.pdf, 1998. [accessed 14 December 2013].

WHO (World Health Organization). Workers health: global plan of action. Sixtieth world health assembly WHA60.26; 2007. [Available: http://www.who.int/occupational_health/WHO_health_assembly_en_web.pdf [accessed 14 December 2013]].

Wild-Scholten MJ, Alsema E. Towards cleaner solar PV: environmental and health impacts of crystalline silicon photovoltaic. Refocus 2004;5(5):46–9.

Wild-Scholten MJ, Schottler M, Schlüter B. Control of life-cycle emissions from crystalline silicon solar cell manufacturing. Proceeding twenty-fourth European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany, 21–25 September; 2009.

Yumoto N. Sustainability conditions for PV hybrid systems: environmental considerations. Report T11-03:2011, International Energy Agency Photovoltaic Power Systems Program Task 11; 2011 [Available: http://www.iea-pvps.org/index.php?id=9&eID=dam_frontend_push&docID=745 [accessed 20 December 2013]].

Zayed J, Phillipe S. Acute oral and inhalation toxicities in rats with cadmium telluride. Int J Toxicol 2009;28(4):259–65.

Zhang WH, Wu YX, Simonnot MO. Soil contamination due to e-waste disposal and recycling activities: a review with special focus on China. Pedosphere 2012;22(4):434–55.

Zimmermann YS, Schäffer A, Hugi C, Fent K, Corvini PFX, Lenz M. Organic photovoltaics: potential fate and effects in the environment. Environ Int 2012;49:128–40.

Applied Geochemistry 108 (2019) 104381

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Release of metal pollutants from corroded and degraded thin-film solar panels extracted by acids and buried in soils

L.C. Su[a], H.D. Ruan[a,*], D.J. Ballantine[a], C.H. Lee[a], Z.W. Cai[b]

[a] Environmental Science Program, Division of Science and Technology, Beijing Normal University-Hong Kong Baptist University United International College, Zhuhai, China
[b] Department of Chemistry, Faculty of Science, Hong Kong Baptist University, Kowloon, Hong Kong

ARTICLE INFO

Editorial handling by Chennai Guest Editor

Keywords:
Acid extraction
Heavy metal
Leaching toxicity
Soil burial
Thin-film solar panel (TFSP)

ABSTRACT

Thin-film solar panels (TFSPs) are widely used in integrated photovoltaic and solar power systems because of their perfect photovoltaic characteristics and ductility. These panels differ from the traditional silicon-based solar panels, in that the metal thin-film layers contain some potentially toxic metals such as zinc (Zn), copper (Cu), nickel (Ni), gallium (Ga), lead (Pb), indium (In) and chromium (Cr). In this study, we examined the environmental pollution that might be caused by disposing of TFSP as domestic trash at the end of their useful life. We used acid extract to simulate metal leaching toxicity and acidic corrosion, and then buried TFSPs in three types of soils to determine if metals might be released into the soil. Our results indicated that the amounts of dissolved metals increased as both the contact time with the acid and the acid concentration in the solution increased during nitric acid extraction. Heavy metals were released from TFSPs in the burial experiment, and the rates of metal release changed with variations in both the amounts of TFSPs in the soil and the soil properties. The increased concentrations of heavy metals such as Zn, Cu, Ni, Ga, Pb, In and Cr in soil samples were correlated to the amounts of TFSPs added. The results of this study confirmed that, when buried, TFSPs polluted the soil.

1. Introduction

Compared to traditional fossil fuels, solar power is considered a clean and renewable energy source with zero carbon emissions (Rahim et al., 2012; Can Sener et al., 2018). In 2015, 234 GW (GW) of photovoltaic (PV) capacity were installed globally (Mondal and Denich, 2010; Kumar Sahu, 2015; Urban et al., 2016). In China, the total energy yield from solar cells grew rapidly from 5 GW in 2007 to 30 GW in 2012, and then to 43 GW in 2015 (Urban et al., 2016). In the USA, solar energy generation grew by about 22% in 2010, with new PV modules generating a total of 8 GW installed in 2015, and continues to grow (Zhao et al., 2013; Urban et al., 2016; Archer et al., 2017). It is pertinent that the market share of thin-film solar panels (TFSP) is increasing more rapidly than that of traditional silicon PV panels because of their perfect PV characteristics and ductility. Thin-film solar panels comprised of single-crystalline GaAs cells (28.8%), polycrystalline CdTe thin-film cells (21.5%), perovskite cells (21.0%), and Cu (In,Ga)Se_2 (known as CIGS) cells (21.7%) offering excellent light absorption and high efficiency (Polman et al., 2016). Lee and Ebong (2017) reported that the module efficiencies of CIGS and CdTe TFSPs almost rival that of crystalline solar cells, which currently account for more than 55% of the market share of TFSPs. The structure (cross section) of a CIGS TFSP is illustrated in Fig. 1. A typical CIGS TFSP contains various layers, including a glass cover, Mo layer, p-type Cu (In,Ga)Se_2 layer, n-type CdS/ZnS layer, TCO(HR-ZnO/n + -ZnO) layer, and an ethylene vinyl acetate (EVA) film, which is always a brown color with a metallic luster. Crystalline silicon or thin-film PV modules have a lifetime between 20 and 30 years and, despite their obvious benefits, their disposal at the end of their useful life may be problematic (Raugei et al., 2007; Shukla et al., 2017). Quite clearly, this is an increasingly urgent issue as there may be as much as 9.57 million tons of end-of-life PV panels to be disposed of by 2050, and the rapid spread of solar power systems means that the potential waste problem is set to increase sharply in the future (Monier and Hestin, 2011).

The vast quantity of waste from spent systems will need to be dealt with properly to avoid environmental problems, and while various solutions for recycling or recovering material from PV cells have already been proposed, researchers are still searching for suitable environmentally friendly and economical methods for recycling TFSPs (Perez-Gallardo et al., 2017). Because of the complexity associated with recycling, TFSPs are generally treated as construction trash, with burial as the preferred disposal option. It is acknowledged that TFSPs should

---

* Corresponding author.
E-mail address: hruan@uic.edu.hk (H.D. Ruan).

https://doi.org/10.1016/j.apgeochem.2019.104381
Received 8 November 2018; Received in revised form 12 June 2019; Accepted 6 July 2019

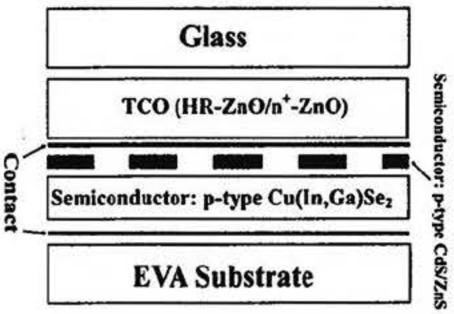


Fig. 1. Structure of a typical CIGS TFSP (cross section); TCO stands transparent conductive oxide, and EVA stands ethylene vinyl acetate.

not be disposed of along with domestic trash as the internal thin-film paint coat contains hazardous metals. Unlike other electrical products, TFSPs are built to resist harsh natural environments, as the toxins in their electrical components are continuously exposed to the environment. The metal thin-film paint coat on a TFSP is well protected by the glass cover and EVA (Fig. 1), but it may become a source of pollution once the glass cover or EVA film is broken. If such damage occurs during the disassembly and transfer stages in a solid waste treatment stream, the internal thin-film paint coat, comprised of the Al/Ni grid, Mo, p-type Cu(In,Ga)Se_2, n-type CdS/ZnS and TCO(HR-ZnO/n^+-ZnO), may be exposed to the environment. Oxygen and water may then permeate into the damaged areas and stimulate corrosion of the thin-film paint coat, resulting in the release of metals.

Previous studies have shown that acid solutions can simulate the leaching toxicity of metal release under acidic environmental conditions, and accelerate the release of metal contaminants from solid waste (Arain et al., 2008; Kazi et al., 2009; Feng et al., 2015). Deng et al. (2009) reported that the expulsion efficiencies of copper (Cu), zinc (Zn), and lead (Pb) from sludge grew as nitric acid concentrations increased (0–0.65 M) and the ideal nitric acid concentration for extracting these metals was 0.325 M (Tyagi et al., 2014). It has also been reported that the release of trace metals from burial of e-waste could contaminate the soil, and the acidic process (vitriolic acid, pH = 1) is the best way to remove cadmium (Cd), chromium (Cr), nickel (Ni) and Zn from domestic and industrial solid waste (Lo and Chen, 1990; Cui et al., 2017).The disposal of TFSPs appears rather harmless and straightforward as long as the toxins inside remain protected by the toughened glass and EVA film. However once the protective layers of TFSPs are damaged, as is inevitable during the waste treatment process, there is the potential for release of heavy metals and other toxins from TFSPs to the surrounding environment, with consequences for soil and water quality. Other types of wastes have been reported to cause similar environmental pollution. For example, investigations of an electronic waste dumpsite showed that the total mean concentrations of heavy metals in the soil decreased with depth in the soil profile and with distance from the dumpsite (Khan et al., 2008; Olafisoye et al., 2013; Adamcová et al., 2017). There are also concerns that the hazardous and toxic metals in the PV modules, such as Cu, Zn, Pb, Cd and selenium (Se), may have serious impacts on human health (da Silva et al., 2017a; da Silva et al., 2017b; Khidkhan et al., 2017; Ngole-Jeme and Fantke, 2017). To date, there have been few studies of the environmental pollution that arises as TFSP is broken down or degraded. One study reported that the predicted environmental concentrations (PEC) of Cd (173.4 $\mu g\,L^{-1}$), molybdenum (Mo) (9.9 mg/L), and Se (9.4 $\mu g\,L^{-1}$) released from thin-film (CIGS) panels during acid rain runoff experiments were considerably greater than the acute toxicity concentrations for some aquatic animals (Zimmermann et al., 2013). Also, very few studies have reported the mechanisms that control the release of toxins into the soil when TFSPs are disposed of. Because of its potential as one of the most promising semi-conductive materials in the thin-film industry, the toxic effects of CIGS and other similar semi-conductive materials need to be investigated. The aim of this study therefore was to determine the mechanisms that controlled metal release from CIGS TFSP material in acidic solutions, and the potential for pollution when TFSP is buried in different types of soils.

human
health

2. Materials and methods

2.1. *Thin-film solar panel extraction*

2.1.1. *Preparation of thin-film solar panel material*

The TFSPs were obtained from a solar energy company in Zhuhai, China. We removed the metal frames, electric cables, and plastic debris (Fig. 1) and then crushed the panel material into small pieces (approximately 9.5 mm * 9.5 mm) with a hammer wrapped in plastic film. The crushed materials were rinsed with deionized (DI) water and air-dried at room temperature for 48 h.

2.1.2. *Determination of metal constituent in thin-film solar panel material*

The metals in TFSP semiconductor layers were extracted by microwave-assisted digestion (Microwave digester MDS-10, Sineo, Shanghai). Approximately 1.00 g of homogenized TFSP semiconductor material that had been ground to less than 0.15 mm was mixed with 10 mL strong acid (4:1 concentrated 65% HNO_3 and 30% H_2O_2 (v/v)) in an airtight Teflon tank (effective volume 50 mL) and heated to 180 °C in the microwave digester (Sineo, MDS-10, Shanghai, China) for 20 min. After digestion the supernatant was separated from the solid particles with a 0.22 μm filter and diluted to 50 mL (Krishnamurty et al., 1976; Farkas, 1993). The concentrations of metals (Al, Ni, Zn, Cu, Na, Ga, V, In, Fe, Pb, Rb, Se, Mn, Mo, Sr and Cr) in semiconductor layers were determined using ICP-OES (Perkin-Elmer Optima 2100 DV, USA).

2.1.3. *Solid waste leaching toxicity*

The leaching toxicity was determined followed the HJ/T299-2007 Solid waste-Extraction procedure for leaching toxicity-Sulphuric acid & nitric acid method. In this experiment, approximate 100.00 g of homogenized TFSP materials that had been further ground to approximate 3 mm were mixed well with 2.00 L leaching reagent (two drops of concentrated 2:1 98% H_2SO_4 and 65% HNO_3 (v/v) in 1 L of DI water, pH ≈ 3.25). The mixture in the flask was agitated on a shaker with a shaking speed of 30 r/min for 18 h at 23 °C, and then filtered with a 0.22 μm filter. The metal concentrations in the solution after filtration and acidification (by HNO_3, to pH less than 2) were determined using ICP-OES (Perkin Elmer Optima 2100DV).

2.1.4. *Nitric acid extraction*

We carried out pre-experiment tests to determine which acid, out of sulphuric acid, ortho-phosphoric acid, hydrochloric acid, nitric acid, and ethylic acid at concentrations of 0.7, 1.4, 2.1, 2.8 and 3.5 M, showed the best ability to corrode TFSP materials and found that the corrosion was best with nitric acid solution (see supplementary material). We then simulated a range of acidic conditions at different nitric acid concentrations and studied the influence of time and acidity on the degree of corrosion of the TFSP materials. Specifically, we placed 10.00 g of the crushed TFSP material (less than 9.5 mm * 9.5 mm), from which the Ni/Al grid was removed to permit a better examination of corrosion for thin-film paint coat, into 250 mL conical flasks and extracted these samples for 1, 6, 12, 24, 48, and 72 h with 100 mL nitric acid at 5 different concentration levels (0.7, 1.4, 2.1, 2.8 and 3.5 M) by shaking (150 rad/min) at room temperature (20 °C). The supernatant was then separated from the solid particles with a 0.22 μm filter and collected in polytetrafluoroethylene (PTFE) bottles. The concentrations of metals (Zn, Ni, Al, Cr, Ga, Pb, Cu and In) in the solution were determined using ICP-OES.

ACID RAIN

Table 1
The properties of the soils used in the experiment.

	Synthetic soil	Mollisol	Oxisol
pH	7.2	5.6	3.9
Organic matter (%)	9.04%	5.30%	8.21%
Sand + silt (> 2 μm)	81.98%	56.24%	49.64%
Clay (< 2 μm)	8.98%	38.46%	42.15%
Pb (mg kg^{-1})	4.00	27.10	193.60
Cu (mg kg^{-1})	12.05	18.80	294.25
Zn (mg kg^{-1})	40.00	28.15	95.50
Ni (mg kg^{-1})	10.80	2.80	20.42
Cr (mg kg^{-1})	7.04	13.45	18.53
Ga (mg kg^{-1})	3.15	9.50	2.05
In (mg kg^{-1})	6.60	1.41	5.28

2.2. Soil burial experiment

2.2.1. Preparation of soil sample

Two soil samples were collected respectively from the upper 20 cm of soil profiles in Zhuhai and Shaoguan, both in Guangdong Province, China. The sample from Zhuhai was a neutral Mollisol that represented a "unpolluted soil" while the sample from Shaoguan was an acid Oxisol with a low pH and high heavy metal background concentrations that represented a "polluted soil". We also prepared a synthetic soil, which was a commercial soil with a neutral pH and low heavy metal concentrations that represented a "garden soil". We air-dried the collected soil samples at room temperature, ground them to less than 2 mm, and then stored in high-density polyethylene (HDPE) buckets. All the soil samples were heated at 121 °C for 24 h to eliminate indigenous microorganisms to avoid bio-leaching of metals. The major properties of these soils are described in Table 1.

2.2.2. Thin-film solar panel burial experiment

Evenly mixed soil samples (2.0 kg) were placed in HDPE pots (250 * 150 * 200 mm). Each pot had 2 small holes (ϕ 5 mm) in its base and a drainage pan underneath into which water drained. This drainage water was returned to the original pot once a day. Different amounts of the crushed TFSP material (with Ni/Al grid) were mixed evenly with the soil samples (0, 50, 100, 150 and 200 g were mixed with 2.0 kg of soil) in the pots, with three pots for each treatment. The samples were left in an open cultivation area under natural environmental conditions (25 ± 5 °C) for 60 days and were soaked with DI water once a day to keep the soil moist (60 ± 5%). After burial, a small amount of the soils in which the remaining TFSP materials had been completely taken out was collected from each pot. These soil samples were air dried at room temperature, then ground to 0.15 mm and stored in a refrigerator at 4 °C. Homogenized soil materials (approximately 200 mg) with 10 mL strong acid (4:1 concentrated 65% HNO_3 and 30% H_2O_2 (v/v)) in an airtight Teflon tank (effective volume 50 mL) were heated at 180 °C in the microwave digester (Sineo, MDS-10, Shanghai, China) for 20 min. After digestion the supernatant was then separated from the solid particles with a 0.22 μm filter and diluted to 50 mL (Krishnamurty et al., 1976; Farkas, 1993). The concentrations of metals (Zn, Ni, Al, Cr, Ga, Pb, Cu and In) were determined using ICP-OES (Perkin-Elmer Optima 2100 DV, USA). The experiments were performed in triplicate. A certified standard reference material GBW07403(GSS-3), obtained from the National Institute of Metrology (NIM), China, was used in the digestion and analysis as part of the QA/QC protocol. Reagent blanks and analytical triplicates comprised 10% of the total samples were used where appropriate to test the accuracy and precision of the analysis. The recovery rates were around 92 ± 6% for all of the metals in the soil reference material (GBW07403(GSS-3)).

2.3. Data analysis

We used the Pollution Index (PI) and Nemerow Contamination Index (P_N) to quantify the pollution and to evaluate the metal pollution levels for soil samples.

2.3.1. Pollution index

The PI ratio was calculated as outlined in the Technical Specifications for Soil Environmental Monitoring HJ/T 166 (2004), and expressed in Equation (Eq.) 2-1.

$$PI = \frac{[C]_{\text{heavy metal}}}{[C]_{\text{background}}} \tag{2.1}$$

where $[C]_{\text{heavy metal}}$ is the heavy metal concentration in a soil sample and $[C]_{\text{background}}$ represents the heavy metal concentration in a blank soil (background).

2.3.2. Nemerow Contamination Index

The Nemerow pollution index (P_N) is exceptionally sensitive and resilient in eclipsing properties, making it a good general-use index on classifying contamination levels of soils (Cai et al., 2015). It considers all the independent pollution indexes and highlights the importance of elements that cause contamination.

$$P_N = \sqrt{\frac{PI_{\text{average}}^2 + PI_{\max}^2}{2}} \tag{2.2}$$

where PI is the pollution index ratio, PI_{average} and $PI_{\max}$ are the average and maximum PI values for each metal, respectively. The relationships between the value of P_N and level of pollution are shown in Table 2. The P_N reflects the combined effects of multiple heavy metals in soils, especially the pollutants with the highest PI.

2.3.3. Statistical analysis

Statistical analysis was performed with SPSS (Ver. 22). We used analysis of variance (ANOVA) to test differences between the concentrations of different metals at different extraction times during the acid extraction experiment, and the relationships between the metal concentrations and the different leaching times for the various soils. Means were separated using the least significant difference option with $\alpha = 0.05$. The correlations between addition of crushed TFSP (g) and Pollution Index (P_I) and Nemerow Contamination Index (P_N) of soils are analyzed using Pearson rank order correlation analysis.

3. Results

3.1. Determination of metal constituent in thin-film solar panel material

The metal constituents in the TFSP semiconductor materials are shown in Fig. 2. As the main elements in Ni/Al grids, aluminum (Al) and Ni, with concentrations of 1270 and 650 mg/kg, respectively, were the two most abundant metals. As expected, Zn, Cu, Ga, and In, the important components of a thin-film paint coat (e.g. TCO (ZnO), p-type $Cu(In,Ga)Se_2$) used for generating electricity, were also present at high concentrations. The main source of sodium (Na) is glass (Fig. 1), while iron (Fe) and vanadium (V) were present in the residual metal frames that were removed in the pre-treatment. The remaining metals, detected at trace concentrations, are added to TFSPs during manufacturing to optimize the optical and photovoltaic properties, or to

Table 2
Nemerow Contamination Index (P_N) for evaluating soil pollution.

Level	Nemerow Contamination Index	Pollution Level
I	$P_N \le 0.7$	Nil
II	$0.7 < P_N \le 1.0$	Light
III	$1.0 < P_N \le 2.0$	Mild
IV	$2.0 < P_N \le 3.0$	Medium
V	$P_N > 3.0$	Heavy

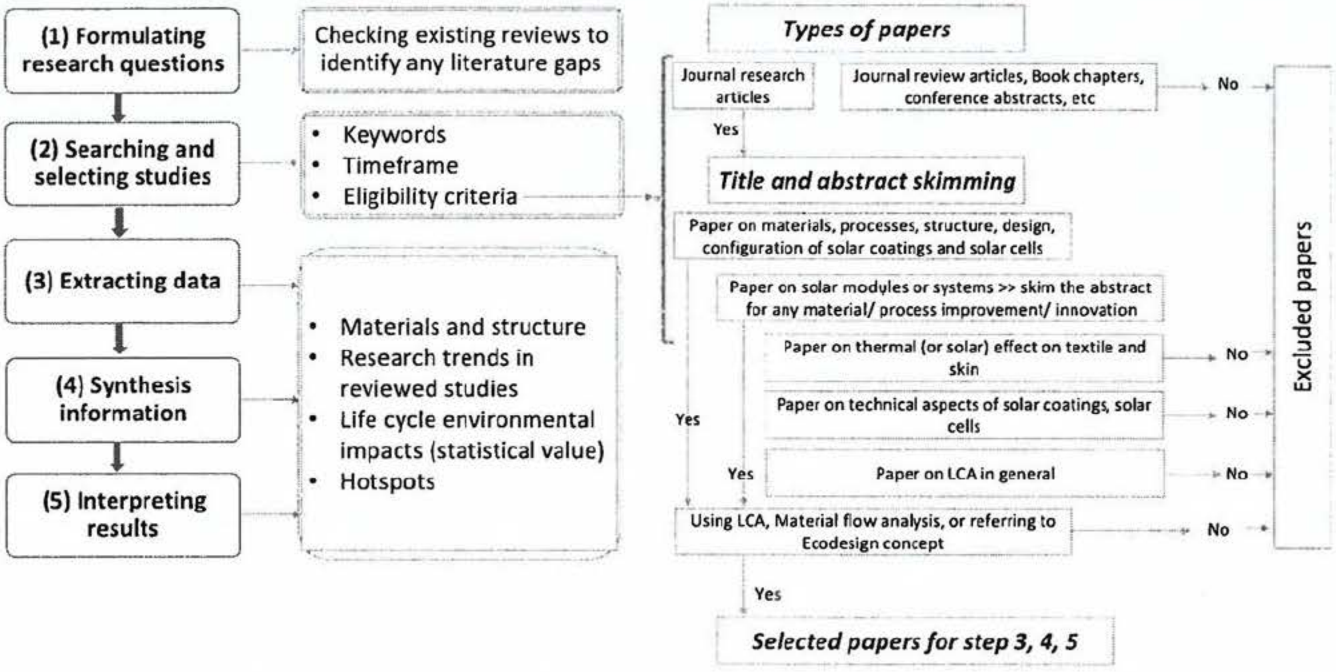


Fig. 1. Logical flow within the review development.

helps to narrow the publications on the "emerging" technologies with improved efficiency, innovative materials, etc. Secondly, because the previous review of Muteri et al. (2020) selected articles being published till 2018, the timeframe from 2017 to 2023 will avoid duplicating the effort of the previous review.

Furthermore, the searched studies are screened and selected based on the three following criteria:

- journal research articles,
- skimming the titles to include studies on materials and structure (layers, configurations, design, etc.) of solar cells (or coatings), and
- screening the abstracts for LCA (or life cycle concepts).

At the end of the skimming and screening process, 24 papers on solar cells, solar coatings and LCA are selected for extracting data. Finally, the extracted data on materials, structure, environmental impacts and hotspots of emerging solar cells will be synthesized and interpreted, as mentioned in steps (4) and (5).

3. Solar technologies

Solar cell is the backbone of solar energy technologies, which converts solar radiation into power. Solar cells are generally classified into three main types of the first generation (crystalline silicon based solar cells), the second generation (thin-film solar cells) and the third generation (non-silicon based solar cells such as organic solar cells, dye sensitized solar cells, etc. (Muteri et al., 2020). Though this classification is popular and convenient, in the past, it discriminated the conventional silicon based solar cells and thin-film solar cells, in which the latter was deemed to be the next generation. However, with the improvement in silicon materials, the cost of silicon based solar cells reduces and their efficiency increases. Recently, many 'third generation' solar cells are silicon based, for example the combination of silicon and perovskite in tandem solar cells. Therefore, instead of describing the solar technologies by the generations, this section will present different solar technologies based on the materials and structure of the solar cells, with some discussion on the improvement in their efficiency and the change in their market share.

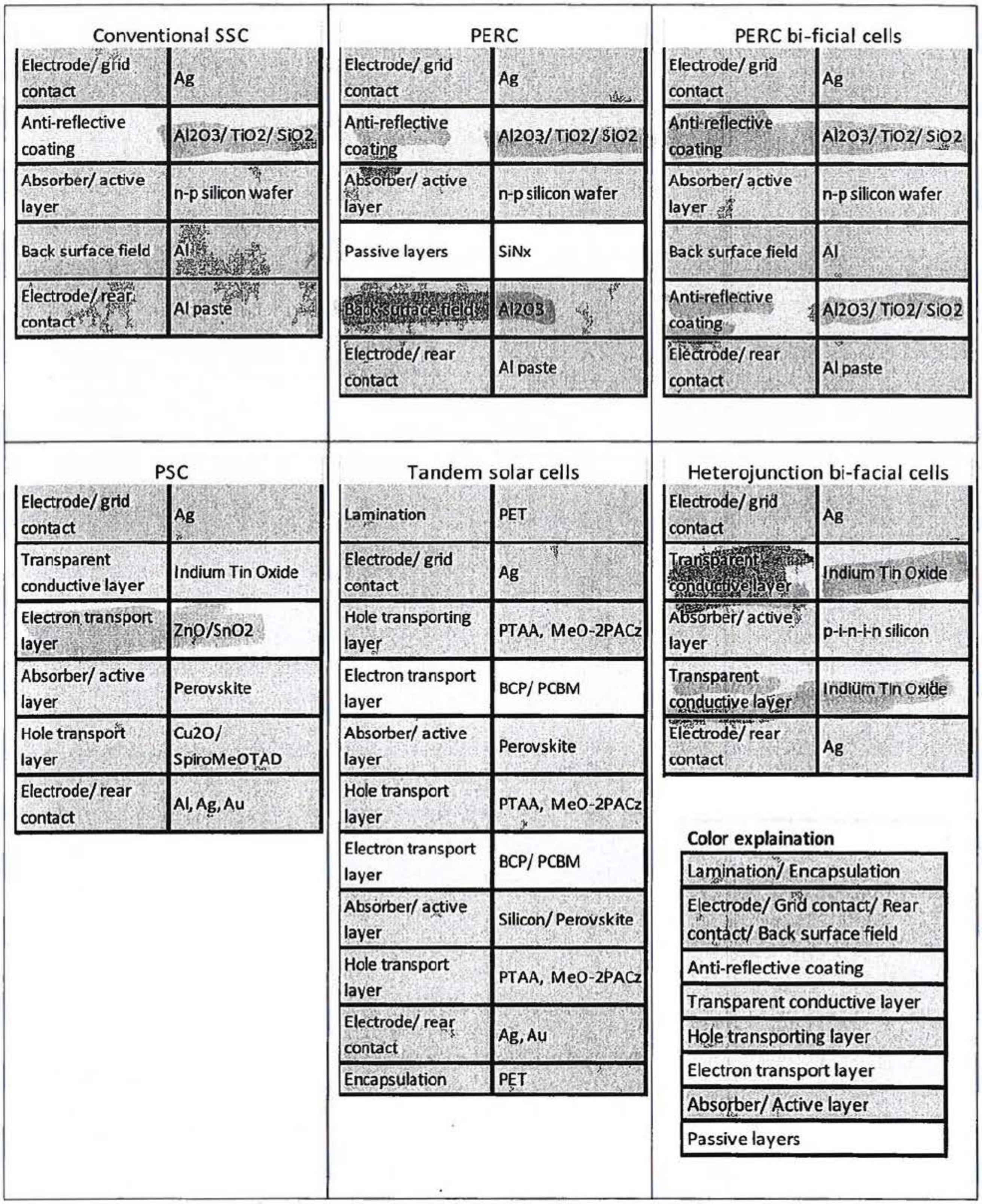
3.1. *Materials for solar cells*

Based on the materials for solar cells, there will be two main categories of materials, silicon based and other non-silicon materials. Most of the existing commercial solar cells are based on silicon (Jungbluth et al., 2012). The silicon based solar cells include mono-Si, multi-Si, ribbon silicon (ribbon-Si) (panel) and a-Si (thin film). Other materials for exploiting solar energy are cadmium telluride (CdTe), copper indium gallium selenide (CIGS), copper indium diselenide (CIS), indium phosphide (InP), photosensitive materials such as titanium dioxide (TiO2), or gallium arsenide (GaAs). Recently, perovskite has been researched as a potential material in the solar energy sector. The classification of solar cells by materials and architecture are summarized in Table 1.

Most of today's solar PV cells are mono-Si and multi-Si, accounting for approximately 80–90 % of the total solar photovoltaic cell market (Jungbluth et al., 2012; Li et al., 2018; IEA, 2022). As of 2008, the shares of commercial solar cells are 51 % of multi-Si, 37 % of mono-Si, 5 % of a-Si, and 1.5 % of ribbon-Si technology (Jungbluth et al., 2012). These shares have recently changed with the decrease of multi-Si to 15 %, and

Table 1
Classification of solar cells by materials and Structure.

Material structure	Silicon (95 % of the market)	Non-silicon (5 % of the market)
Conventional (single junction, mono facial)	Mono-Si Multi-Si (dead) Ribbon-Si (never born)	
Passivated	PERC (86–88 % of the market)	
Bi-faciality and passivated	PERC bi-faciality	
Thin-film (heterojunction)	a-Si	CdTe (going to finish) CIGS/CIS (going to finish) GaAs (space application) Perovskite (lab scale)
Bi-faciality and heterojunction	Silicon based bi-faciality heterojunction	
Tandem (multijunction)	Silicon based tandem	CIGS-based tandem Perovskite based tandem (Maybe in future)



Conventional SSC

Electrode/ grid contact	Ag
Anti-reflective coating	Al2O3/ TiO2/ SiO2
Absorber/ active layer	n-p silicon wafer
Back surface field	Al
Electrode/ rear contact	Al paste

PERC

Electrode/ grid contact	Ag
Anti-reflective coating	Al2O3/ TiO2/ SiO2
Absorber/ active layer	n-p silicon wafer
Passive layers	SiNx
Back surface field	Al2O3
Electrode/ rear contact	Al paste

PERC bi-ficial cells

Electrode/ grid contact	Ag
Anti-reflective coating	Al2O3/ TiO2/ SiO2
Absorber/ active layer	n-p silicon wafer
Back surface field	Al
Anti-reflective coating	Al2O3/ TiO2/ SiO2
Electrode/ rear contact	Al paste

PSC

Electrode/ grid contact	Ag
Transparent conductive layer	Indium Tin Oxide
Electron transport layer	ZnO/SnO2
Absorber/ active layer	Perovskite
Hole transport layer	Cu2O/ SpiroMeOTAD
Electrode/ rear contact	Al, Ag, Au

Tandem solar cells

Lamination	PET
Electrode/ grid contact	Ag
Hole transporting layer	PTAA, MeO-2PACz
Electron transport layer	BCP/ PCBM
Absorber/ active layer	Perovskite
Hole transport layer	PTAA, MeO-2PACz
Electron transport layer	BCP/ PCBM
Absorber/ active layer	Silicon/ Perovskite
Hole transport layer	PTAA, MeO-2PACz
Electrode/ rear contact	Ag, Au
Encapsulation	PET

Heterojunction bi-facial cells

Electrode/ grid contact	Ag
Transparent conductive layer	Indium Tin Oxide
Absorber/ active layer	p-i-n-i-n silicon
Transparent conductive layer	Indium Tin Oxide
Electrode/ rear contact	Ag

Color explaination

- Lamination/ Encapsulation
- Electrode/ Grid contact/ Rear contact/ Back surface field
- Anti-reflective coating
- Transparent conductive layer
- Hole transporting layer
- Electron transport layer
- Absorber/ Active layer
- Passive layers

Fig. 2. Layers and materials of various solar PV cells.

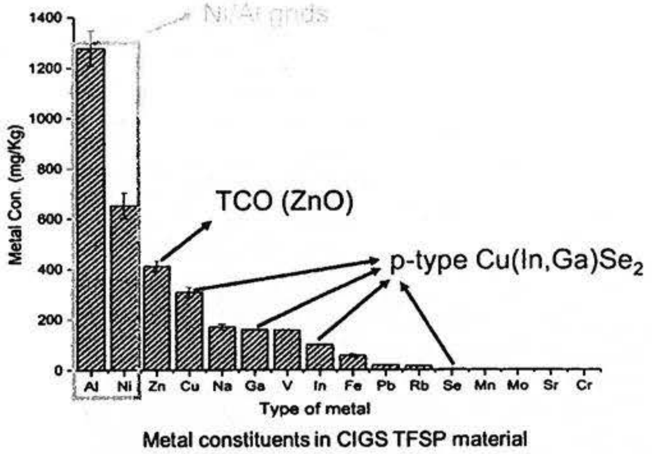


Fig. 2. Metal concentrations of TFSP after microwave-assisted digestion. (Values in the bar chart are expressed as the mean and error bars represent the SD. Three samples were analyzed for each metal. SD = standard deviation).

prevent corrosion of the paint coats.

3.2. Metal leaching toxicity from TFSP material

Fig. 3 demonstrates the metal leaching toxicity of TFSPs. As the main elements in a thin-film panel coat (e.g. ZnO), the concentration of Zn (3.66 mg/L) showed the highest value among all metals. The other important components in Ni/Al grids, aluminum (Al) and nickel (Ni), also showed high concentration of 1.69 and 1.25 mg/L, respectively. Since none of the metal leaching toxicity of TFSP exceeded the related national standard (GB 5085.3–2007 Identification standards for hazardous wastes – Identification for extraction toxicity), the TFSP materials can be defined as solid waste s below the national level of leaching toxicity based on this experiment.

3.3. Nitric acid extraction of metals from TFSP material

Fig. 4 shows the four major metal components of TFSP, especially of the thin-film paint coat (without glass cover and Ni/Al grid) after acid extraction. During the first 24 h of extraction, the concentration of Zn in solution increased significantly ($p < 0.05$), after which the concentrations increased very slowly. As shown in Fig. 4a, the concentration of Zn extracted by 3.5 M nitric acid solution was 30% higher than that extracted by 0.7 M nitric acid during the first hour of extraction. The pattern of Zn extraction was different from those of Ga, In and Cu, as shown in Fig. 4. Zinc showed a rapid increasing trend in the early stages of extraction while Ga, In and Cu followed a contrasting pattern. After extraction for 6 h, Ga, In and Cu were dissolved slowly in the solution, and the increases in their concentrations were not significant ($p > 0.05$). Dissolution of Ga, In and Cu started to increase in 1.4, 2.1, 2.8, and 3.5 M nitric acid solutions between 6 and 24 h of extraction. It was noticed that even Ga and In started to increase in 0.7 M nitric acid solution after 24 h of extraction. After 48 h of extraction, the concentrations of Ga, In and Cu had increased significantly ($p < 0.05$) in all nitric acid concentrations (Fig. 4b, c & 4d), and the dissolution rates of Ga, In and Cu showed obvious increases after 48 h of extraction in 2.1, 2.8, and 3.5 M nitric acid solutions. As shown in Fig. 4d, the Cu concentration peaked after 72 h of extraction, but the Cu peak concentration was much lower than those of other metals. Only 0.64 mg/L of Cu was extracted in 2.1 M nitric acid solution, and after extracting with 2.1, 2.8, and 3.5 M nitric acid solutions, the Cu concentrations were almost the same. The 1.4 and 0.7 M nitric acid solutions showed weaker extraction abilities, and they extracted only half as much Cu as the 2.1 M nitric acid after 72 h.

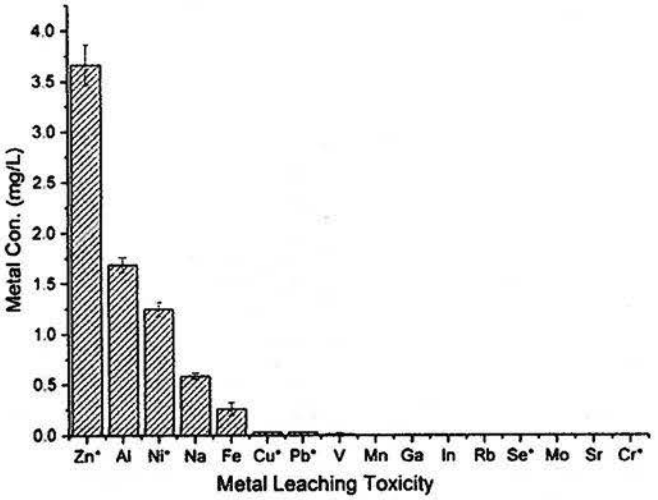


Fig. 3. Metal leaching toxicity of TFSPs. *Denotes the metals that ought to be targeted during leaching toxicity evaluation. Values of metal concentrations are expressed as the mean with error bars representing the standard deviation (SD). Five replicates were analyzed.

3.4. Thin-film solar panel burial experiment

The metal concentrations in the synthetic soil, Mollisol, and Oxisol increased as the amounts of TFSP added increased over a 60-day burial period. The metals presented the highest concentrations in these three soils were Ga, Zn, Pb, Cu, Ni, In and Cr (Fig. 5).

3.4.1. Burial experiment of synthetic soil

Of the heavy metals studied, the Ni concentration was the highest in the synthetic soil after 60-day burial (Fig. 5a). The concentration of Ni increased 12 times from a background level of 10.8–137 mg/kg in the synthetic soil where 200 g of TFSP (with Al/Ni grid) was added, which indicated that the release of Ni was significantly ($p < 0.05$) correlated to the amount of TFSP added. The background concentrations of Zn and Cu in the synthetic soil were 40 and 13 mg/kg, respectively. For example, after 60 days of burial with addition of 200 g of TFSP, the concentration of Zn in the soil increased to approximately 82 mg/kg. This was approximately twice the concentration in the blank soil sample, and corresponded well with the amount of TFSP added. The Cu concentration was 39 mg/kg in the soil where 200 g of TFSP was added, which was 3 times the concentration in the blank (Fig. 5a). The In and Ga concentrations also increased as the amount of TFSP added increased, from a background concentration of 6.6–16.5 mg/kg for In and 3.2–5.2 mg/kg for Ga in the soil where 200 g of TFSP was added after 60 days of burial (Fig. 5a).

3.4.2. Burial experiment of Mollisol

After burial for 60 days, we found that the concentrations of Zn, Cu, Ni, Ga, In and Cr in Mollisol were higher than those at the beginning of burial period, reflecting the release of metals from TFSP (Fig. 5b). Of these metals, the concentration of Zn was the highest, and had increased from a background level of 28 mg/kg to a maximum of 131 mg/kg as the amounts of TFSP added increased to 200 g. The concentration of Ni was initially 2.8 mg/kg but increased to 13.6 mg/kg, 4 times its background concentration, and the concentration of Pb increased by approximately 18.5% from 27.1 to 32.7 mg/kg in the soil where 200 g of TFSP was added after the 60-day burial, due to soldering that contains Pb was used in TFSP and contributed to Pb release into the soil. The concentrations of Ga and Cr in Mollisol changed only slightly when different quantities of TFSP were added.

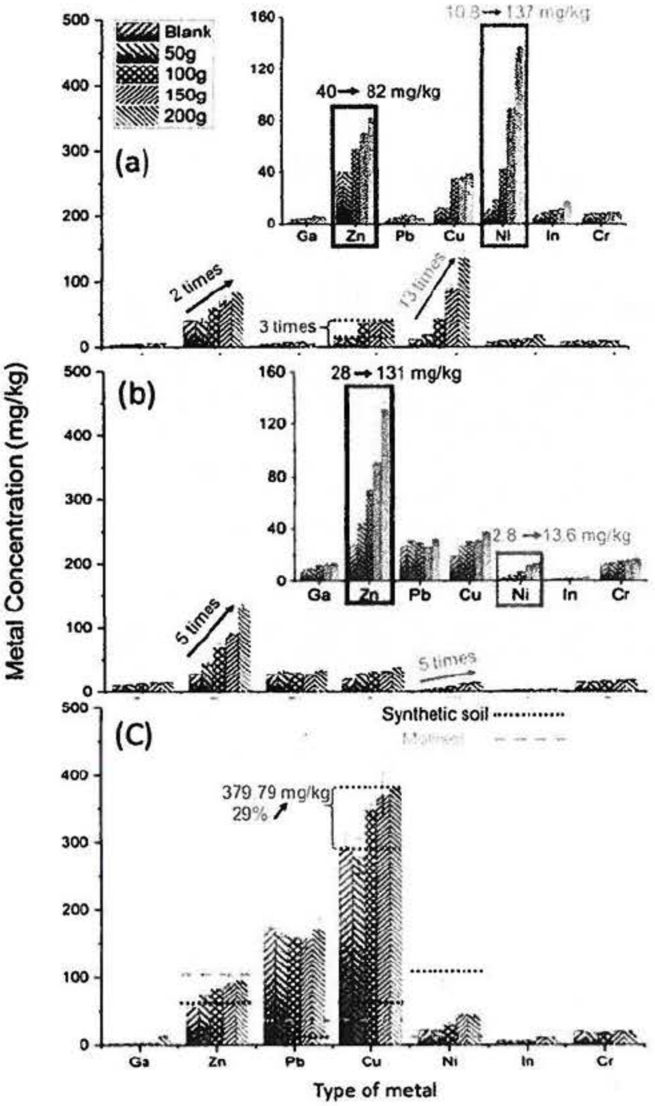


Fig. 5. Metal concentrations in soils contaminated by TFSP: (a) synthetic soil, (b) mollisol, and (c) oxisol. The inset graphs in Fig. 5-a & b have been included to show the results more clearly. Labels in (a) indicate the amounts of TFSP added. Values are expressed as the mean ± SD. Samples were analyzed in triplicate.

different periods of time indicated that the metals in TFSP could be released under acidic conditions, and that the duration of the exposure to the acidic environment was an important parameter of influence on the amounts of metals released. Hazardous metals may be released to the environment from the thin-film paint coat inside TFSP when the protective layers are broken, and the release may be accelerated by the acidity of the surrounding environment.

4.3. Thin-film solar panel burial experiment

4.3.1. Burial experiment of synthetic soil

Indium and Ga are key elements in the p-type Cu (In, Ga) Se_2 layer of a CIGS TFSP, so the increases in their concentrations in the soil indicated that the paint coat of the thin-film was corroded. The internal thin film layer can therefore be corroded easily once the glass or EVA film is broken. The results of increases in the total concentrations of Ga, Zn, Pb, Cu, Ni, In and Cr in the synthetic soil samples as shown in Fig. 5a demonstrate that heavy metals were released from TFSP during the 60-day burial period.

Table 3
Pollution Index (PI) and Nemerow Contamination Index (P_N) of soils.

Soil type	Addition of crushed CIGS TFSP (g)				Correlation factor (r)
Synthetic soil	50 g	100 g	150 g	200 g	
P_{Ga} [a]	1.26	1.45	1.88	1.64	0.764
P_{Zn}	1.01	1.46	1.74	2.05	0.994**
P_{Pb}	1.20	1.69	1.72	1.05	−0.159
P_{Cu}	1.02	2.96	3.05	3.23	0.837
P_{Ni}	1.65	3.92	8.24	12.69	0.990**
P_{In}	1.29	1.56	1.70	2.50	0.935*
P_{Cr}	1.16	1.14	1.23	1.19	0.593
P_{AVG}	1.24	2.17	3.06	3.86	0.999**
P_N	1.46	3.17	6.21	9.38	0.992**
Pollution level	*Mild*	*Heavy*	*Heavy*	*Heavy*	-
Mollisol	50 g	100 g	150 g	200 g	–
P_{Ga}	1.06	1.30	1.40	1.47	0.958*
P_{Zn}	1.57	2.47	3.22	4.68	0.989**
P_{Pb}	1.17	1.10	0.96	1.21	−0.024
P_{Cu}	1.47	1.64	1.69	2.01	0.956*
P_{Ni}	1.80	2.66	4.30	4.84	0.983**
P_{In}	1.86	2.06	1.76	2.55	0.651
P_{Cr}	1.35	1.35	1.42	1.63	0.887
P_{AVG}	1.49	1.87	2.22	2.79	0.993**
P_N	1.69	2.30	3.42	3.95	0.990**
Pollution level	*Mild*	*Medium*	*Heavy*	*Heavy*	–
Oxisol	50 g	100 g	150 g	200 g	–
P_{Ga}	0.94	1.57	1.60	6.04	0.84
P_{Zn}	0.92	1.22	1.38	1.51	0.980**
P_{Pb}	0.92	0.90	0.89	0.97	0.508
P_{Cu}	0.95	1.18	1.26	1.29	0.923*
P_{Ni}	0.98	1.50	2.22	2.14	0.929*
P_{In}	0.98	1.07	1.86	1.89	0.923*
P_{Cr}	0.92	0.92	1.00	0.99	0.861
P_{AVG}	0.94	1.19	1.46	2.12	0.968*
P_N	0.96	1.39	1.88	4.52	0.901*
Pollution level	*Light*	*Mild*	*Mild*	*Heavy*	–

[a] P_{metal} stands for the pollution factor of metal in soil and P_{AVG} is the average value of P_{metal}; and P_N stands for Nemerow contamination index of the soil. The correlations are between the P_N and the amounts of TFSP materials added; *, $p < 0.05$ and **, $p < 0.01$.

Synthetic soil with addition of 100, 150, and 200 g of TFSP was classified as heavily contaminated (P_N values of 3.17_{100g}, 6.21_{150g}, and 9.38_{200g}, as shown in Table 3). The Ni concentration in synthetic soil was higher than the limit of the Environmental Quality Standards for Soil in China GB15618 (2018), while the concentrations of other metals did not exceed the standard. Nickel was the primary metal contaminant released from TFSPs when buried in synthetic soil. The different leaching patterns of synthetic soil and Mollisol were mainly attributed to the soil properties, including pH and organic matter. The organic matter in synthetic soil ($OM_{Synthetic} = 9\%$) was higher than in Mollisol ($OM_{Mollisol} = 5.3\%$), which was added in for enrich the soil nutrient (e.g. peat). The organic matter showed a good Ni adsorption ability, which led to the equilibrium concentration of Ni in synthetic soil much higher than that in Mollisol. It is notice that the concentration of Ni in synthetic soil increased with the amount of TFSP added.

4.3.2. Burial experiment of Mollisol

The background concentration of Zn in Mollisol was approximately 30% less than that in synthetic soil, but after 200 g of TFSP was added and buried for 60 days, the Zn concentration in Mollisol was 1.5 times higher than that in synthetic soil. The concentrations of Ni followed a different pattern. The background concentration of Ni in Mollisol was only 1/3 of the concentration in synthetic soil. After 60 days, the Ni concentration in Mollisol to which 200 g of TFSP was added had increased from 2.8 to 13.6 mg/kg but was only 10% of the concentration in synthetic soil. After 60 days, the Cu concentration had doubled from 18.8 to 37.7 mg/kg in Mollisol to which 200 g of TFSP was added (Fig. 5b); this was comparable to the concentration of Cu extracted from synthetic soil with 200 g of material added (Fig. 5a). These results suggest that it was easier to extract Zn, but more difficult to extract Ni, from the Mollisols (pH 5.6) than from the synthetic soil (pH 7.2) with TFSP added. According to Barać et al. (2016), soil contamination by heavy metals not only significantly increased the concentrations of heavy metals in the soil but also their mobile and potentially bioavailable amounts (Abdu et al., 2017; Xiao et al., 2017). Our results may reflect the characteristics of these soils, including their pH, humic acid and hydrous ferric oxide contents, particle size and shape, ionic strength, specific surface area, surface bonding, cation exchange capacity, and their affinity to accelerate or retard the release of metals from TFSP. The Mollisol used in this experiment was a kind of natural soil collected in Zhuhai, with less organic matter ($OM_{Synthetic} = 9\%$; $OM_{Mollisol} = 5.3\%$) than synthetic soil but with much higher clay content ($Clay_{Synthetic} = 8.98\%$; $Clay_{Mollisol} = 39.46\%$). The selective adsorption of Zn on the clay increased the total adsorption capacity of Zn by Mollisol. The Zn concentration was higher than the limit of the Environmental Quality Standards for Soil in China GB15618 (2018) in the soil where 200 g of TFSP was added after 60 days of burial, indicating that the Mollisol was contaminated. Zinc was the primary metal contaminant released from TFSP when buried in Mollisol. According to Strachel et al. (2017), high concentration of Zn in contaminated soil can significantly modify the soil properties by accelerating or retarding the release of other metals from TFSP.

4.3.3. Burial experiment of oxisol

As shown in Fig. 5c, the patterns of metal concentrations in Oxisol were different from those in synthetic soil and Mollisol (Fig. 5a and b). The Oxisol used in this study was already polluted by various metals, especially Pb. For this circumstance, the initial high pollutant concentrations may suggest that there was ongoing gradual release of pollutants (Fig. 5c). For example, the concentrations of Cu and Zn in Oxisol with only 50 g TFSP added were not significantly different from those in the blank. However the concentrations of Cu and Zn were approximately 29% and 70% higher, respectively, in Oxisol where 200 g of TFSP was added, indicating that the metals released from TFSP caused the metal concentrations to increase in the soil. Compared with synthetic soil and Mollisol, Oxisol showed the highest background concentration of metal contaminant with the lowest pH value. For example, high concentrations of metal contaminants especially of Cu and Pb were obtained. It should be noted that the low pH value can lead to a high leaching efficiency of metal from TFSP, but the results of soil burial experiment figured out the leaching efficiency of Oxisol was much lower than those of synthetic soil and Mollisol. The concentration of Cu increased approximate 29% and the concentration of Pb seemed to be unchanged. It was attributed to the equilibrium of metal contaminants in soil mainly from the background but few from the newly released metals. This was why much lower concentrations of metals were extracted by Oxisol even at a lower pH value. In addition, the concentration of Pb in Oxisol burial experiment decreased slightly, and its concentration did not vary significantly either in the burial experiments of synthetic soil and Mollisol. According to Ma et al. (2007), corroding mechanisms of metallic Pb can be separated into three steps: oxidation, carbonation and dissolution, and soil properties especially pH can significantly influence these processes. This phenomenon possibly reflects differences in the equilibrium status between adsorption and desorption of Pb (including Pb-carbonates and Pb-oxides) and its interaction with other metals. After 60 days of burial, the concentrations of Ni, In and Ga in Oxisol were higher than their initial concentrations increased 114.2%, 89.2% and 492.4%, respectively with 200 g of TFSP being added. The concentration of Cr stabilized at approximately 18 mg/kg. Therefore, the increases in metal concentrations in these three types of soils reflect the states of metals released from TFSP.

It is noteworthy that, in the same type of soil, the metal concentrations were higher after TFSP was added over the same time interval. In this experiment, by comparing three types of soils after 60 days of burial experiment, the metal concentrations were the lowest in synthetic soil with the highest pH (7.2), followed by Mollisol with a pH value of 5.6, and were the highest in Oxisol with a pH of 3.9, which indicates that pH is one of parameters influences the dissolution of metals in different types of soils, and that metal release from TFSP is enhanced under acidic conditions.

4.4. Mechanism of metal release from TFSP

There are various mechanisms contributed to metal release from TFSP, as follows. First, dissolution and oxidation occurred at the broken interface of TFSP, resulted in metal release into the soil. Second, the ionic strength influenced the rate of metal dissolution, as shown by the variations in dissolution rate after different amounts of TFSP were added related to the background concentrations of metals in three types of soils. Hydrogen ions contributed significantly to the changes in cation exchange capacity in the soil, such that metal release from TFSP was accelerated. Finally, soil properties and surface bonding of soil minerals, for example water molecules, may have facilitated metal adsorption when the H^+ was released, so that metals built up new bonds with oxygen left over on the surface of a mineral (Jiang et al., 2013). The larger amount of hydrogen ion penetrated in the broken TFSP may facilitate corrosion of TFSP, resulting in more metal release into the soil.

4.5. Assessment of soil contamination caused by thin-film solar panel

We used P_N to assess the degree of metal pollution in soils caused by the metals released from TFSP.

The values of PI for the most abundant metals and the values of P_N of soil contamination after TFSP was added are shown in Table 3. The synthetic soil, Mollisol, and Oxisol with additions of 200 g of TFSP were classed as heavily contaminated. The P_{AVG} showed a strongly positive correlation with addition of crushed TFSP in three types of soils ($r_{Syn} = 0.999$, $p < 0.01$; $r_{Mollisol} = 0.993$, $p < 0.01$; $r_{Oxisol} = 0.968$ $p < 0.05$), indicating that P_{AVG} increased with addition of crushed TFSP. This illustrated that more pollutants could be released when more crushed TFSP materials were buried. There was a strong positive relationship between P_N and addition of crushed TFSP in synthetic soil and Mollisol ($r_{Syn} = 0.992$, $p < 0.01$; $r_{Mollisol} = 0.990$, $p < 0.01$), indicating that the P_N increased as the amount of crushed TFSP increased. This suggests that the contamination levels of synthetic soil and Mollisol increase with the addition of crushed TFSP. The Oxisol with 50 g of TFSP added was lightly polluted, and the lower PI (P_{metal}) for this soil may reflect the fact that it had a higher background of metal concentrations than other soils. The other soils with 50 g of TFSP added were classified as mildly contaminated. The soil samples with TFSP added between 100 and 200 g showed mild, medium, and heavy contaminations, and the contamination level increased as the amount of TFSP added increased. The P_N values show that TFSP had adverse effects of pollution on the different types of soil.

5. Conclusion

Our results demonstrate that metal pollutants were released into the soil from the buried TFSP. The observations and results show that heavy metals may be released into the surrounding environment once the protective layers are broken and exposed to acidic conditions. We detected 16 metals in TFSPs, of which Ni, Zn, and Cu were released at the highest concentrations in three different types of soils studied. We examined the mechanisms of metal release from TFSP and found that, All soils contaminated

from the rates of metal dissolution and the affinity of metals to the reaction media (e.g. soil minerals), they were related to the soil properties. In this study, three various soils showed different abilities to leach pollutants from TFSPs. The synthetic soil showed the best ability for leaching Ni whereas the Mollisol showed the greatest Zn leaching ability. Although the background metal concentrations were highest in the Oxisol, the amount of Cu leached by Oxisol was greatest when the same amount of TFSP was added. The Nemerow Contamination Index showed that all the soils were contaminated to different levels, from light, mild, medium, to heavy, depending on the amounts of TFSPs added. The increases in metal concentrations in the soil were therefore related to the amounts of TFSPs added and the soil properties.

Declarations of interest

None.

Acknowledgements

This research was financially supported by the Beijing Normal University-Hong Kong University United International College (UIC), under the Research Project R201625 and the Zhuhai Key Laboratory Research Fund R1053. The authors thank Mr Helmut Warmenhoven and Ms Helen Ann Thompson of UIC who provided useful comments for this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.104381.

References

Abdu, N., Abdullahi, A.A., Abdulkadir, A., 2017. Heavy metals and soil microbes. Environ. Chem. Lett. 15 (1), 65–84.

Adamcová, Dana, Radziemska, Maja, Ridošková, Andrea, Bartoň, Stanislav, Pelcová, Pavlína, Elbl, Jakub, Kynický, Jindřich, Martin, Brtnický, Vaverková, Magdalena Daria, 2017. Environmental assessment of the effects of a municipal landfill on the content and distribution of heavy metals in Tanacetum vulgare L. Chemosphere 185, 1011–1018.

Arain, M.B., Kazi, T.G., Jamali, M.K., Jalbani, N., Afridi, H.I., Baig, J.A., 2008. Speciation of heavy metals in sediment by conventional, ultrasound and microwave assisted single extraction methods: a comparison with modified sequential extraction procedure. J. Hazard Mater. 154 (1), 998–1006.

Archer, C.L., Simao, H.P., Kempton, W., Powell, W.B., Dvorak, M.J., 2017. The challenge of integrating offshore wind power in the US electric grid. Part I: wind forecast error. Renew. Energy 103, 346–360.

Barać, N., Škrivanj, S., Mutić, J., Manojlović, D., Bukumirić, Z., Živojinović, D., Petrović, r., Ćorac, A., 2016. Heavy metals fractionation in agricultural soils of Pb/Zn mining region and their transfer to selected vegetables. Water, Air, Soil Pollut. 227 (12), 481.

Cai, C., Xiong, B., Zhang, Y., Li, X., Nunes, L.M., 2015. Critical comparison of soil pollution indices for assessing contamination with toxic metals. Water, Air, Soil Pollut. 226 (10), 352.

Can Sener, S.E., Sharp, J.L., Anctil, A., 2018. Factors impacting diverging paths of renewable energy: a review. Renew. Sustain. Energy Rev. 81 (P2), 2335–2342.

Cui, J.L., Luo, C.L., Tang, C.W.Y., Chan, T.S., Li, X.D., 2017. Speciation and leaching of trace metal contaminants from e-waste contaminated soils. J. Hazard Mater. 329, 150–158.

da Silva, F.B.V., do Nascimento, C.W.A., Araújo, P.R.M., da Silva, F.L., Lima, L.H.V., 2017a. Soil contamination by metals with high ecological risk in urban and rural areas. Int. J. Environ. Sci. Technol. 14 (3), 553–562.

da Silva, W.R., da Silva, F.B.V., Araújo, P.R.M., do Nascimento, C.W.A., 2017b. Assessing human health risks and strategies for phytoremediation in soils contaminated with As, Cd, Pb, and Zn by slag disposal. Ecotoxicol. Environ. Saf. 144, 522–530.

Deng, J., Feng, X., Qiu, X., 2009. Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid. Chem. Eng. J. 152 (1), 177–182.

Farkas, A., 1993. Preparation of samples for heavy metal analyses and measuring heavy metals. *Limnological bases of lake management*. In: Proceedings of the ILEC UNEP international training course. 24. pp. 160–163.

Feng, L., Luo, J., Chen, Y., 2015. Dilemma of sewage sludge treatment and disposal in China. Environ. Sci. Technol. 49 (8), 4781–4782. https://doi.org/10.1021/acs.est.5b01455. 2015.

Hala, M., Kato, H., Algasinger, M., Inoue, Y., Rey, G., Werner, F., Schubbert, Ch, Dalibor T., Siebentritt, S., 2017. Improved environmental stability of highly conductive nominally undoped ZnO layers suitable for n-type windows in thin film solar cells. Sol. Energy Mater. Sol. Cells 161, 232–239.

Jiang, Y., Ruan, H., Lai, S., Lee, C., Yu, C., Wu, Z., Chen, X., He, S., 2013. Recycling of solid waste material in Hong Kong: I. properties of modified clay mineral waste material and its application for removal of cadmium in water. Earth Sci. 2 (2), 40–46.

Kazi, T.G., Jamali, M.K., Arain, M.B., Afridi, H.I., Jalbani, N., Sarfraz, R.A., Ansari, R., 2009. Evaluation of an ultrasonic acid digestion procedure for total heavy metals determination in environmental and biological samples. J. Hazard Mater. 161 (2), 1391–1398.

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in beijing, China. Environ. Pollut. 152 (3), 686–692.

Khidkhan, K., Imsilp, K., Poapolathep, A., Poapolathep, S., Tanhan, P., 2017. Potential human health risk from consumption of metallic elements-contaminated benthic mollusks from Don Hoi Lot sandbar, Thailand. Sci. Total Environ. 584, 1239–1247.

Krishnamurty, K.V., Shpirt, E., Reddy, M.M., 1976. Trace metal extraction of soils and sediments by nitric acid-hydrogen peroxide. At. Absorpt. Newsl. 15 (3), 68.

Kumar Sahu, B., 2015. A study on global solar PV energy developments and policies with special focus on the top ten solar PV power producing countries. Renew. Sustain. Energy Rev. 43, 621–634. https://doi.org/10.1016/j.rser.2014.11.058.

le Reinders, A., Verlinden, P., Freundlich, A., 2017. Photovoltaic Solar Energy: from Fundamentals to Applications. John Wiley & Sons., pp. 169.

Lee, T.D., Ebong, A.U., 2017. A review of thin film solar cell technologies and challenges. Renew. Sustain. Energy Rev. 70, 1286–1297.

Lo, K.S.L., Chen, Y.H., 1990. Extracting heavy metals from municipal and industrial sludges. Sci. Total Environ. 90, 99–116.

Ma, L.Q., Hardison, D.W., Harris, W.G., Cao, X., Zhou, Q., 2007. Effects of soil property and soil amendment on weathering of abraded metallic Pb in shooting ranges. Water, Air, Soil Pollut. 178 (1–4), 297–307.

Mondal, M.A.H., Denich, M., 2010. Assessment of renewable energy resources potential for electricity generation in Bangladesh. Renew. Sustain. Energy Rev. 14 (8), 2401–2413. https://doi.org/10.1016/j.rser.2010.05.006.

Monier, V., Hestin, M., 2011. Study on Photovoltaic Panels Supplementing the Impact Assessment for a Recast of the WEEE Directive. European Commission Studies on Waste Electrical and Electronic Equipment. Final Report, ENV.G. 4, 6/FRA/2007 0067.

Ngole-Jeme, V.M., Fantke, P., 2017. Ecological and human health risks associated with abandoned gold mine tailings contaminated soil. PLoS One 12 (2), e0172517.

Olafisoye, O.B., Adefioye, T., Osibote, O.A., 2013. Heavy metals contamination of water, soil, and plants around an electronic waste dumpsite. Pol. J. Environ. Stud. 22 (5), 1431–1439.

Perez-Gallardo, J.R., Azzaro-Pantel, C., Astier, S., 2017. A multi-objective framework for assessment of recycling strategies for photovoltaic modules based on life cycle assessment. Waste Biomass Valorization 9 (1), 147–159.

Polman, A., Knight, M., Garnett, E.C., Ehrler, B., Sinke, W.C., 2016. Photovoltaic materials: present efficiencies and future challenges. Science 352 (6283), aad4424.

Rahim, M., Yoshino, J., Yasuda, T., 2012. Evaluation of solar radiation abundance and electricity production capacity for application and development of solar energy. Int. J. Energy Environ. 3, 687–700.

Raugei, M., Bargigli, S., Ulgiati, S., 2007. Life cycle assessment and energy pay-back time of advanced photovoltaic modules: CdTe and CIS compared to poly-si. Energy 32 (8), 1310–1318. https://doi.org/10.1016/j.energy.2006.10.003.

Strachel, R., Wyszkowska, J., Baćmaga, M., 2017. The role of compost in stabilizing the microbiological and biochemical properties of zinc-stressed soil. Water, Air, Soil Pollut. 228 (9), 349.

Shukla, A.K., Sudhakar, K., Baredar, P., 2017. Recent advancement in BIPV product technologies: a review. Energy Build. 140, 188–195.

Tyagi, V.K., Lo, S.L., Appels, L., Dewil, R., 2014. Ultrasonic treatment of waste sludge: a review on mechanisms and applications. Crit. Rev. Environ. Sci. Technol. 44 (11), 1220–1288.

Urban, F., Geall, S., Wang, Y., 2016. Solar PV and solar water heaters in China: different pathways to low carbon energy. Renew. Sustain. Energy Rev. 64, 531–542.

Xiao, L., Guan, D., Peart, M.R., Chen, Y., Li, Q., Dai, J., 2017. The influence of bioavailable heavy metals and microbial parameters of soil on the metal accumulation in rice grain. Chemosphere 185, 868–878.

Zhao, Z., Zhang, S., Hubbard, B., Yao, X., 2013. The emergence of the solar photovoltaic power industry in China. Renew. Sustain. Energy Rev. 21, 229–236. https://doi.org/10.1016/j.rser.2012.12.066.

Zimmermann, Y., Schäffer, A., Corvini, P.F.-., Lenz, M., 2013. Thin-film photovoltaic cells: long-term metal (loid) leaching at their end-of-life. Environ. Sci. Technol. 47 (22), 13151–13159. https://doi.org/10.1021/es402969c.

more environmental-friendly way for their final disposal. In fact, although the actual toxic effects of today's commercialized PV panels on environment are objectively low, many PV companies have volunteered to recycle their end-of-life modules. The purpose of this gesture is not only to reduce the risk of toxic materials outflow, but also to make the new generation of PV technologies more acceptable to the public (Kadro and Hagfeldt, 2017). For example, First Solar, the leading company in sustainable energy in the world, particularly in CdTe thin film solar modules, offers global PV recycling services for its modules. They give guidance to customers on how to return the end-of-life modules by labeling the information on each one. Furthermore, their recycling recovery rate is significantly high with up to 90% for both glass and semiconductor materials. Therefore, it is environmentally friendly and available to promote the recycling and reuse of lead halide PSCs when it comes to large-scale implementation. More importantly, the proof of concept for recycling materials in Pb-containing PSCs has already been reported.

There are many demonstrations on the reuse of transparent conducting glass/TiO_2 substrates, PbI_2 and the metal electrodes after the functional lifetime of PSCs is exhausted. Particularly, the recycling and reuse of PbI_2 is proved to avoid lead waste at the stage of disposal and the related methods can be basically categorized as two types, as shown in Fig. 8. One is to make use of waste lead to reproduce the lead-containing raw materials via solvent extraction, chemical precipitation and electrochemical deposition. The regeneration of PbI_2 can be reused for the fabrication of new devices, while other lead-containing materials such as metallic lead are fed back into the lead trading market. The other is to recycle PbI_2 from pristine PSCs and regenerate new devices in situ. It worth mentioning that PbI_2 recycled from other industries such as lead-acid battery is also qualified for PSCs preparation.

A typical metal-based PSC consists of a metal electrode, a HTL, a light-harvesting perovskite layer, an ETL and a transparent electrode. Aside from HTL materials, almost all other major components in metal-based PSCs can be recycled layer by layer. The organic HTL can be selectively dissolved in non-polar solvents such as toluene, diethyl ether, dichloromethane, and chlorobenzene. Meanwhile, the gold electrode was peeled off from the device followed by separation and recycling process (Kadro et al., 2016; Kim et al., 2016). After dismantling the metal electrode and HTL, there are two steps for PbI_2 collection. The first one is to remove CH_3NH_3I using polar protic solvents (methanol, ethanol, 2-propanol, or water) and then extract the remaining PbI_2 layer using polar aprotic solvents (acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, or g-butyrolactone), as the representative schematic procedures shown in Fig. 9a (Kadro et al., 2016; Kim et al., 2016). Though $CH_3NH_3PbI_3$ decomposes into CH_3NH_3I and PbI_2 in both kinds of polar solvents, the solubility of PbI_2 in polar protic solvents is very low. It was also proved that perovskite could be completely dissolved in polar aprotic solvents owing to their reaction with Pb^{2+} (Kim et al., 2016). Kadro et al. (2016) also compared the selectivity of four solvents for CH_3NH_3I dissolution. They found that the order of $CH_3NH_3PbI_3$ decomposition rate in solvents was ranked as methanol > deionized water > ethanol > 2-propanol, while the ordering for segregation efficiency was deionized water > 2-propanol > ethanol > methanol. With all factors considered, ethanol was eventually chosen as the proper solvent because it is less toxic than methanol and evaporates faster than water with reduced processing time (Kadro et al., 2016). As for the recycled PbI_2 in polar aprotic solvents such dimethylformamide (DMF), it can be reused in regenerating perovskites after removing DMF under vacuum. It has also been found that the photovoltaic performance of PSCs directly utilizing the recycled PbI_2 was not as good as that of PSCs using fresh PbI_2 (Binek et al., 2016). This was understandable since the recycled PbI_2 may contain some impurities such as CH_3NH_3I and TiO_2. However, it was encouraging that after being recrystallized from water to remove impurities, the purified PbI_2 exhibited comparable performances to the fresh PbI_2 for preparing PSCs (Binek et al., 2016). A new adsorbent, Fe-decorated hydroxyapatite hollow composite, was reported very recently to separate and recycle lead from PSCs (Park et al., 2020). Owing to its negative surface charge and magnetic property, this composite could effectively absorb lead from non-aqueous solvents such as DMF and easily be separated in magnetic field. The following recycling of PbI_2 was achieved by dissolving the Pb-absorbed composite into nitric acid and then adding KI to recrystallize PbI_2, the detailed recycling process is presented in Fig. 9b. The Pb recovery rate was up to 99.97% using this method. Moreover, the recycled PbI_2 showed almost no difference to commercial PbI_2 on device efficiency when fabricated into PSCs (Park et al., 2020). Aside from recrystallization to obtain highly purified PbI_2, there is another dissolving-precipitating method to extract PbI_2 from carbon-based PSCs to avoid solvent evaporation, which may have potential health risks to human and as environmental pollution (Zhang et al., 2018). In this case, PSC was firstly immersed in DMF solution to dissolve perovskite since there is no HTL in carbon-based PSCs and the carbon electrode does not react with DMF solvent. Then ammonium hydroxide was added into DMF to precipitate Pb^{2+} and HI was subsequently used to form PbI_2. Related chemical reactions are shown as following:

$$Pb^{2+}+2NH_3\cdot H_2O \rightleftharpoons Pb(OH)_2(s)+2NH_4^+ \quad (5)$$

Fig. 8. Illustration for cyclic utilization of lead in end-of-life PSCs.

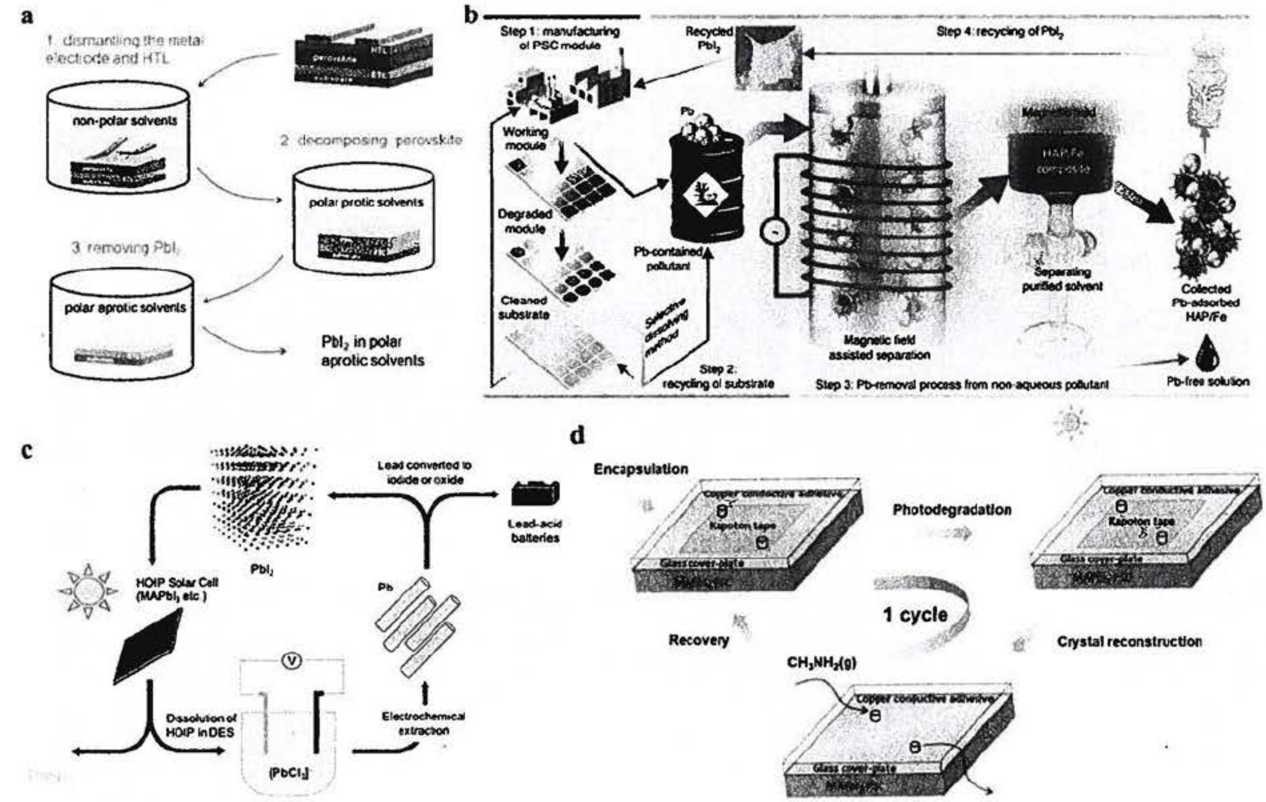


Fig. 9. **(a)** Schematic procedures for PSCs recycling. Non-polar solvent is used to dissolve HTL and extract gold electrode, polar protic solvent is used to dissolve $CH_3NH_3PbI_3$, and polar aprotic solvent is used to extract PbI_2. **(b)** The recycling process of lead in PSCs by using Fe-decorated hydroxyapatite hollow composite. The first step is the fabrication of PSCs. The second step is to recycle the substrate from degraded devices via selective dissolving method. The third is to extract lead using Fe-decorated hydroxyapatite hollow composite and an electromagnetic separating system. The last step is dissolving the collected Pb-adsorbed composite with HNO_3 solution and then adding KI to recrystallize PbI_2 for the refabrication of PSCs. Adapted with permission from Park et al. (2020), copyright 2020 Springer Nature. **(c)** Demonstration of the deep eutectic solvent based electrochemical recycling process for lead. Adapted from Poll et al. (2016) with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry. **(d)** Illustration of regeneration of encapsulated $CH_3NH_3PbI_3$ PSCs via methylamine gas post-treatment. Reproduced with permission from Hong et al. (2017), copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

$$Pb(OH)_2 + 2HI \rightleftharpoons PbI_2 + 2H_2O \tag{6}$$

The recovery rate for PbI_2 from DMF solution was up to 95.7% and the performance of the recycled PbI_2 can also compete with commercial PbI_2 (Zhang et al., 2018). The Pb content in perovskite can also be effectively recycled by electrochemical method (Poll et al., 2016). In an electrochemical process, shown in Fig. 9c, a deep eutectic solvent consisted of choline chloride and ethylene glycol was used to dissolve the perovskite films. Lead was then electrodeposited on the Pb foil as working electrode with up to 99.8% recovery rate (Poll et al., 2016). More recently, a bleacher solution contained methylamine and tetrahydrofuran was used to recycle the whole PSCs (Wang et al., 2021). Especially, perovskite recovered in the bleacher solution can be dispersed in nonionic solvents and then recast the perovskite film (Wang et al., 2021).

The other way to achieve the cyclic utilization of PbI_2 is the in situ recycling of PbI_2 from pristine PSCs and regenerating new devices (Jena et al., 2018; Xu et al., 2017). Xu et al. (2017) transformed $CH_3NH_3PbI_3$ film to pure PbI_2 by thermal decomposition and then introduced CH_3NH_3I from an isopropanol solution to form a new absorber layer. The first step is to remove the electrode with adhesive tape and then soak the devices in chlorobenzene solvent to wash off the HTL. The third step is a vital one to decompose $CH_3NH_3PbI_3$ at appropriate temperature. It was proved that 250 °C was the proper temperature to degrade $CH_3NH_3PbI_3$ and sublime CH_3NH_3I as confirmed by thermogravimetric analysis. Then CH_3NH_3I solution was spin-coated on the recycled PbI_2 films and heated to regenerate a new perovskite film. At last, a new HTL was spin-coated and top electrode was thermally evaporated on the device under vacuum. It is noteworthy that the in-situ recycled PSCs has comparable photovoltaic performance to the PSCs made by pristine PbI_2 (Xu et al., 2017). Jena et al. (2018) also studied the reuse of perovskite films by reconversion of PbI_2 to perovskite. After washing off the Au layer and HTL (spiro-OMeTAD layer) using chlorobenzene solvent, the degraded perovskite film was heated at 80 °C for 15 min to complete the transformation into PbI_2. Then the film was spin coated with CH_3NH_3I solution followed by annealing, spin-coating fresh spiro-OMeTAD layer and depositing Au electrodes. However, in their findings, the power conversion efficiency of recycled PSCs decreased, mainly owing to a significant drop of the fill factor, and greater hysteresis in J-V curves was observed as well. They also proved that the not-fully-restored performance of recycled PSCs was because the newly formed interface between perovskite and spiro-OMeTAD layer became worse after recycling, which resulted in inefficient carrier transport (Jena et al., 2018). The two works mentioned above both recovered the perovskite by introducing CH_3NH_3I solution on pre-decomposed PbI_2 with the need to remove and reconstruct the metal electrode and HTL. Another work demonstrated a different and unusual route to regenerate the degraded PSCs via methylamine gas post-treatment without component reconstruction (Hong et al., 2017). The recovery procedure is shown in Fig. 9d. Purging CH_3NH_2 gas into the decomposed devices could make $CH_3NH_3PbI_3$ recrystallized. This post-treatment process includes a solid-liquid-solid phase transition for perovskite reconstruction as shown in following equations:

$$CH_3NH_3PbI_3(s) + CH_3NH_2(g) \rightarrow CH_3NH_3PbI_3 \cdot xCH_3NH_2(l) \quad (7)$$

$$CH_3NH_3PbI_3 \cdot xCH_3NH_2(l) \rightarrow CH_3NH_3PbI_3(s) + CH_3NH_2(g) \quad (8)$$

It is worth mentioning that according to this study, the efficiency of encapsulated PSCs after two cycles of photodegradation-recovery treatment can still reach 91% of the original devices (Hong et al., 2017).

Overall, works have proven that the major components of Pb-based PSCs can be recycled and reused, and the efficiency of regenerated PSCs can compete with the ones fabricated by fresh materials. More importantly, the recycle and reuse of PbI_2 effectively avoid the Pb waste and prevent lead contamination, which makes PSC-based photovoltaic technology more environmentally friendly. Additionally, the PbI_2 used in PSCs not only can be commercial PbI_2 or recycled PbI_2 from degraded PSCs, but can also be recycled PbI_2 from other industries such as car batteries (Chen et al., 2014; Li et al., 2021). Vice versa, the recycled lead from degraded PSCs can be used for the production of other lead-containing products (Poll et al., 2016). In this way, it enables the cyclic utilization of lead and consequently cuts down the fabrication cost and reduces the risk of lead outflow. Therefore, the development of lead recycling technology for PSCs is clearly beneficial to the practical application of lead-based PSCs. Nevertheless, further improvement is still needed to ensure the high efficiency and long-term stability of the regenerated PSCs.

5. Summary and outlook

As discussed above, the overall lead content used in PSCs is actually pretty low. However, considering the high toxicity of lead, the negative impacts on animal and human health, as well as on plant growth and the entire ecosystem are still non-negligible. In the case of damaged encapsulation, the majority of lead in PSCs would be washed off into environment by rain. Furthermore, the improper disposal of end-of-life PSCs also causes lead leaching problems. Though catastrophic encapsulation failure for panels is uncommon, controlling the lead loss in midlife and end-of-life is significantly important because lead in PSCs is soluble, which is different from lead-containing solder in the conventional c-Si modules. To date, several solutions to PSCs lead leakage in midlife and a good number of recycling methods for PbI_2 have been proposed. However, in term of implementation, many other factors should be taken into account such as cost and manufacturing process at larger scale.

In future, there is still a need to explore more cost-effective and efficient solutions to reduce lead leakage. In fact, lead extraction and lead removal have been widely investigated in the field of wastewater treatment and contaminated soil remediation, and many techniques have been proved to be efficient such as chemical precipitation, adsorption, electrochemical technics, solvent extraction and ion exchange (Feng et al., 2020; Hirayama, 2012; Hu et al., 2015; Huang et al., 2018; Ihsanullah et al., 2016; Samiey et al., 2014; Tuzen et al., 2016). Therefore, it is promising to apply some of these technologies to reduce lead leakage in PSCs. For example, given that the major degradation product of lead perovskites is PbI_2 with a high solubility of about 340 mg/L Pb^{2+} in water, the solubility value far exceeds the limit of allowed Pb^{2+} concentration of 0.015 mg/L, therefore, it would be a good strategy to transform the highly soluble lead iodide into other insoluble lead compounds such as PbS to reduce their potential bioavailability. The highly insoluble PbS has a K_{sp} value of 3.0×10^{-28} and the calculated solubility is about 3.6×10^{-9} mg/L for Pb^{2+}, which is about 11 orders of magnitude lower than that in PbI_2 and also far below the safety limit of lead in water. Utilizing phosphate materials such as apatite and hydroxyapatite to immobilize lead is also a good strategy, because the leaching lead can react with phosphate to form pyromorphite $Pb_5(PO_4)_3X$ ($X = F^-, Cl^-, Br^-, OH^-$), which is the most stable Pb compound in nature over a wide range of pH. For instance, the $\log_{10}K_{sp}$ value of chloropyromorphite $Pb_5(PO_4)_3Cl$ varies from -18.69 in pH range of 0–2.12, to -84.4 in pH range of 12.38–14. More importantly, it has been found that even if the formed pyromorphite is consumed by human by mistake, it cannot be absorbed by the digestion system (Miretzky and Fernandez-Cirelli, 2008). On the other hand, as previously mentioned in Section 4.1, introducing Pb-absorbing materials with phosphonic acid and thiol groups in PSCs has been verified as an available approach to prevent lead leakage. In fact, there are many other functionalized groups acting as Lewis bases that can strongly bond with Pb^{2+} (acting as Lewis acid) to form metal complex, such as hydroxyl, carboxyl and amine groups (Aguado et al., 2009; Chiariza et al., 1997; Manousi et al., 2019; Peng et al., 2014; Shen and Fan, 2013; Yantasee et al., 2007; Zhu et al., 2019). Thus, there is a great possibility to explore other materials with one or more kinds of Pb-chelating groups to reduce lead leakage. However, it is worth noting that the introduced materials should be environmentally friendly and have no negative impact on the performance of PSCs. It is also important that they are insoluble in water and cannot be washed off except that lead has been transformed into non-toxic compounds. Last but not least, speeding up the legislation process on PV waste recycling around the world is still one of the most effective strategies to control lead leakage for end-of-life PSCs.

CRediT authorship contribution statement

Meng Ren: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing. **Xufang Qian**: Conceptualization, Methodology, Resources, Supervision, Writing – review & editing. **Yuetian Chen**: Methodology, Supervision, Writing – review & editing. **Tianfu Wang**: Supervision, Writing – review & editing. **Yixin Zhao**: Conceptualization, Formal analysis, Methodology, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China Grant (22025505, 51861145101), Program of Shanghai Academic/Technology Research Leader (Grant no. 20XD1422200) and Cultivating Fund of Frontiers Science Center for Transformative Molecules (2019PT02).

References

Aguado, J., Arsuaga, J.M., Arencibia, A., Lindo, M., Gascón, V., 2009. Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. J. Hazard. Mater. 163 (1), 213–221. https://doi.org/10.1016/j.jhazmat.2008.06.080.

Babayigit, A., Boyen, H.-G., Conings, B., 2018. Environment versus sustainable energy: the case of lead halide perovskite-based solar cells. MRS Energy Sustain. 5, E1 https://doi.org/10.1557/mre.2017.17.

Babayigit, A., Duy Thanh, D., Ethirajan, A., Manca, J., Muller, M., Boyen, H.-G., Conings, B., 2016a. Assessing the toxicity of Pb- and Sn-based perovskite solar cells in model organism Danio rerio. Sci. Rep. 6 (1), 18721. https://doi.org/10.1038/srep18721.

Babayigit, A., Ethirajan, A., Muller, M., Conings, B., 2016b. Toxicity of organometal halide perovskite solar cells. Nat. Mater. 15 (3), 247–251. https://doi.org/10.1038/nmat4572.

Bae, S.-Y., Lee, S.Y., Kim, J.-w, Umh, H.N., Jeong, J., Bae, S., Yi, J., Kim, Y., Choi, J., 2019. Hazard potential of perovskite solar cell technology for potential implementation of "safe-by-design" approach. Sci. Rep. 9 (1), 4242. https://doi.org/10.1038/s41598-018-37229-8.

Benmessaoud, I.R., Mahul-Mellier, A.-L., Horváth, E., Maco, B., Spina, M., Lashuel, H.A., Forró, L., 2015. Health hazards of methylammonium lead iodide based perovskites: cytotoxicity studies. Toxicol. Res. 5 (2), 407–419. https://doi.org/10.1039/c5tx00303b.

Journal of Hazardous Materials 426 (2022) 127848

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Review

Potential lead toxicity and leakage issues on lead halide perovskite photovoltaics

Meng Ren, Xufang Qian, Yuetian Chen, Tianfu Wang, Yixin Zhao*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Rd., Shanghai 200240, China

ARTICLE INFO

Editor: Yang Deng

Keywords:
Lead
Toxicity
Lead leakage
Silicon Photovoltaics
Perovskite solar cells

ABSTRACT

Recently, lead halide perovskite solar cells have become a promising next-generation photovoltaics candidate for large-scale application to realize low-cost renewable electricity generation. Although perovskite solar cells have tremendous advantages such as high photovoltaic performance, low cost and facile solution-based fabrication, the issues involving lead could be one of the main obstacles for its commercialization and large-scale applications. Lead has been widely used in photovoltaics industry, yielding its environmental and health issues of vital importance because of the widespread application of photovoltaics. When the solar cell panels especially perovskite solar cells are damaged, lead would possibly leak into the surrounding environment, causing air, soil and groundwater contamination. Therefore, lots of research efforts have been put into evaluating the lead toxicity and potential leakage issues, as well as studying the encapsulation of lead to deal with leakage issue during fire hazard and precipitation in photovoltaics. In this review, we summarize the latest progress on investigating the lead safety issue on photovoltaics, especially lead halide perovskite solar cells, and the corresponding solutions. We also outlook the future development towards solving the lead safety issues from different aspects.

1. Introduction

The photovoltaics (PV) industry has grown at unprecedented rates over the last two decades, with hundreds of thousands of PV systems installed worldwide. The cumulative installed electricity generation from photovoltaic technology has increased rapidly from only 805 GW h in 2000 to 549,833 GW h in 2018, while the annual and accumulative installed electricity capacities in 2019 were up to 97 GW and 578 GW, respectively (Padoan et al., 2019). Compared with conventional energy technologies, PV is considered to be more environmental-friendly. It has been analyzed that, PV technology can help to reduce around 90% of the pollution associated with greenhouse gas emission, criteria pollutant emission, as well as emissions originated from heavy metals and radioactive species (Fthenakis et al., 2008). Although the PV is generally considered as a form of green energy, the usage of lead in PV cannot be neglected with the fast development of photovoltaics due to the potential environment risks. Over the last decade, perovskite solar cells (PSCs) have become the most promising next-generation photovoltaic technology because of its unprecedentedly superb properties such as suitable bandgap, high absorption coefficient, well-balanced charge transfer, long carrier diffusion length and easy solution processing method (Cheng et al., 2021; Green et al., 2014). Halide perovskite crystals have the general chemical formula of ABX_3, where A sites are organic or inorganic cations like methylammonium (MA, $CH_3NH_3^+$), formamidinium (FA, $NHCHNH_3^+$) and Cs^+, B sites are divalent metal cations like Pb^{2+} and Sn^{2+}, and X sites are halogen anions like Cl^-, Br^- and I^-. The latest certified efficiency of laboratory-scale ($\sim 0.1\ cm^2$) PSCs has achieved 25.5% in 2020, exceeding that of other commercialized solar cells such as multi-crystalline silicon (mc-Si, 23.3%), thin-film solar cells of cadmium telluride (CdTe, 22.1%) and copper indium gallium selenide (CIGS, 23.4%) (Green et al., 2020; Kojima et al., 2009; NREL, 2021). Nevertheless, there is still much potential on efficiency improvement. In fact, the efficiency of single-junction PSCs is expected to approach 30% toward the theoretical value in the next decade by light management and defect control (Ma and Park, 2020; Park, 2019). Therefore, the emerging perovskite solar cell is becoming a more and more popular, potentially a game changer in the photovoltaics industry. It usually requires at least 20-year operational lifetime with less than 10% efficiency drop in performance for marketable photovoltaic technology (Grancini et al., 2017). To improve both intrinsic stability and extrinsic

---

* Corresponding author.
E-mail address: yixin.zhao@sjtu.edu.cn (Y. Zhao).

https://doi.org/10.1016/j.jhazmat.2021.127848
Received 11 August 2021; Received in revised form 5 November 2021; Accepted 16 November 2021
Available online 20 November 2021

10X more dangerous

- Dangerous to animal
Health
-Food chain

environmental stability of perovskite, a lot of efforts have been devoted to compositional engineering, interface engineering, as well as developing all-inorganic perovskites and encapsulation methods, and thereby significant successes have been achieved (Boyd et al., 2019). To date, some perovskite solar cells and modules are capable of reaching an equal of 10-year lifetime, while the effective worktime of the most stable PSCs was estimated to 87 years, achieved by inorganic cation tuning and using FA-based perovskites (He et al., 2020; Turren-Cruz et al., 2018).

However, the lead toxicity of PSCs has become an emerging environmental issue for its practical application owing to the inclusion of Pb^{2+} (Mallick and Visoly-Fisher, 2021; Ravi et al., 2020; Sheikh et al., 2021). Compared with great successes achieved to improve PSCs device stability, there is still a long way to go on exploring effective ways to address lead toxicity issue of PSCs. One approach is the development of lead-free perovskites by replacing toxic Pb with other environmental-friendly cations such as Sn^{2+}, Ge^{2+}, Mg^{2+}, V^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+}, but their performance and stability are far behind the lead-based PSCs (Hoefler et al., 2017; Jena et al., 2019). Among them, tin has been explored as a less toxic alternative because of their similar ionic radii (1.35 Å for Sn^{2+}, 1.49 Å for Pb^{2+}) and comparably good semiconductor characteristics (Jena et al., 2019; Ke et al., 2019). However, they are not as stable and efficient as Pb-based perovskites owing to the easy oxidation of Sn^{2+} to Sn^{4+} in ambient environment (Konstantakou and Stergiopoulos, 2017). So far, the highest efficiency of $FASnI_3$ based PSCs was up to 14.81%, achieved by the introduction of 4-fluoro-phenethylammonium bromide based 2D tin-perovskite capping layer (Yu et al., 2021). To date, high efficiency PSCs were achieved by lead-containing perovskites (Min et al., 2021), and Pb-based PSCs would be more likely to be the first to enter the PV market for large-scale production (Lyu et al., 2017; Park and Zhu, 2020; Wang et al., 2019). Therefore, it is vital and necessary to assess the toxicity of Pb-based PSCs and find some ways to solve the problem before it goes to the market.

In this review, we summarize the use of lead in photovoltaics, especially its application and toxicity issue in lead halide perovskite solar cells. We also discuss the potential lead leakage related issues in midlife and end-of-life of Pb-based PSCs and summarize the corresponding solutions to manage lead loss, including designing fail-safe encapsulation and device structure and making cyclic utilization of lead in end-of-life PSCs. In the last, we also outlook the prospects of potential approaches for lead management of Pb-based PSCs.

2. Lead issue in photovoltaics

Lead is a toxic heavy metal and is generally found in bedrock and soils in the mineral form of ore galena (lead sulfide, PbS) with a natural concentration of 12–20 ppm, while the amounts in stream water and sea water are pretty low with 0.03 μg/L and 1.0 μg/L, respectively (van der Voet et al., 2013). Lead level in atmosphere had experienced an increase because of the use of leaded petrol, but it eventually dropped once lead was phased out of petrol and related products (Tsai and Hatfield, 2011). Lead has become one of the most widely used and vital metals in shielding, electronic solder and battery technologies, owing to the advantages of low cost, high density, malleability, low melting point, ductility and high resistance to corrosion (Babayigit et al., 2018). According to International Lead and Zinc Study Group, in 2019, the lead mining production was 4,650,000 ton and the total lead production was up to 11,942,000 ton (International Lead and Zinc Study Group, 2019). Though lead has versatile properties, its toxicity has been limiting its broader application. Exposure to lead can cause many adverse effects to human health, ranging from hypertension, anemia, impaired nerve conduction, encephalopathy and even death (Babayigit et al., 2016b; Needleman, 2004). Therefore, legislations in many countries have strict regulations on lead production and recycling, aiming to eliminate lead contamination. According to the U.S. Environmental Protection Agency (EPA), the upper limit of lead concentrations in drinking water and air are 0.015 mg/L (USA Environmental Protection Agency,) and 0.15 μg/m^3 (USA Environmental Protection Agency,) respectively. In China, Ministry of Ecology and Environment (MEE) regulates that the threshold of lead concentrations in drinking water and air (annual average) are 0.01 mg/L and 0.5 μg/m^3, respectively (China MEE, 2006, 2012). Because of the potential toxicity of lead to human beings and ecosystem, as well as the drastic upsurge on the generation of electronic waste, recent years have seen an increase in the concerns about public safety associated with lead-containing products, especially with the emerging electronic waste (Huo et al., 2007). Thereby, it is crucial to develop lead-free alternatives or to manage the life cycle of lead-based products to avoid lead leakage.

2.1. *Application and toxicity issues of lead in silicon PV*

Though some hazardous materials are used in PV panels, such as cadmium in CdTe solar cells and lead-containing solder in crystalline silicon (c-Si) modules, the PV deployment has grown at an unprecedented rate over the last two decades. Among all the commercial solar photovoltaics (PVs), c-Si modules dominate the PV market with a share of annual production of 94% in 2019 (Fraunhofer Institute for Solar Energy Systems, 2020). With the use of lead-containing solder coated ribbons in c-Si modules, PV market has been consuming large amount of lead. The PV ribbons are copper flat wires coated with solder alloy, and the commonly used commercial solders on PV ribbons are Sn37Pb and Sn36Pb2Ag alloys (Moon and Yoo, 2017; Song et al., 2019). PV ribbons in the modules are soldered onto the Ag electrodes to interconnect individual solar cells in series and therefore to collect the electrical current (Eslami Majd and Ekere, 2020; Geipel et al., 2019). The amount of lead in a c-Si module varies from zero to several hundreds of grams depending on soldering material, while the estimated usage of lead for a typical 60-cell module was around 10 g based on the consumption of a 95-m-long ribbon coated with 15-μm-thick SnPb solder (Geipel et al., 2019; Malandrino et al., 2017; Mulvaney, 2019). Therefore, the calculated lead content in current c-Si panel is about 6.1 g/m^2 (based on 10 g in a typical 60-cell module with dimensions of 1650 mm × 992 mm). Meanwhile, the percentage of lead presents in the total module varies from zero to 0.689% by weight (Nain and Kumar, 2020). Though the amount of lead in c-Si panels is relatively low, with the worldwide implementation of PV deployment, the world total lead used in PV panels was consequently and dramatically increasing. As shown in

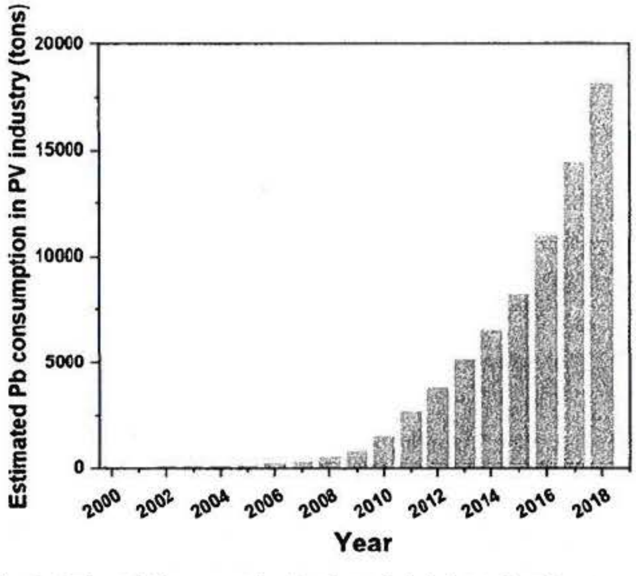


Fig. 1. Estimated Pb consumption in photovoltaic industry based on annual electricity capacity. The data of electricity capacity generated by photovoltaics is from International renewable energy agency.

Fig. 1, the lead consumption used in PV industry was estimated according to the annual electricity capacity, assuming that a 60-cell module contains 10 g of lead and has an average output power of 265 W. The calculated lead usage was up to 18,150 ton in 2018. Moreover, given that c-Si PV has been accounting for the highest share of production over the years and very possibly in the next decades, lead is identified as the most widespread hazardous material in PV industry (Mulvaney, 2019).

Given an average panel lifetime of 25 years, a dramatic increase of exhausted PV modules will turn into PV waste by 2025. However, PV panels may suffer from incompetent installation, degradation of anti-reflective coating, glass breakage, microcracks in interconnectors and other damages even before reaching their warranty lifetime, and those cannot be repaired will participate in PV waste stream ahead of the normal lifetime. In fact, the amount of PV waste is increasing rapidly in recent years, whereas the majority of end-of-life modules are currently dumped in landfills because of the little economic incentive to collect and recycle them (Masoumian and Kopacek, 2015; Monteiro Lunardi et al., 2018; Smith and Bogust, 2018). From the perspective of environmental impact, PV waste should be treated with caution because they contain hazardous Pb based materials. Thereby, it is important to evaluate the leaching potential of PV panels and some laboratory leaching tests for c-Si panels have been conducted (Collins and Anctil, 2017; Eberspacher and Fthenakis, 1997; Nover et al., 2017; Sinha and Wade, 2015; Tammaro et al., 2016; Zapf-Gottwick et al., 2015). The toxic characteristic leaching procedure (TCLP) test for commercial c-Si modules showed that, the lead leaching out modules varied from 3 to 11 mg/L while some of the modules exceeded the regulatory limits (5 mg/L), which may make end-of-life c-Si panels classified as hazardous wastes (Eberspacher and Fthenakis, 1997; Sinha and Wade, 2015). Some c-Si panels also failed the Japanese leaching test No.13 (JLT-13) which use distilled water as leaching solvent to evaluate the leaching potential of heavy metals such as Pb in incinerator ash. The resulted leachate lead concentration varied from nondetective to 0.9 mg/L while the regulatory limits is 0.3 mg/L (Sakai et al., 1995; Sinha and Wade, 2015). With regard to lead toxicity issues in PV panels, much effort has been devoted to developing environmental-friendly lead-free soldering. However, due to the high soldering temperature and high cost, there is no perfect substitute to the lead-coated ribbon in PV industry yet. Fortunately, as PV panels are becoming lighter and more efficient, the use of hazardous material per unit of power is expected to reduce (IEA International Energy Agency, 2016). Tammaro et al. studied the potential release of metals and the corresponding ecotoxicological effects of 26c-Si panels produced in the last 30 years (Tammaro et al., 2016). Bioassays were conducted with different organisms, including ISO 11348-3 for bacterium *Vibrio fischeri*, ISO 6341 for crustacea *Daphnia magna*, and ISO 8692 for algae *Pseudochirneriella subcapitata*. The leachate was classified as ecotoxic: $EC_{50} < 10$ vol% for *Daphnia magna* and *Vibrio fischeri*, and $EC_{20} < 20$ vol% for *Pseudochirneriella subcapitata*, where EC_{50} and EC_{20} represented effective concentration of different percentages. Just one threshold exceedance was enough to judge a sample as ecotoxic. Results showed that more than 80% of the leachates were ecotoxic with at least one threshold exceedance. The toxicity of leachate from c-Si panels was mainly relevant to the high amount of lead. However, recent years have seen a decrease on the amount of leachate lead from c-Si panels because of the replacement of lead with silver in solder (Tammaro et al., 2016). Therefore, even though the use of lead in photovoltaics poses challenges regarding the element's toxicity and leakage potential, there still are on-going approaches to tackle these issues.

2.2. *Application and toxicity issue of lead in PSCs*

The Pb content in PSC with a 400-nm-thick $CH_3NH_3PbI_3$ light absorber is estimated to be about 0.4 g/m^2, which is equivalent to that in 1-cm-thick natural soil per square meter, as shown in Fig. 2**a** (Park et al., 2016). The lead concentration by weight of PSCs with different substrates has also been evaluated (Moody et al., 2020). The establishment of this rubric is from the European Union's Restriction of Hazardous Substances (RoHS) Directive, which regulates the use of hazardous materials in electrical and electronic equipment and the allowed maximum concentration for lead is 0.1% by weight in homogenous materials (EU, 2011). It is worth noting that fixed PV panels are exempt from this regulation as it only applies to portable PV panels. The evaluated lead concentration is 344 ± 4 mg/kg and 22,400 ± 100 mg/kg for perovskite thin films on glass and flexible polyethylene terephthalate (PET) substrates, respectively, as shown in Fig. 2**b**. It is evident that lead concentration of perovskite on heavier glass substrates is below RoHS limit while that on lighter PET substrates cannot satisfy the criteria, indicating that portable PSCs characterized with lightweight and flexibility would not be made available on European Union market if without additional exemption (Moody et al., 2020). As for the U.S. market, work from Douglas qualified the upper limit of total lead consumption and possible lead leakage based on a hypothetical widespread application of this technology in the U.S. He assumed that, if all the U.S. electricity is supplied by PV technology associated with perovskite/c-Si tandem solar cells with assumed 25-year lifetime and 25% PV conversion efficiency, around 160 t/year lead will be required for the solar panel production (Douglas, 2015). That is to say, if 1% of the PV devices are damaged due to extreme weather, there would be 1.6 t/year of lead leaching into the environment. A comparison to some other lead emission sources and lead containing products is also given as shown in Fig. 2c. It is encouraging to find that the hypothetical lead consumption of perovskite PV is

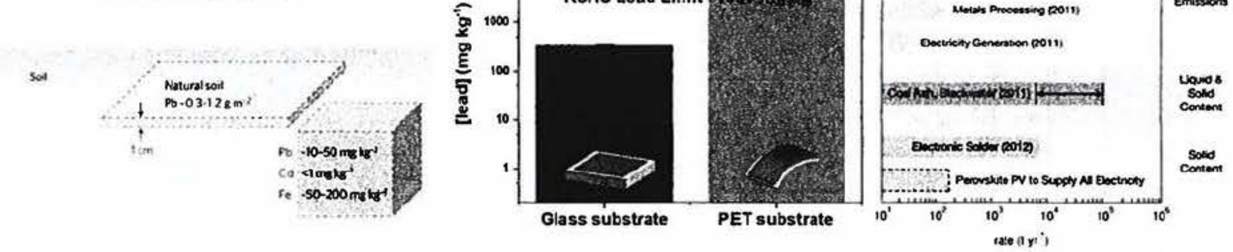


Fig. 2. (a) Amount of lead used in PSCs and in 1-cm-thick natural soil. The lower right legend shows the weight content of Pb, Cd and Fe in natural soil. Adapted with permission from Park et al. (2016), copyright 2016 Springer Nature. (b) Lead concentration by weight of PSCs on glass and PET substrates. Reproduced with permission from Moody et al. (2020), copyright 2020 Elsevier Inc. (c) The quantities (metric: tons per year) of lead emission in air, liquid, solid, including the hypothetical consumption of lead in PSCs to supply all electricity in the U.S. Adapted with permission from Douglas (2015), copyright 2015 American Chemical Society

10X

much lower than that in electronic solder, or the lead content in coal ash and blackwater (Douglas, 2015). However, some studies suggested that lead in perovskite PV is ten times more bioavailable than those other sources, making it more dangerous for raising toxicity issues (J. Li et al., 2020).

With the intensive development of PSCs, a number of toxicity studies on Pb-based PSCs have been conducted (Babayigit et al., 2016a; Bae et al., 2019; Benmessaoud et al., 2015; J. Li et al., 2020; Wang et al., 2020; Zhai et al., 2017, 2020). A cytotoxicity study found that different kinds of cells have different responses to perovskite exposure in terms of cellular properties, metabolic activity, morphology and viability (Benmessaoud et al., 2015). For murine primary hippocampal neurons and human dopaminergic neuroblastoma cells, they suffered a massive apoptotic cell death after $CH_3NH_3PbI_3$ treatment. While for human lung epithelial cells, only were the proliferation capacity and mitochondrial activity changed without noticeable cell death (Benmessaoud et al., 2015). Some research investigated the potential harmful effects of PSC and its lead-containing degradation products (Bae et al., 2019; Wang et al., 2020). One study showed that the order of toxicity was ranked as $Pb^{2+} > CH_3NH_3PbI_3 > PbI_2 = PbO$, unveiling that $CH_3NH_3PbI_3$ was more toxic than its decomposition products (Bae et al., 2019). Here, PbI_2 and PbO represent the main lead-based degradation compounds of perovskite resulting from water and fire exposure (Bae et al., 2019), which will be discussed in next section. But it cannot be ignored that PbI_2 is already listed as acutely toxic based on Regulation (EC) No. 1907/2006. More detailed information about hazardous classification and toxicity of PbI_2 has been summarized by Goetz et al. (2021), EU (2008). Additionally, systematic toxicity bioassays for three typical Pb-based perovskites, $CH_3NH_3PbI_3$, $NHCHNH_3PbBr_3$ and $CH_3NH_3PbBr_3$, has been conducted, using samples from single aquatic and soil bacterial species to invertebrate animals and more complex forms of life (Wang et al., 2020). Results show that $NHCHNH_3PbBr_3$ and $CH_3NH_3PbBr_3$ were more toxic than $CH_3NH_3PbI_3$ for the tested organisms. This may relate to the more Pb^{2+} released from the former two lead halide perovskites in the exposure medium. The authors also examined the toxicity sensitivity of some organisms for leaded perovskite and found that V. *fischeri* exhibited the most sensitivity to toxicants with EC_{50} (50% effective concentration) values ranging from 1.45 to 2.91 mg/L within 30 min of exposure, as shown in Fig. 3 (Wang et al., 2020). Soil bacterial communities and *C. elegans* were found to be less sensitive than V. *fischeri*, but all these three were highly sensitive species to lead-based PSCs. They further classified the following organisms as low sensitive species with an order of sensitivity based on extra toxicity data from the other reports: Danio rerio > human colonic epithelial cells (Caco–2/TC7) > human lung adenocarcinoma epithelial cells (A549) > human dopaminergic neuroblastoma cells (SH-SY5Y) > mice primary neurons (Benmessaoud et al., 2015). Therefore, bacterium V. *fischeri* was recommended as the most appropriate organism to assess the toxicity of Pb-based perovskites (Wang et al., 2020).

The impacts on natural environmental conditions and physicochemical properties from the toxicity of perovskite nanoparticles have also been studied in several researches (Zhai et al., 2017, 2020). It was found that the fate and toxicity of lead perovskite nanoparticles on soil microorganisms were influenced by pH, humic acid and divalent cations (Zhai et al., 2020). Generally speaking, the formation of perovskite aggregates, the released Pb^{2+} ions and the interaction between microbial community with leaded materials in different exposure medium all contribute to the overall toxicity of perovskite nanoparticles. Lower pH value accelerated the aggregation of perovskite nanoparticles but increased the lead ion release and led to higher toxicity to bacterial cells. The impact of divalent cations on the perovskite toxicity depends on its concentration. When at low concentrations, toxicity increased with more perovskite nanoparticles absorbed on the bacteria. This was because a small number of cations could neutralize the surface charge of perovskites and form ion bridges enhancing the interaction between perovskite nanoparticles and bacteria. Nevertheless, large number of divalent cations reduced toxicity due to the compression of electric double layers of perovskite nanoparticles associated with the formation of larger aggregates. Humic acid alleviated the toxicity of perovskite. The reason for this toxicity alleviation was that, humic acid coating on perovskite nanoparticle surface not only prevented the active sites on nanoparticle surface from releasing Pb^{2+}, but also increased the negative surface potential of perovskite nanoparticles, which associated with increased charge repulsion to bacteria. Moreover, the formation of humic acid-Pb^{2+} complexes decreased the Pb-ion induced toxicity. It is also noteworthy that the concentration of divalent cations has a major impact on the toxicity of perovskites when coexisting with humic acid (Zhai et al., 2020). The dynamics between perovskite concentration with different particle sizes and their toxicity to soil bacterial communities have also been reported (Zhai et al., 2017). Results show that the toxicity of perovskites to bacteria mainly come from their ionic forms (74–81%) rather than particulate forms (16–26%). Perovskites with smaller particle size were more toxic than larger ones because of the higher percentage of surface area supplying the release of more Pb^{2+}

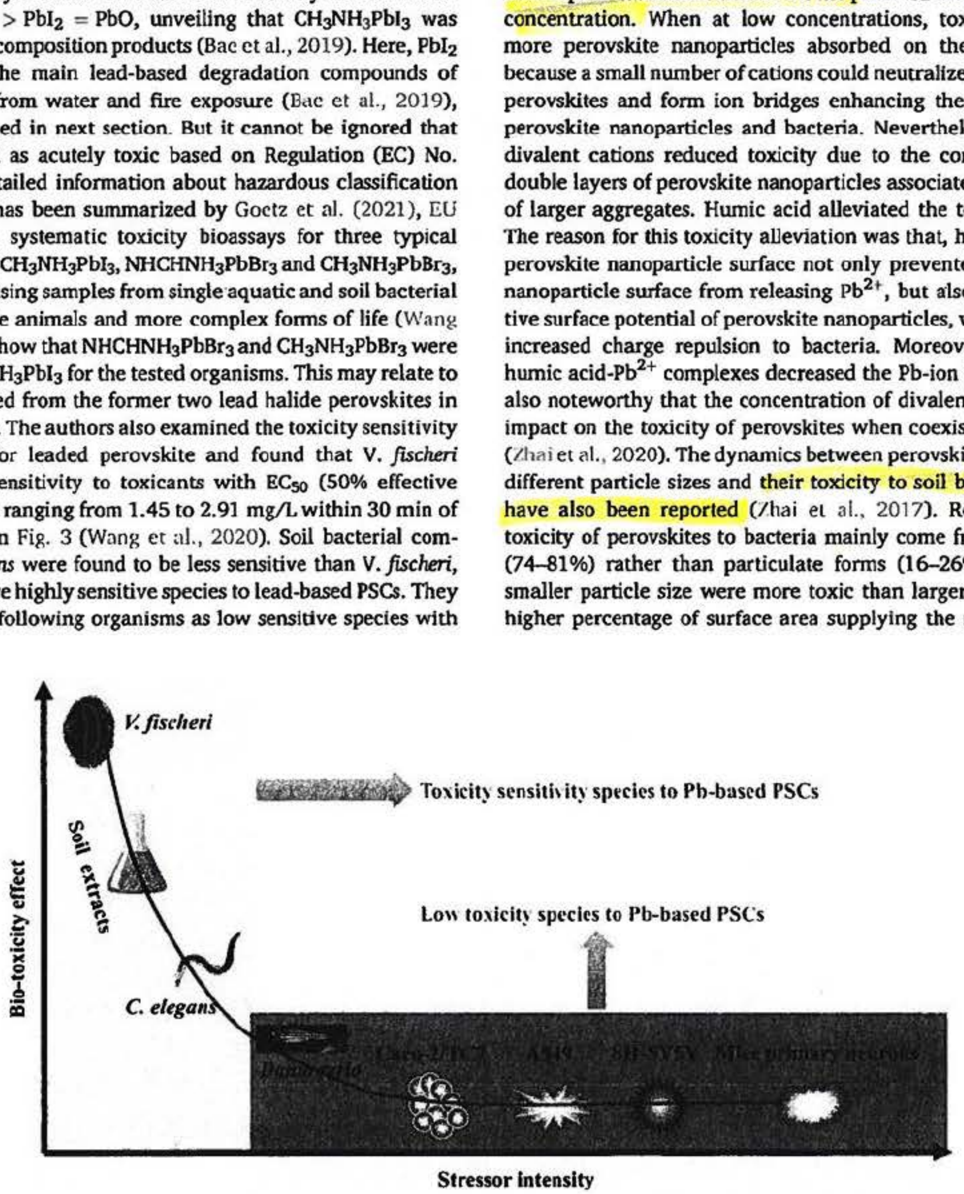


Fig. 3. Diagram of toxicity sensitivity species to lead-PSCs based on EC_{50} values. A549 represented for human lung adenocarcinoma epithelial cells, SH-SY5Y represented for human dopaminergic neuroblastoma cells, Caco–2/TC7 represented for human colonic epithelial cells.
Adapted with permission from Wang et al. (2020), copyright 2019 Elsevier B.V.

ions (Zhai et al., 2017).

Given that the concern on the inclusion of toxic lead in perovskite might be an obstacle for industrialization of PSCs, many environmentally benign metals have been considered as replacements for Pb to develop lead-free perovskites. Among them, tin has been explored as a popular less-toxic alternative (Jena et al., 2019; Ke et al., 2019). A toxicological assessment of PbI_2 and SnI_2, the main degradation products of Pb- and Sn-based perovskites, was also conducted by employing the zebrafish embryo acute toxicity testing protocol (Babayigit et al., 2016a). It was surprisingly found that SnI_2 exposure was more toxic than PbI_2 attributed to the lower pH values in aqueous medium. This is because Sn^{2+} is highly unstable and can be easily oxidized into Sn^{4+} with the generation of hydroiodic acid (HI), while exposure to acidification has been reported to be detrimental to animal health. The reactions are proposed as following (Babayigit et al., 2016a):

$$8SnI_2 + 4H_2O + O_2 \rightarrow 2SnI_4 + 6Sn(OH)I + 2HI \quad (1)$$

$$SnI_4 + 2H_2O \rightarrow SnO_2 + 4HI \quad (2)$$

The biological impact of lead from PSCs has been investigated as well very recently (J. Li et al., 2020). Lead uptake by mint plants from the perovskite-contaminated soil was observed even at a very low concentration (Pb^{2+}: 5 mg/kg), screening the bioavailability of lead in the form of perovskite. The lead taken by plants deposited in roots, stems and leaves, and demonstrated a noticeable difference compared to plants grown in natural soil, indicating a bioaccumulation potential of lead in food chains (Fig. 4). However, the lead bioavailability was mainly caused by organic cations of lead-based perovskite associated with changed pH values of soil, as the researchers found that mints grown in PbI_2-contaminated-only soil didn't show similar bioavailable effect. Furthermore, the bioavailability of lead-free perovskite was also investigated, where Sn-based perovskite and SnI_2 was found to be much less effective in accumulating in mint plants than lead-based perovskite (J. Li et al., 2020).

Therefore, lead-based perovskites pose significant risks to animal and human health as well as ecosystem. These toxic effects of perovskites are mainly caused by the released Pb^{2+} ions with toxicity proved to be higher than their individual degradation products PbI_2 and PbO. On the other hand, the safety issue and potential risks of Sn-based perovskites, which are commonly considered to be less toxic and more environmentally friendly, should also be comprehensively evaluated before its broader application.

3. Lead leakage in PSCs

In general, lead in PSCs would leach from damaged encapsulation at three stages throughout their entire lifetime: (1) panel production, (2) panel use in midlife, and (3) end-of-life disposal of PSCs. Among three stages, the lead leakage mechanism and solutions in midlife and end-of-life stages will be the focus on our discussion. In midlife, the PSCs may suffer from mechanical load cycles such wind and snow loads and temperature changes which may cause microcracks or breakage to panels (IEA International Energy Agency, 2016). Those undiscovered cracks on PSCs pose potential risks of lead leakage in rainy days. For end-of-life PV waste, specific regulations are lacked for PV waste in most countries so far, even for the commercially widely used silicon modules.

3.1. Lead leakage in midlife PSCs

As we know, a proper encapsulation is necessary for improving the long-term stability of PSCs, preventing the devices from exposing to external environmental factors such as humidity and oxygen, and against lead leakage. However, during the midlife of PSCs, the package could be damaged when it comes to extremely bad weather such as hailstorm, hurricane and fires. In these extreme conditions, lead in damaged PSCs would find its way into surrounding water and soil through rainfall, or evaporating into atmosphere due to the high temperature in fires. Therefore, it is necessary to investigate the environmental impact in the case of catastrophic module failure before the commercialization of lead PSCs. Several studies simulating such scenarios have thus been conducted, including exposing damaged PSC devices to rain and a fire safety assessment to evaluate the lead loss.

In the case of rains, $CH_3NH_3PbI_3$ perovskite films decomposed into PbI_2 immediately with the initial black color changing into yellow phase as an irreversible degradation process (Hailegnaw et al., 2015). The percentage of lead loss was up to 72% after 5 min of exposure to the simulated rain, while it showed almost no difference with pH values ranging from 4.2 to 8.1. Moreover, the leaching lead not only existed in the form of Pb^{2+} but also as PbI_2 solid or colloids (Hailegnaw et al., 2015). Jiang et al. (2019) reported Pb leakage from damaged cells with different encapsulation methods. At very serious condition where the simulated heavy rain lasted for 72 h, lead in perovskite films entirely leached out with the leaking amounts of 0.54 g/m^2 for the damaged PSCs both without encapsulation and with only the bottom glass encapsulation (Jiang et al., 2019). In fact, perovskite films are very sensitive to humidity and the decomposition is much different in the presence of moisture and liquid water. When exposing to water vapor,

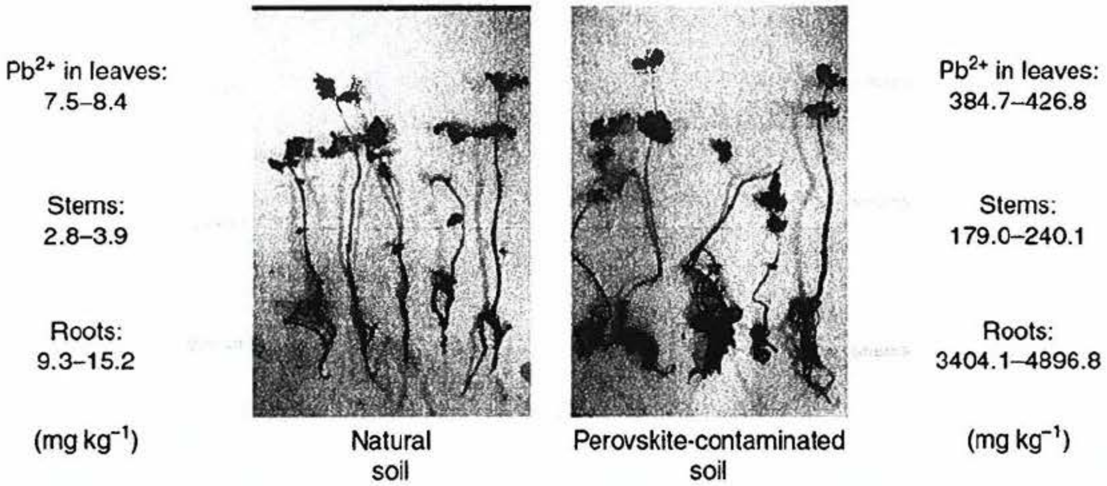


Fig. 4. Pictures of mint plants grown in natural soil and perovskite-contaminated soil.
Adapted with permission from J. Li et al. (2020), copyright. The Authors, published from 2020 Springer Nature.

monohydrate and dihydrate are formed, resulting in detrimental effects on device performances. However, it has been found that these hydrate compounds can be converted back to perovskite phases after soaked in nitrogen. Meanwhile, the decreased device performances can be fully reversed as well, following the reaction shown in Eq. (3). Nevertheless, liquid water induced degradation of $CH_3NH_3PbI_3$ is irreversible, because the dihydrate products will degrade into aqueous $CH_3NH_3^+$, as shown in Eq. (4) (Leguy et al., 2015).

$$4(CH_3NH_3)PbI_3 + 4H_2O(g) \rightleftharpoons 4[CH_3NH_3PbI_3 \cdot H_2O] \rightleftharpoons (CH_3NH_3)_4PbI_6 \cdot 2H_2O + 3PbI_2 + 2H_2O \tag{3}$$

$$(CH_3NH_3)_4PbI_6 \cdot 2H_2O \xrightarrow{H_2O(l)} 4CH_3NH_3I + PbI_2 + 2H_2O \tag{4}$$

A fire safety assessment of Si/perovskite miniature PV modules was also conducted (Conings et al., 2019). In the simulated fire scenario, which is annealing at 760 °C with constant fresh air supply, perovskite decomposed into PbI_2 and volatile organic components. Nearly all the PbI_2 products from the exposed perovskite film without glass-glass cover evaporated into atmosphere with a small remainder oxidized in place. Nevertheless, with glass-glass encapsulation in present, PbI_2 was oxidized into PbO and PbO_2 species with 81% of lead remained in the glass cover, which could prevent the Pb-containing vapor contamination (Conings et al., 2019). In sum, lead will leach from PSCs mainly in the form of PbI_2 in the case of damaged encapsulation. However, given the soil sequestration behavior of Pb^{2+}, there is still a need to investigate the outdoor fate of PSCs through leaching and emission to rain water and soil under natural weather conditions.

3.2. Lead leakage in end-of-life PSCs

As an emerging technology, specific regulation on the collection and recycling of PV waste are lacked so far in most countries and regions. The disposal of PV waste depends on its classification as non-hazardous waste or hazardous waste. In China, the classification of hazardous waste relies on its toxicity, corrosivity, ignitability, reactivity, and infectivity. As for PV waste, identification standards for hazardous wastes-identification for extraction procedure toxicity (GB 5085.3—2007) regulates that the threshold value for lead leaching concentration is 5 mg/L for a solid waste to be classified as hazardous waste. The leaching procedure is performed according to Solid waste - Extraction procedure for leaching toxicity-Sulfuric acid & nitric acid method (HJ/T 299–2007) (China MEE, 2007a, 2007b). In the US, Resource Conservation and Recovery Act (RCRA) regulations prescribe the management and disposal of both non-hazardous waste and hazardous waste (US EPA, RCRA). The classification of PSCs relies on their toxic characteristic leaching procedure (TCLP) results. The RCRA threshold value for TCLP lead leaching concentration is also 5 mg/L for a solid waste to be classified as hazardous waste. Moody et al. conducted the TCLP tests for PSCs on glass and PET substrates, and the lead leaching result is shown in Fig. 5**a** (Moody et al., 2020). The leachate lead concentration on both kinds of substrates exceeded the RCRA limit with 14.2 ± 0.2 mg/L and 713 ± 5 mg/L for PSCs based on glass and flexible PET substrates, respectively, suggesting that the end-of-life PSCs should be treated as hazardous wastes (Moody et al., 2020). Both the EU RoHS and the US RCRA aim to reduce the risk of harm caused by hazardous materials with different criteria, i.e. lead content by weight for EU RoHS and lead leaching by TCLP test for the US RCRA. The researchers further simulated a scenario, in which hypothetically 5 MW_p perovskite modules with flexible substrates were dumped in an unlined landfill to evaluate whether the total lead content or the leached lead poses a greater risk to human beings (Moody et al., 2020). The total concentration of lead in soil, air and surface water were calculated by weight based on the exposure results from physical erosion and material migration, while the lead concentration in groundwater was determined by TCLP test. Results showed that all of the lead concentrations were below the regulatory limits, but the one in groundwater had the highest potential to exceed the threshold value (Fig. 5**b**). Thereby, the lead leaching of PSCs posed greater health risks to human beings and ecosystem than the lead content in the landfill scenario. Therefore, it is of great importance to reduce lead leakage throughout the lifetime of PSCs.

4. Solutions to lead leakage

4.1. Fail-safe encapsulation and device structure

Recent years, researchers started looking at the safety issue of the potential lead leakage in the case of damaged encapsulation and several solutions have been proposed, as shown in Fig. 6. One is to enhance the physical encapsulation to better protect the device, for example, a self-healing coating could heal itself if there is a scratch. The other is chemical approaches by introducing lead adsorbents in device structure. Even if the encapsulation is failed, lead can be captured by the adsorbents incorporated into devices.

To the best of our knowledge, there have been limited amount of research on avoiding lead leaching from damaged PSCs via the strategy of fail-safe encapsulation. Jiang et al. reported using self-healing polymer-based encapsulation to minimize Pb leakage from damaged lead

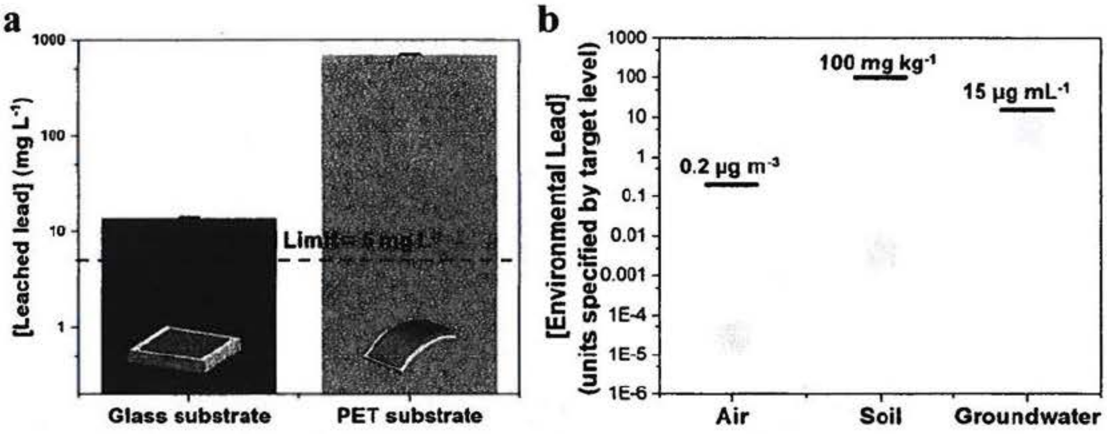


Fig. 5. (a) Leachate lead concentration in TCLP tests for PSCs based on glass and PET substrates, (b) Estimated lead concentration distribution (green squares) in air, soil and groundwater based on a hypothetical 5 MWp end-of-life PSCs dumped in an unlined landfill. The black lines represent the EPA threshold value in environment.

Reproduced with permission from Moody et al. (2020), copyright 2020 Elsevier Inc.

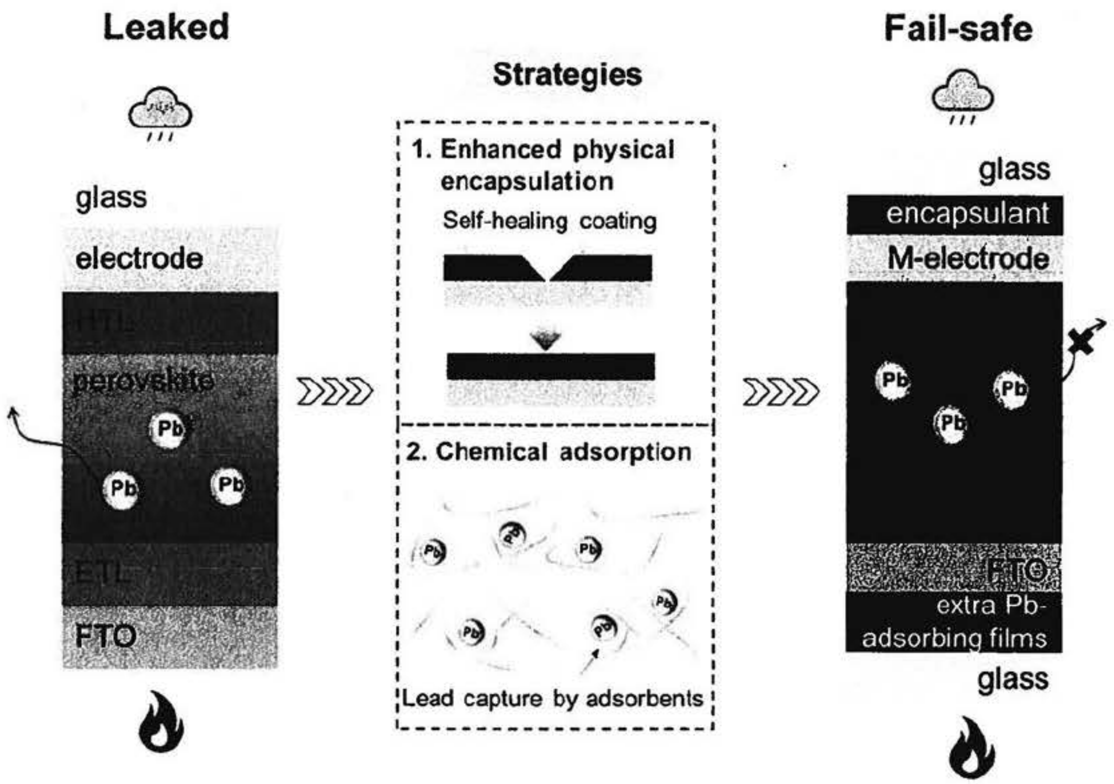


Fig. 6. Illustration of the control of lead leakage during the use of PSC with a damaged encapsulation. M in M-electrode, M-HTL and M-ETL represents for multifunctional.

halide PSCs (Jiang et al., 2019). This particular polymer is epoxy resin with a glass transition temperature (T_g) at around 42 °C, which is sandwiched between fluorine-doped tin oxide (FTO) and the top glass cover, as the illustration shown in Fig. 7a. Test results have proved that star-shaped microcracks due to mechanical attack with damaged hydrophobicity on devices can be recovered after heating, thus effectively preventing the ingress of water and limiting lead loss. Furthermore, experiments assessing the quantity of lead leaching from damaged modules under rainy and sunny weather were conducted. Results show that the epoxy resin encapsulated devices could significantly reduce lead loss from 30 to 0.08 mg h^{-1} m^{-2} when compared with the only bottom encapsulated ones (Jiang et al., 2019).

In addition to the physical fail-safe encapsulation to prevent lead leakage, there are some chemical approaches by designing hole transport layer (HTL), electron transport layer (ETL) and electrodes with lead-absorbing ability, or introducing additional lead-sequestrating materials into the PSC device structure. Lee et al. reported a novel polymeric HTL material, which has the structure based on benzo[1,2-b:4,5:b′]dithiophene and tetraethylene glycol-substituted 2,1,3-benzothiadiazole and can be denoted as alkoxy-PTEG. This HTL material is designated to exhibit green processing and lead capturing ability (Lee et al., 2020). The lead capture function was ascribed to the tetraethylene glycol groups chelating with Pb^{2+}, which was confirmed by ^{1}H NMR, UV–vis and secondary ion mass spectroscopy results. The binding constant of alkoxy-PTEG and Pb^{2+} was calculated with a value 2.76 M^{-1}, which reflects a moderate strength that can be nondestructive to the perovskite lattice while preventing the lead leakage (Lee et al., 2020). Our group has developed a strategy to form an inorganic PbS_x layer in situ on perovskite film via ammonium sulfide post-treatment (Xie et al., 2020). Because of the strong binding energy between Pb and S, the sulfide quickly reacted with the Pb-halide framework and formed the compact PbS_x layer. Thereby, ammonium sulfide post-treatment could effectively immobilize the surface lead on the perovskite film and also improve the device performance and stability (Xie et al., 2020). Very recently, a thiol functionalized metal-organic framework, ZrL3, was chosen to work as ETL material in PSC and has been proved not only to enhance the device stability but also to reduce the lead leakage (Fig. 7b) (Wu et al., 2020). The addition of ZrL3 can cause a more than 80% reduction in lead leakage because of the formation of insoluble Pb-ZrL3 complex between the thiol and the disulfide groups on ZrL3. The ZrL3 showed a lead adsorption capacity of 355 mg/g (Wu et al., 2020). Cao et al. also reported the introduction of thiol copper(II) porphyrin on the perovskite surface could prevent lead leakage by forming Pb—S bond between the thiol group of copper(II) porphyrin and Pb ion on the perovskite film (Xiao et al., 2020). Huang et al. employed a low-cost sodium form cation-exchange resin to minimize lead loss in perovskite solar modules (Chen et al., 2020). The sulfonate groups on cation-exchange resin could strongly bind Pb^{2+} in aqueous solution and it showed a maximum lead adsorption capacity of 410 mg/g. The cation-exchange resin could be directly blade-coated on the surface of glass substrates and metal electrodes of perovskite solar modules with positive-intrinsic-negative architecture for leaked lead absorption, while it had a negligible influence on the device performance. Besides, the cation-exchange resin could be added into carbon paste to make carbon electrodes and it exhibited unchanged conductance for carbon electrodes with suitable proportion. In water-dripping tests, the reduction of lead leakage reached 98% by the integration of cation-exchange resin in carbon electrodes and the coating on the glass surface (Chen et al., 2020). More recently, a sulfonic acid cation exchange resin with mesoporous structure was also reported to be incorporated into perovskite layer as a scaffold, shown in Fig. 7c and d (Chen et al., 2021). The function of preventing lead leakage in PSCs comes from the sulfonic acid groups which would selectively and strongly bond with Pb^{2+} as well as the mesoporous structure with high internal surface area (Fig. 7e) (Chen et al., 2021). X. Li et al. (2020) reported a chemical approach for on-device sequestration of lead for PSCs. They integrated two Pb-sequestrating materials, DMDP and EDTMP-PEO, into a standard PSC device as shown in Fig. 7f (DMDP represents P,P′-di(2-ethylhexyl)

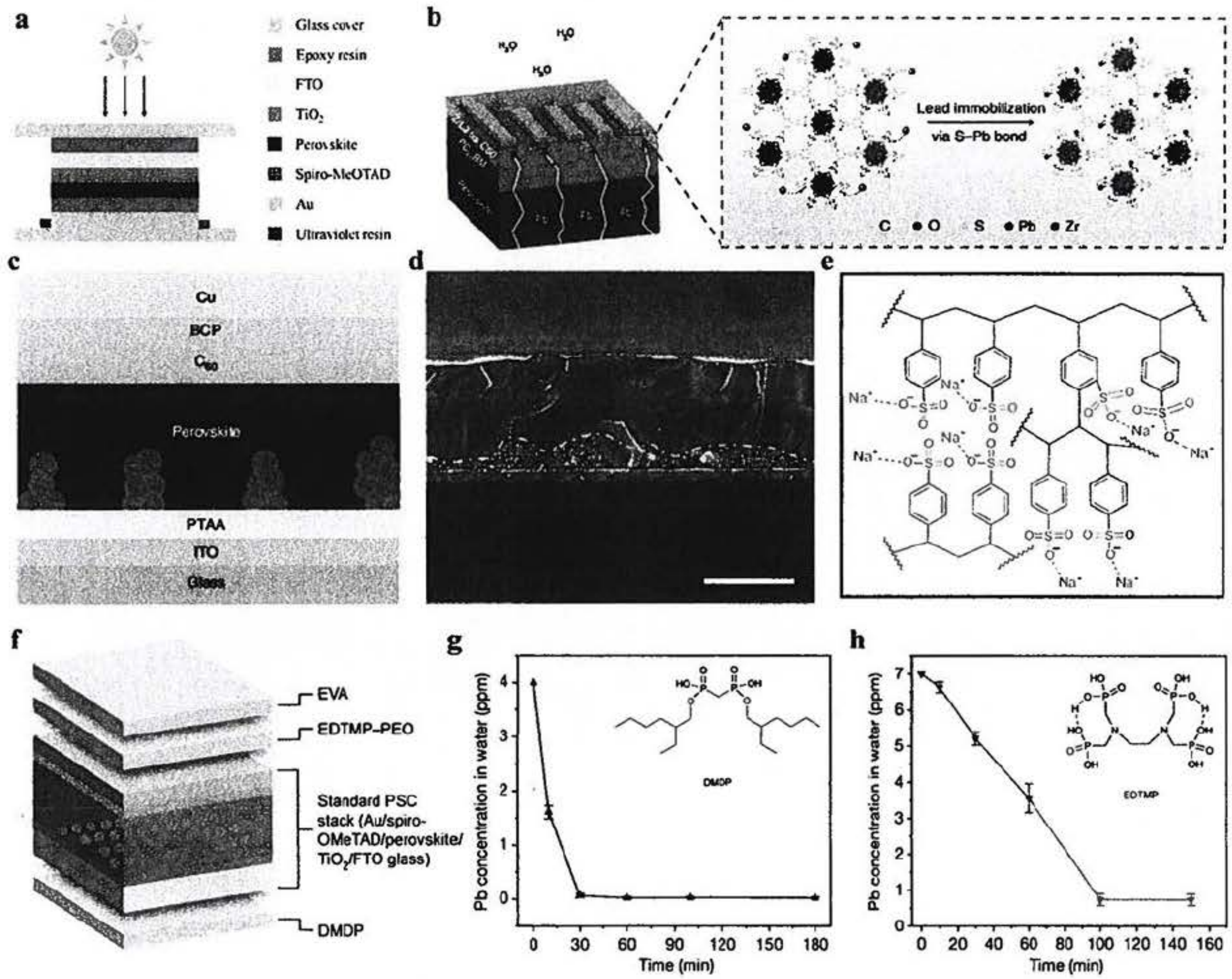


Fig. 7. (a) The self-healing encapsulation method for PSCs. Reproduced with permission from Jiang et al. (2019), copyright 2019 Springer Nature. (b) Schematic illustration of the prevention mechanism for lead leakage through chemical absorption between Pb^{2+} and thiols of ZrL3 in PSCs. Adapted with permission from Wu et al. (2020), copyright 2020 The Authors, published by Spring Nature. (c) Schematic illustration of the resin-scaffold device (blue bars represent the cation exchange resin). (d) Scanning electron microscope (SEM) image of the resin-scaffold device. (e) The chemical structure of sulfonic acid cation exchange resin. Adapted with permission from Chen et al. (2021), copyright 2021 The Authors, published by Spring Nature. (f) The device structure with the incorporation of two lead absorbing films, DMDP and EDTMP-PEO. (g) and (h) Diagrams reflecting the lead capture abilities of 4-cm^2 DMDP and EDTMP-PEO films immersed in 50 mL PbI_2, and the top right inset of each plot is the chemical structure of DMDP and EDTMP, respectively. Reproduced with permission from X. Li et al. (2020), copyright 2020 Springer Nature.

methanediphosphonic acid; EDTMP represents N,N,N′,N′-ethyl enediaminetetrakis(methylenephosphonic acid); PEO represents poly(ethylene oxide)). DMDP films on the glass side are transparent with each DMDP molecule containing two phosphonic acid groups that can strongly bind with a Pb^{2+} ion. EDTMP-PEO films on the metal side are a mixture of EDTMP with good Pb-chelating ability blended in a host PEO. The lead absorbing capacity of DMDP and EDTMP-PEO films is shown in Fig. 7g and **h**, respectively. Furthermore, it is worth noting that when soaked in water, these two Pb-absorbing films could swell and remain inside the damaged devices rather than dissolving. Therefore, with such device architecture, more than 96% of the lead leakage could be sequestrated on-device. It was also proved that these integrated lead-capturing films almost had no impact on the device performances and long-term stability (X. Li et al., 2020).

On the other hand, fire safety of lead perovskite has been investigated as discussed earlier in Section 3.1 (Conings et al., 2019). A glass-glass encapsulation has been proven to be an effective approach for capturing lead in perovskite under fire because the majority of the evaporated PbI_2 could be oxidized into PbO and PbO_2 species and retain inside the glass cover (Conings et al., 2019).

To sum up these reported approaches on controlling lead leaching, progress has been made on establishing enhanced physical encapsulation, developing multifunctional HTL, ETL, electrodes and incorporating extra Pb-chelating films into the device structures. It is also important that these strategies have no negative influence on perovskites' optical properties and device performance. However, more improvements are desirable to a scalable, more efficient and cost-effective method for solving lead toxicity and potential leakage problems.

4.2. Cyclic utilization of lead in end-of-life PSCs

Aside from taking precautionary measures against potential lead leaching problem, selecting appropriate disposal method for exhausted PSCs is also important to avoid lead contamination at their end of life. Being landfilled would cause 70% of lead at worst leaching to soil and water during the first year (Serrano-Luján et al., 2015; Spalvins et al., 2008). Though 98% of lead can be recovered in ashes, the waste treatment of substrate and electrodes during incineration process has negative impacts on human health (Serrano-Luján et al., 2015). Compared with landfill and incineration, recycling lead-based PSCs is obviously a

70% year 1

more environmental-friendly way for their final disposal. In fact, although the actual toxic effects of today's commercialized PV panels on environment are objectively low, many PV companies have volunteered to recycle their end-of-life modules. The purpose of this gesture is not only to reduce the risk of toxic materials outflow, but also to make the new generation of PV technologies more acceptable to the public (Kadro and Hagfeldt, 2017). For example, First Solar, the leading company in sustainable energy in the world, particularly in CdTe thin film solar modules, offers global PV recycling services for its modules. They give guidance to customers on how to return the end-of-life modules by labeling the information on each one. Furthermore, their recycling recovery rate is significantly high with up to 90% for both glass and semiconductor materials. Therefore, it is environmentally friendly and available to promote the recycling and reuse of lead halide PSCs when it comes to large-scale implementation. More importantly, the proof of concept for recycling materials in Pb-containing PSCs has already been reported.

There are many demonstrations on the reuse of transparent conducting glass/TiO_2 substrates, PbI_2 and the metal electrodes after the functional lifetime of PSCs is exhausted. Particularly, the recycling and reuse of PbI_2 is proved to avoid lead waste at the stage of disposal and the related methods can be basically categorized as two types, as shown in Fig. 8. One is to make use of waste lead to reproduce the lead-containing raw materials via solvent extraction, chemical precipitation and electrochemical deposition. The regeneration of PbI_2 can be reused for the fabrication of new devices, while other lead-containing materials such as metallic lead are fed back into the lead trading market. The other is to recycle PbI_2 from pristine PSCs and regenerate new devices in situ. It worth mentioning that PbI_2 recycled from other industries such as lead-acid battery is also qualified for PSCs preparation.

A typical metal-based PSC consists of a metal electrode, a HTL, a light-harvesting perovskite layer, an ETL and a transparent electrode. Aside from HTL materials, almost all other major components in metal-based PSCs can be recycled layer by layer. The organic HTL can be selectively dissolved in non-polar solvents such as toluene, diethyl ether, dichloromethane, and chlorobenzene. Meanwhile, the gold electrode was peeled off from the device followed by separation and recycling process (Kadro et al., 2016; Kim et al., 2016). After dismantling the metal electrode and HTL, there are two steps for PbI_2 collection. The first one is to remove CH_3NH_3I using polar protic solvents (methanol, ethanol, 2-propanol, or water) and then extract the remaining PbI_2 layer using polar aprotic solvents (acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, or g-butyrolactone), as the representative schematic procedures shown in Fig. 9a (Kadro et al., 2016; Kim et al., 2016). Though $CH_3NH_3PbI_3$ decomposes into CH_3NH_3I and PbI_2 in both kinds of polar solvents, the solubility of PbI_2 in polar protic solvents is very low. It was also proved that perovskite could be completely dissolved in polar aprotic solvents owing to their reaction with Pb^{2+} (Kim et al., 2016). Kadro et al. (2016) also compared the selectivity of four solvents for CH_3NH_3I dissolution. They found that the order of $CH_3NH_3PbI_3$ decomposition rate in solvents was ranked as methanol > deionized water > ethanol > 2-propanol, while the ordering for segregation efficiency was deionized water > 2-propanol > ethanol > methanol. With all factors considered, ethanol was eventually chosen as the proper solvent because it is less toxic than methanol and evaporates faster than water with reduced processing time (Kadro et al., 2016). As for the recycled PbI_2 in polar aprotic solvents such dimethylformamide (DMF), it can be reused in regenerating perovskites after removing DMF under vacuum. It has also been found that the photovoltaic performance of PSCs directly utilizing the recycled PbI_2 was not as good as that of PSCs using fresh PbI_2 (Binek et al., 2016). This was understandable since the recycled PbI_2 may contain some impurities such as CH_3NH_3I and TiO_2. However, it was encouraging that after being recrystallized from water to remove impurities, the purified PbI_2 exhibited comparable performances to the fresh PbI_2 for preparing PSCs (Binek et al., 2016). A new adsorbent, Fe-decorated hydroxyapatite hollow composite, was reported very recently to separate and recycle lead from PSCs (Park et al., 2020). Owing to its negative surface charge and magnetic property, this composite could effectively absorb lead from non-aqueous solvents such as DMF and easily be separated in magnetic field. The following recycling of PbI_2 was achieved by dissolving the Pb-absorbed composite into nitric acid and then adding KI to recrystallize PbI_2, the detailed recycling process is presented in Fig. 9b. The Pb recovery rate was up to 99.97% using this method. Moreover, the recycled PbI_2 showed almost no difference to commercial PbI_2 on device efficiency when fabricated into PSCs (Park et al., 2020). Aside from recrystallization to obtain highly purified PbI_2, there is another dissolving-precipitating method to extract PbI_2 from carbon-based PSCs to avoid solvent evaporation, which may have potential health risks to human and as environmental pollution (Zhang et al., 2018). In this case, PSC was firstly immersed in DMF solution to dissolve perovskite since there is no HTL in carbon-based PSCs and the carbon electrode does not react with DMF solvent. Then ammonium hydroxide was added into DMF to precipitate Pb^{2+} and HI was subsequently used to form PbI_2. Related chemical reactions are shown as following:

$$Pb^{2+}+2NH_3\cdot H_2O \rightleftharpoons Pb(OH)_2(s)+2NH_4^+ \quad (5)$$

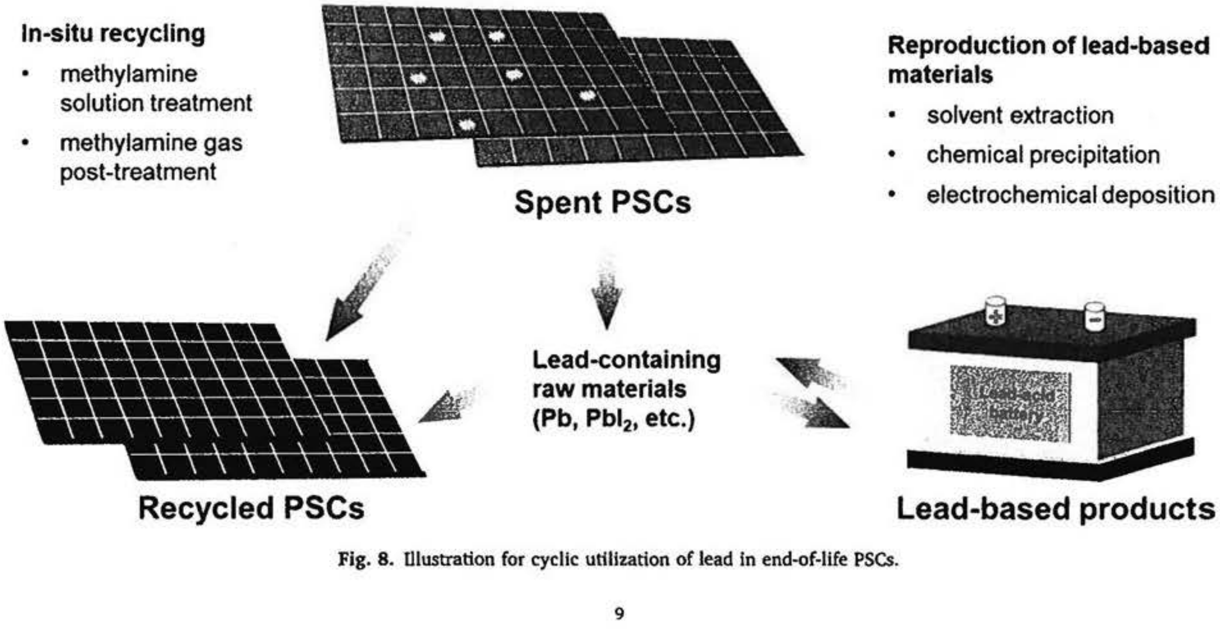


Fig. 8. Illustration for cyclic utilization of lead in end-of-life PSCs.

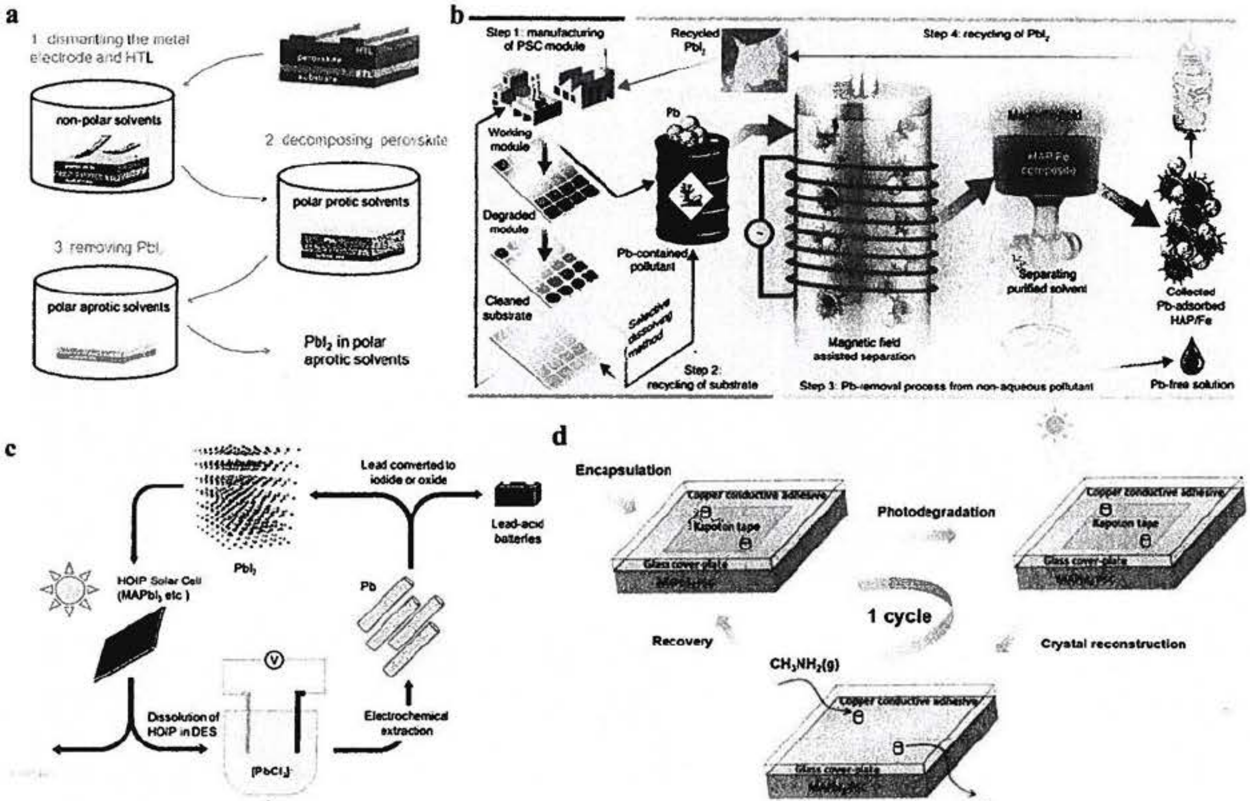


Fig. 9. (a) Schematic procedures for PSCs recycling. Non-polar solvent is used to dissolve HTL and extract gold electrode, polar protic solvent is used to dissolve $CH_3NH_3PbI_3$, and polar aprotic solvent is used to extract PbI_2. (b) The recycling process of lead in PSCs by using Fe-decorated hydroxyapatite hollow composite. The first step is the fabrication of PSCs. The second step is to recycle the substrate from degraded devices via selective dissolving method. The third is to extract lead using Fe-decorated hydroxyapatite hollow composite and an electromagnetic separating system. The last step is dissolving the collected Pb-adsorbed composite with HNO_3 solution and then adding KI to recrystallize PbI_2 for the refabrication of PSCs. Adapted with permission from Park et al. (2020), copyright 2020 Springer Nature. (c) Demonstration of the deep eutectic solvent based electrochemical recycling process for lead. Adapted from Poll et al. (2016) with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry. (d) Illustration of regeneration of encapsulated $CH_3NH_3PbI_3$ PSCs via methylamine gas post-treatment. Reproduced with permission from Hong et al. (2017), copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

$$Pb(OH)_2 + 2HI \rightleftharpoons PbI_2 + 2H_2O \tag{6}$$

The recovery rate for PbI_2 from DMF solution was up to 95.7% and the performance of the recycled PbI_2 can also compete with commercial PbI_2 (Zhang et al., 2018). The Pb content in perovskite can also be effectively recycled by electrochemical method (Poll et al., 2016). In an electrochemical process, shown in Fig. 9c, a deep eutectic solvent consisted of choline chloride and ethylene glycol was used to dissolve the perovskite films. Lead was then electrodeposited on the Pb foil as working electrode with up to 99.8% recovery rate (Poll et al., 2016). More recently, a bleacher solution contained methylamine and tetrahydrofuran was used to recycle the whole PSCs (Wang et al., 2021). Especially, perovskite recovered in the bleacher solution can be dispersed in nonionic solvents and then recast the perovskite film (Wang et al., 2021).

The other way to achieve the cyclic utilization of PbI_2 is the in situ recycling of PbI_2 from pristine PSCs and regenerating new devices (Jena et al., 2018; Xu et al., 2017). Xu et al. (2017) transformed $CH_3NH_3PbI_3$ film to pure PbI_2 by thermal decomposition and then introduced CH_3NH_3I from an isopropanol solution to form a new absorber layer. The first step is to remove the electrode with adhesive tape and then soak the devices in chlorobenzene solvent to wash off the HTL. The third step is a vital one to decompose $CH_3NH_3PbI_3$ at appropriate temperature. It was proved that 250 °C was the proper temperature to degrade $CH_3NH_3PbI_3$ and sublime CH_3NH_3I as confirmed by thermogravimetric analysis. Then CH_3NH_3I solution was spin-coated on the recycled PbI_2 films and heated to regenerate a new perovskite film. At last, a new HTL was spin-coated and top electrode was thermally evaporated on the device under vacuum. It is noteworthy that the in-situ recycled PSCs has comparable photovoltaic performance to the PSCs made by pristine PbI_2 (Xu et al., 2017). Jena et al. (2018) also studied the reuse of perovskite films by reconversion of PbI_2 to perovskite. After washing off the Au layer and HTL (spiro-OMeTAD layer) using chlorobenzene solvent, the degraded perovskite film was heated at 80 °C for 15 min to complete the transformation into PbI_2. Then the film was spin coated with CH_3NH_3I solution followed by annealing, spin-coating fresh spiro-OMeTAD layer and depositing Au electrodes. However, in their findings, the power conversion efficiency of recycled PSCs decreased, mainly owing to a significant drop of the fill factor, and greater hysteresis in J-V curves was observed as well. They also proved that the not-fully-restored performance of recycled PSCs was because the newly formed interface between perovskite and spiro-OMeTAD layer became worse after recycling, which resulted in inefficient carrier transport (Jena et al., 2018). The two works mentioned above both recovered the perovskite by introducing CH_3NH_3I solution on pre-decomposed PbI_2 with the need to remove and reconstruct the metal electrode and HTL. Another work demonstrated a different and unusual route to regenerate the degraded PSCs via methylamine gas post-treatment without component reconstruction (Hong et al., 2017). The recovery procedure is shown in Fig. 9d. Purging CH_3NH_2 gas into the decomposed devices could make $CH_3NH_3PbI_3$ recrystallized. This post-treatment process includes a solid-liquid-solid phase transition for perovskite reconstruction as shown in following equations:

$$CH_3NH_3PbI_3(s) + CH_3NH_2(g) \rightarrow CH_3NH_3PbI_3 \cdot xCH_3NH_2(l) \tag{7}$$

$$CH_3NH_3PbI_3 \cdot xCH_3NH_2(l) \rightarrow CH_3NH_3PbI_3(s) + CH_3NH_2(g) \tag{8}$$

It is worth mentioning that according to this study, the efficiency of encapsulated PSCs after two cycles of photodegradation-recovery treatment can still reach 91% of the original devices (Hong et al., 2017).

Overall, works have proven that the major components of Pb-based PSCs can be recycled and reused, and the efficiency of regenerated PSCs can compete with the ones fabricated by fresh materials. More importantly, the recycle and reuse of PbI_2 effectively avoid the Pb waste and prevent lead contamination, which makes PSC-based photovoltaic technology more environmentally friendly. Additionally, the PbI_2 used in PSCs not only can be commercial PbI_2 or recycled PbI_2 from degraded PSCs, but can also be recycled PbI_2 from other industries such as car batteries (Chen et al., 2014; Li et al., 2021). Vice versa, the recycled lead from degraded PSCs can be used for the production of other lead-containing products (Poll et al., 2016). In this way, it enables the cyclic utilization of lead and consequently cuts down the fabrication cost and reduces the risk of lead outflow. Therefore, the development of lead recycling technology for PSCs is clearly beneficial to the practical application of lead-based PSCs. Nevertheless, further improvement is still needed to ensure the high efficiency and long-term stability of the regenerated PSCs.

5. Summary and outlook

As discussed above, the overall lead content used in PSCs is actually pretty low. However, considering the high toxicity of lead, the negative impacts on animal and human health, as well as on plant growth and the entire ecosystem are still non-negligible. In the case of damaged encapsulation, the majority of lead in PSCs would be washed off into environment by rain. Furthermore, the improper disposal of end-of-life PSCs also causes lead leaching problems. Though catastrophic encapsulation failure for panels is uncommon, controlling the lead loss in midlife and end-of-life is significantly important because lead in PSCs is soluble, which is different from lead-containing solder in the conventional c-Si modules. To date, several solutions to PSCs lead leakage in midlife and a good number of recycling methods for PbI_2 have been proposed. However, in term of implementation, many other factors should be taken into account such as cost and manufacturing process at larger scale.

In future, there is still a need to explore more cost-effective and efficient solutions to reduce lead leakage. In fact, lead extraction and lead removal have been widely investigated in the field of wastewater treatment and contaminated soil remediation, and many techniques have been proved to be efficient such as chemical precipitation, adsorption, electrochemical technics, solvent extraction and ion exchange (Feng et al., 2020; Hirayama, 2012; Hu et al., 2015; Huang et al., 2018; Ihsanullah et al., 2016; Samiey et al., 2014; Tuzen et al., 2016). Therefore, it is promising to apply some of these technologies to reduce lead leakage in PSCs. For example, given that the major degradation product of lead perovskites is PbI_2 with a high solubility of about 340 mg/L Pb^{2+} in water, the solubility value far exceeds the limit of allowed Pb^{2+} concentration of 0.015 mg/L, therefore, it would be a good strategy to transform the highly soluble lead iodide into other insoluble lead compounds such as PbS to reduce their potential bioavailability. The highly insoluble PbS has a K_{sp} value of 3.0×10^{-28} and the calculated solubility is about 3.6×10^{-9} mg/L for Pb^{2+}, which is about 11 orders of magnitude lower than that in PbI_2 and also far below the safety limit of lead in water. Utilizing phosphate materials such as apatite and hydroxyapatite to immobilize lead is also a good strategy, because the leaching lead can react with phosphate to form pyromorphite $Pb_5(PO_4)_3X$ ($X = F^-, Cl^-, Br^-, OH^-$), which is the most stable Pb compound in nature over a wide range of pH. For instance, the $\log_{10}K_{sp}$ value of chloropyromorphite $Pb_5(PO_4)_3Cl$ varies from -18.69 in pH range of 0–2.12, to -84.4 in pH range of 12.38–14. More importantly, it has been found that even if the formed pyromorphite is consumed by human by mistake, it cannot be absorbed by the digestion system (Miretzky and Fernandez-Cirelli, 2008). On the other hand, as previously mentioned in Section 4.1, introducing Pb-absorbing materials with phosphonic acid and thiol groups in PSCs has been verified as an available approach to prevent lead leakage. In fact, there are many other functionalized groups acting as Lewis bases that can strongly bond with Pb^{2+} (acting as Lewis acid) to form metal complex, such as hydroxyl, carboxyl and amine groups (Aguado et al., 2009; Chiariza et al., 1997; Manousi et al., 2019; Peng et al., 2014; Shen and Fan, 2013; Yantasee et al., 2007; Zhu et al., 2019). Thus, there is a great possibility to explore other materials with one or more kinds of Pb-chelating groups to reduce lead leakage. However, it is worth noting that the introduced materials should be environmentally friendly and have no negative impact on the performance of PSCs. It is also important that they are insoluble in water and cannot be washed off except that lead has been transformed into non-toxic compounds. Last but not least, speeding up the legislation process on PV waste recycling around the world is still one of the most effective strategies to control lead leakage for end-of-life PSCs.

CRediT authorship contribution statement

Meng Ren: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing. **Xufang Qian**: Conceptualization, Methodology, Resources, Supervision, Writing – review & editing. **Yuetian Chen**: Methodology, Supervision, Writing – review & editing. **Tianfu Wang**: Supervision, Writing – review & editing. **Yixin Zhao**: Conceptualization, Formal analysis, Methodology, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China Grant (22025505, 51861145101), Program of Shanghai Academic/Technology Research Leader (Grant no. 20XD1422200) and Cultivating Fund of Frontiers Science Center for Transformative Molecules (2019PT02).

References

Aguado, J., Arsuaga, J.M., Arencibia, A., Lindo, M., Gascón, V., 2009. Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. J. Hazard. Mater. 163 (1), 213–221. https://doi.org/10.1016/j.jhazmat.2008.06.080.

Babayigit, A., Boyen, H.-G., Conings, B., 2018. Environment versus sustainable energy: the case of lead halide perovskite-based solar cells. MRS Energy Sustain. 5, E1 https://doi.org/10.1557/mre.2017.17.

Babayigit, A., Duy Thanh, D., Ethirajan, A., Manca, J., Muller, M., Boyen, H.-G., Conings, B., 2016a. Assessing the toxicity of Pb- and Sn-based perovskite solar cells in model organism Danio rerio. Sci. Rep. 6 (1), 18721. https://doi.org/10.1038/srep18721.

Babayigit, A., Ethirajan, A., Muller, M., Conings, B., 2016b. Toxicity of organometal halide perovskite solar cells. Nat. Mater. 15 (3), 247–251. https://doi.org/10.1038/nmat4572.

Bae, S.-Y., Lee, S.Y., Kim, J.-w, Umh, H.N., Jeong, J., Bae, S., Yi, J., Kim, Y., Choi, J., 2019. Hazard potential of perovskite solar cell technology for potential implementation of "safe-by-design" approach. Sci. Rep. 9 (1), 4242. https://doi.org/10.1038/s41598-018-37229-8.

Benmessaoud, I.R., Mahul-Mellier, A.-L., Horváth, E., Maco, B., Spina, M., Lashuel, H.A., Forró, L., 2015. Health hazards of methylammonium lead iodide based perovskites: cytotoxicity studies. Toxicol. Res. 5 (2), 407–419. https://doi.org/10.1039/c5tx00303b.

Science of the Total Environment 908 (2024) 168019

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

A review on life cycle environmental impacts of emerging solar cells

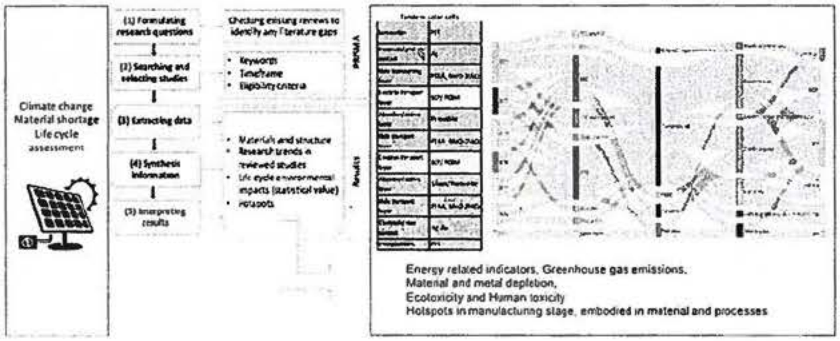
Maurizio Cellura, Le Quyen Luu *, Francesco Guarino, Sonia Longo

Department of Engineering, University of Palermo, Viale delle Scienze Ed.9, 90128 Palermo, Italy

HIGHLIGHTS

- Common indicators include energy, greenhouse gas, material, and toxicity.
- Manufacturing process is the hotspot for conventional and emerging solar cells.
- LCA method and production scales cause large range in environmental results.
- Eco-design is crucial in solar cell development to minimize environmental impacts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jacopo Bacenetti

Keywords:
Solar PV
Solar thermal
LCA
Eco-design
Material

ABSTRACT

The development of solar technologies requires increased efficiency in converting solar radiation to energy, as well as innovative materials and structure to go beyond the conventional power conversion ratio. In line with these innovations, there are concerns about greenhouse gas emissions of the solar cells, materials for the solar technologies and other relevant environmental impacts of the manufacturing processes. This review is conducted on life cycle assessments of solar cells, considering the climate change and natural resource shortage context. It is identified that the majority of existing life cycle assessments on solar cells take into account four typical environmental impacts: energy consumption, greenhouse gas emissions, material depletion, and toxicity. Though the diverse methodological aspects make it difficult to directly compare these environmental impacts among various types of solar cells, the obtained results hinder that emerging solar cells such as perovskite solar cells or tandem solar cells are likely to have better environmental profiles than conventional silicon based and thin film solar cells, in terms of energy consumption, greenhouse gas emissions and material consumption. However, the emerging solar cells may utilize toxic materials in which their eco-toxicity and human toxicity should be further considered during the design of the technologies. Moreover, it is identified that the energy and environmental hotspot lies in the manufacturing process, regardless of impact indicators and types of solar cells.

---

* Corresponding author.

E-mail addresses: maurizio.cellura@unipa.it (M. Cellura), lequyen.luu@unipa.it (L.Q. Luu), francesco.guarino@unipa.it (F. Guarino), sonia.longo@unipa.it (S. Longo).

https://doi.org/10.1016/j.scitotenv.2023.168019
Received 7 September 2023; Received in revised form 19 October 2023; Accepted 20 October 2023

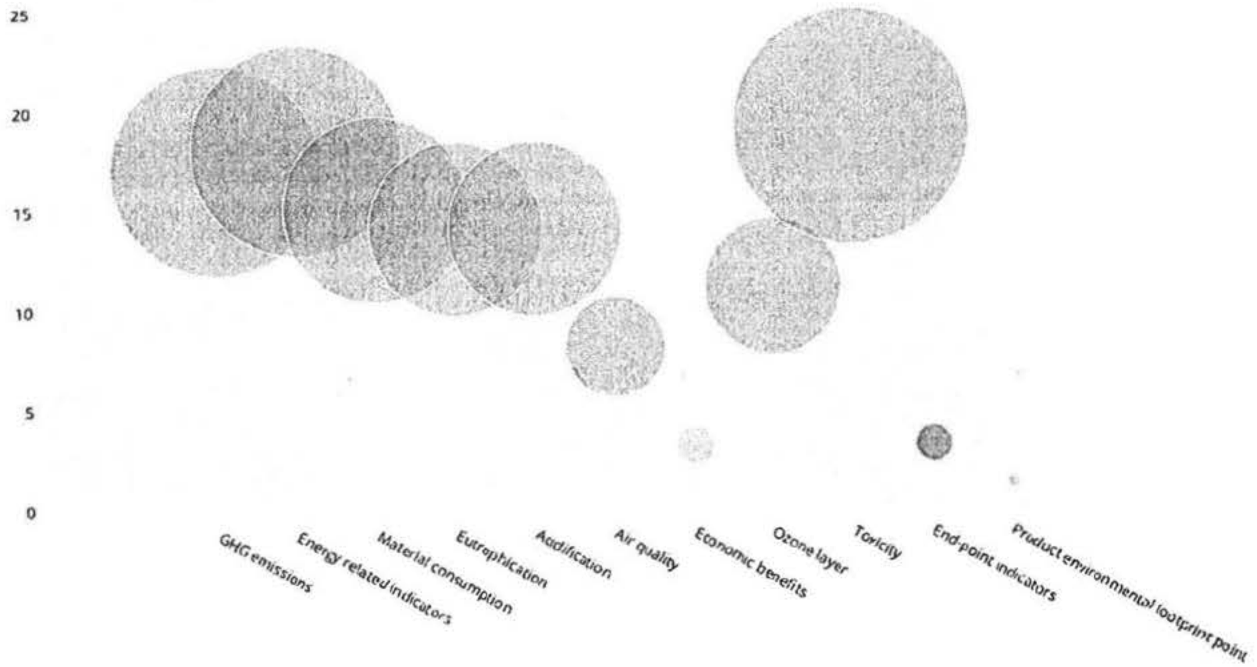


Fig. 3b. Methodological aspect in selecting life cycle impact indicators.

module (Li et al., 2022). However, when being converted into the FU of kWh, the CED reported by Li et al. (2022) dropped significantly 3.07E-02 MJ per kWh, much lower than the results of other studies.

The cradle to grave CED was 6.59E+03 to 9.32E+03 MJ per m^2 of active area of PSC (Alberola-Borras et al., 2018b), being equivalent to 1.03E+00 to 1.46E+00 MJ per kWh. These numbers were in the range of the reported cradle to gate CED of (Alberola-Borràs et al., 2018a; Sánchez et al., 2019).

The cradle to gate CED of organic transparent PV ranged from 3.1 to 11.4 MJ per Wp, depending on materials of glass or plastics and efficiencies of the current or future technologies (Anctil et al., 2020).

While CED is used to measure the energy consumption, CEY considers the energy production. It is the amount of energy production during the life cycle of the product, presented in MJ of energy or kWh of electricity. CEY depends on the total energy output of the system, consequently on the efficiency of the module, the tilt of the cells, solar radiation, temperature in the installation site, and many other technical parameters of the system as well as the installation site (Hosseinian Ahangharnejhad et al., 2019). Though it is a 'life cycle' indicator, CEY originates from the 'use' stage of the module, in other words, generating electricity or thermal energy during the operation of the solar cells. CEY was applied by only one author, in which the CEY of solar cells ranged from 7.8 MWh to 12.6 MWh per m^2 of PV module (Hosseinian Ahangharnejhad et al., 2020).

EROI or NER is the ratio of the amount of energy delivered in relation to the amount of energy invested to explore, extract, process, produce, generate, transmit and transport it (Raugei et al., 2016). Though these indicators are called by different names, they are the same by nature, and being calculated by applying Eq. (3). These two indicators are dimensionless. EROI was applied in Jia et al.'s study, which is 9.4 to 13.17 for SSCs (Jia et al., 2021). NER indicator was applied in Rao et al.'s study for PSCs, which is calculated at 3.08 (Ramamurthy Rao et al., 2021). Both studies of Jia et al. and Rao et al. covered the system boundary from cradle to grave, meaning that they include energy production and consumption from the material extraction to end of life of the product system. The Eq. (2) is presented as followings:

$$EROI = \frac{Energy_{out}}{Energy_{in}} \quad (3)$$

in which:

$Energy_{out}$ is the amount of energy generated (MJ or kWh)
$Energy_{in}$ is the amount of energy used in the processes along the life cycle (MJ or kWh)

EPBT is the amount of time it takes for an energy system to generate the amount of energy equivalent to the amount that took to produce the system (Frischknecht et al., 2016). The EPBT of PSC is 2.17 years considering cradle to gate (Okoroafor et al., 2022), and 1.41 to 2.12 considering gate to gate system boundary (Correa Guerrero et al., 2021). The EPBT of PSC reduces to 0.97 years (Ramamurthy Rao et al., 2021), when the system boundary is extended to cover the whole life cycle of the cells, e.g. from cradle to grave. For CdTe module, the cradle to grave EPBT is around 1.3 and 1.34 years, depending on whether recycling is applied in the end of life treatment of the product (Vellini et al., 2017). The cradle to grave EPBT of Si module is 2.6 years, but may be reduced to 1.6 years if recycling is applied (Vellini et al., 2017).

Fossil fuel depletion is a life cycle environmental impact indicator being similar to CED, but it only limits to fossil energy sources. The fossil fuel depletion of different types of solar cells is converted into the FU of kWh and presented in Table 2.

The cradle to gate fossil fuel depletion of SSC was from 7.83E+00 to 1.54E+01 g oil eq per kWh of electricity depending on type of solar cells, mono or multi crystalline (Stamford and Azapagic, 2019), and 1.44 MJ surplus per kg of c-Si, being equivalent to 6.05E+00 kg oil eq per kg c-Si (Klugmann-Radziemska and Kuczyńska-Łażewska, 2020). The cradle to end use resource depletion of SSC was 1.98E+02 MJ per m^2 PV module (Hosseinian Ahangharnejhad et al., 2020). The end of life fossil fuel depletion of SSC was 8.11E+00 kg oil eq per m^2 of end of life PV panel treated (Corcelli et al., 2018). Meanwhile, the end of life treatment of SSCs was from 4.00E-01 to 1.48E+00 kg oil eq per kg of PV material depending on end-of life treatment (Contreras Lisperguer et al., 2020).

The life cycle emissions from manufacturing process accounted for a significant part of the whole life cycle emission, which ranged from 2.57E-02 to 5.05E-02 kgCO$_2$eq per kWh (Stamford and Azapagic, 2019). The high range of 4.42E-02 to 5.05E-02 kgCO$_2$eq per kWh for multi and mono SSCs lies in SSCs installed in low radiation areas, for example UK (Stamford and Azapagic, 2019). It should be noted that the results of Bogacka et al.'s study did not fall within the range, and being higher, at 1.17E-01 kgCO$_2$eq per kWh (Bogacka et al., 2017), because this number indicated the highest avoided emissions by substituting the standard energy mix of either Poland, France or Norway with energy generated from SSC with recycled materials.

The emissions of tandem SSC fall within the range of SSCs, at 2.25E-02 kgCO$_2$eq per kWh for cradle to grave emissions of LSC-Si devices (Lunardi et al., 2019). For non-silicon, thin film solar cells, such as CIGS and CdTe, the life cycle emissions are a bit lower, ranging from 1.46E-02 to 2.50E-02 kgCO$_2$eq per kWh for CIGS cradle to gate emissions and 1.74E-02 to 2.98E-02 kgCO$_2$eq per kWh for CdTe cradle to gate emissions (Stamford and Azapagic, 2019).

For PSC, the cradle to grave GHG emissions ranged from 1.82E-01 to 6.78 kgCO$_2$eq per kWh (Ramamurthy Rao et al., 2021; Zhang et al., 2017). The range is quite large due to different end of life treatments of the cells. At the same time, the higher end of PSC was reported by (Zhang et al., 2017), who quantified the environmental impacts per kWh with the assumption of one year lifetime. The cradle to gate GHG emissions of this type of solar cells were between 3.01E-02 to 9.50 kgCO$_2$eq per kWh (Alberola-Borràs et al., 2018a; Sánchez et al., 2019). This significant difference can be explained by the manufacturing processes and scale of production.

Per m^2 of PV module, the results in cradle to gate emissions are diverse, from 4.17E+01 to 5.22E+01 in mono facial PSC, 7.45E+01 to 8.34E+01 in bifacial PSC, 7.60E+01 to 1.24E+02 in mono facial tandem PSC, and from 1.07E+02 to 1.56E+02 in bifacial tandem PSC (Hosseinian Ahangharnejhad et al., 2020). The emissions may be up to 9.4 kgCO$_2$eq per m^2 of PV module (Li et al., 2022). Even the higher end of the PSC's GHG emissions is lower than that of OSC, at 9.5 kgCO$_2$eq per m^2 of PV module (Li et al., 2022); and much lower than that of SSC, at 1.49E+02 kgCO$_2$eq per m^2 of PV module (Hosseinian Ahangharnejhad et al., 2020). As mentioned above, the FU of m^2 will be converted into kWh, for statistical analysis. In this case, the cradle to gate emissions of PSC in (Hosseinian Ahangharnejhad et al., 2020) are in the range of 5.28E-03 to 9.27E-03 for mono facial and bi-facial PSCs, and 7.71E-03 to 1.24E-02 for mono facial and bi-facial tandem PSCs, which are the lower ends of GHG emissions of PSC in all reviewed case studies (see Fig. 4).

Per kg of PV material, the end of life emissions of Si based PVs are 1.38 and 5.39 kgCO$_2$eq, for recycling and landfill treatment, respectively (Contreras Lisperguer et al., 2020). Recycling different materials (CdTe) has reduced the end of life emissions by half, at 0.57 kgCO$_2$eq (Contreras Lisperguer et al., 2020).

For electronic grade silicon, the cradle to gate emissions are much smaller, at 3.10E-05 to 5.25E-05 kgCO$_2$eq per kg of c-Si, depending on input materials for manufacturing the silicon, from recycled or virgin materials (Klugmann-Radziemska and Kuczyńska-Łażewska, 2020).

4.4. *Material consumption*

The material consumption is indicated by the abiotic depletion potential (ADP). This impact category measures the availability of resources including fossil fuel, metal and mineral depletion. As the fossil fuel depletion has been reported in the previous section in energy related indicators, this section only presents the metal or mineral depletion of solar cells.

Depending on the life cycle impact assessment methods, ADP is quantified in various units. For example, CML method quantifies the ADP in kg Sb eq, meaning that the consumption of all resources are normalized into antimony. ReCiPe method quantifies metal, mineral depletion and fossil fuel depletion separately, in which metal and mineral depletions are measured in kg Fe eq and kg Cu eq, respectively. The metal and mineral depletion of solar cells in kg Sb eq are presented in Fig. 5.

Per kWh of electricity, the ADP of mono facial SSC was 4.00E-04 to 4.10E-04 kg Sb eq (Jia et al., 2021), a little lower for bifacial Si solar cell was 2.60E-04 to 2.75E-04 kg Sb eq (Jia et al., 2021), and lowest for PSC. Zhang et al. (2017) reported the ADP of PSC ranged from 3.20E-05 to 1.32E-05 kg Sb eq per cm^2 of active area, depending on the input materials of the cells and end of life treatment practice, which are equivalent to 1.36E-05 to 7.23E-05 kg Sb eq per kWh. According to (Alberola-Borràs et al., 2018b; Okoroafor et al., 2022), the ADPs of PSC are lower, at 5.11E-06 and 1.76E-06 kg Sb eq per kWh, respectively. It should be noted that the case study of Okoroafor et al. (2022) was conducted within cradle to gate, while other case studies covered from cradle to grave. Therefore, it can be expected that the lower end of cradle to grave ADP of PSC should be higher than 1.76E-06 kg Sb eq per kWh.

The unit of kg Cu eq was only applied in one case study of Stamford and Azapagic (2019). In this case study, the authors reported the cradle to gate metal/mineral depletion of SSC were 6.17E-01 to 1.08E+00 g Cu eq per kWh of electricity depending on mono or multi Si solar cell. These numbers are similar to those of CdTe, at 5.94E-01 to 1.02E+00 g Cu eq per kWh; and lower than those of CIGS, at 3.31E+00 to 5.52E+00 g Cu eq per kWh (Stamford and Azapagic, 2019).

Two case studies used the unit of kg Fe eq for assessing metal/mineral depletion. Both these case studies focus on the end of life of the solar cells, but they are different in terms of system boundary and FU. While the case study of Corcelli et al. (2018) quantified the impacts from end of life impacts per m^2 of treated panel, the system boundary of Lisperguer et al.'s study (Contreras Lisperguer et al., 2020) covered from gate to grave and the impacts are calculated per kg of PV materials. According to (Corcelli et al., 2018), the metal/mineral depletion of SSC was 2.17E+00 kg Fe eq per m^2 of end-of-life PV panel treated. Meanwhile, the gate to grave metal/mineral depletion of SSC was from 1.35E+00 to 2.63E+00 kg Fe eq per kg of PV material depending on end of life treatment practice, in which recycling consumes less metal/mineral than landfill practice (Contreras Lisperguer et al., 2020). Lisperguer et al. also reported the metal depletion of recycling CdTe solar cells, which was at 2.05E-01 kg Fe eq per kg PV material (Contreras Lisperguer et al., 2020).

4.5. *Toxicity*

Toxicity includes the impacts on the health of species (ecotoxicity) and human (human toxicity) due to the persistence and accumulation of emissions in the environment, causing the increasing exposure of species and human to harmful substances and eventually causing the disease and death in species as well as human. Depending on environmental impact assessment methods, toxicity is measured in CTU (CTUe for ecotoxicity and CTUh for human toxicity), kg 1,4 DB eq, PAF/(m^2·day), PAF/(m^3·year), cases, DALY. Among these units, CTU and kg 1,4 DB eq are the most popular ones. CTU is used in the USETox model, which was developed by UNEP/SETAC to quantify ecotoxicity and human toxicity impacts based on the exposure, risks and impacts of thousands of chemicals in products and in environment. Meanwhile, the unit of kg 1,4 DB eq is applied in CML and ReCiPe methods to normalize the impacts of different chemicals to the reference flow of 1,4 dichlorobenzene. The following section describes the ecotoxicity and human toxicity of solar cells.

The ecotoxicity of SSCs generally lower than emerging solar cells. The cradle to grave ecotoxicity of SSC was 1.35E-05 kg 1,4 DB eq per kWh (Bogacka et al., 2017) and 4.51E-07 kg 1,4 DB eq per kWh (Corcelli et al., 2018). These numbers are even lower than the cradle to gate ecotoxicity of PSC, at 5.91E+00 to 4.23E+01 kg 1,4 DB eq per kWh (Li et al., 2022; Okoroafor et al., 2022) and that of OSC, at 4.66E+01 kg 1,4 DB eq per kWh (Li et al., 2022).

The same pattern is identified in the case of quantifying ecotoxicity

CTUe per kWh (Lunardi et al., 2019). The tandem SSCs had the lowest ecotoxicity, at 2.20E-05 CTUe per kWh (Lunardi et al., 2019). The ecotoxicities of solar cells are presented in Fig. 6.

With regards to human toxicity, per kWh, PERC Si device has the lowest human toxicity from cradle to grave, at 1.80E-11 CTUh per kWh (Lunardi et al., 2019), then tandem LSC-Si, at 1.00E-11 CTUh (Lunardi et al., 2019). The cradle to gate human toxicity of PSC is even higher than that of cradle to grave human toxicity of SSC, at 4.45E-09 to 1.35E-05 CTUh per kWh (Alberola-Borràs et al., 2018a) and 1.02E-08 to 1.38E-07 CTUh per kWh (Sánchez et al., 2019). However, in other studies, the human toxicity of PSC was at 1.00E-03 kg 1,4 DB eq per kWh (Okoroafor et al., 2022), which is much lower than those of Si solar cell at 7.84E-01 kg 1,4 DB eq per kWh (Bogacka et al., 2017), or CIGS at 1.47E-01 to 2.53E-01 kg 1,4 DB eq per kWh (Stamford and Azapagic, 2019). It should be noted that the human toxicity of SSC is from cradle to grave, while the reported numbers for PSC and CIGS are from cradle to gate.

The contrary results can be explained by the nature of life cycle impact assessment methods and the materials used in different types of cells. While the human toxicity which is measured in CTUh focuses on the cancer impacts of the solar cells, the human toxicity which is measured in kg 1,4 DB eq includes both cancer and non-cancer effects of the solar cells. Considering the cancer impacts, the PSCs are most lead-based, with high cancer impact factor. This causes its higher human toxicity compared to SSC which uses no (or almost no) materials that may cause cancer. In contrast, considering both cancer and non-cancer impacts, the CIGS and SSC cause high human toxicity potential, in which non-cancer impact accounts for the majority of the total impact (Stamford and Azapagic, 2019; Bogacka et al., 2017) and the cancer impact is negligible.

Human toxicity of different types of solar cells (based on materials), cradle to grave SSC was at 7.74E+00 kg 1,4 DB eq per m^2 of end-of-life PV panel treated (Corcelli et al., 2018). The cradle to gate human toxicity of OSC was from 2.32E+02 to 5.80E+00 kg 1,4 DB eq per m^2 (Li et al., 2022). The cradle to gate human toxicity of PSC was from 2.30E+02 to 3.94E+00 kg 1,4 DB eq per m^2 (Li et al., 2022), 1.00E-03 kg 1,4 DB eq per kWh (Okoroafor et al., 2022), 4.45E-09 to 1.35E-05 CTUh per kWh (Alberola-Borràs et al., 2018a), 1.02E-08 to 1.38E-07 CTUh per kWh (Sánchez et al., 2019), and 1.16E+00 DALY per kWh (Okoroafor et al., 2022). Fig. 7 illustrates the human toxicity of different solar cells.

4.6. Hotspots identification

The manufacturing stage is identified as the hotspot during the whole life cycle of the solar cells. This stage is responsible for a large share of several environmental impacts, regardless of the type of solar cells. Fig. 8a and b presents the contribution of manufacturing stages to various environmental impact indicators of PSC and SSC. In terms of GWP, the manufacturing stage accounted for 95 % to 97 % of the whole life cycle GHG emissions, depending on types of perovskite solar cells (Zhang et al., 2017). This also occurs with silicon based solar cells, and others. For example, the review in Heath et al. indicated that silicon wafers accounted for around half of the GWP (Heath, 2020). Similarly, Jia et al.'s case study identified that silicon wafers accounted for the largest share, at about 47 %–51 % of life cycle GHG emissions of mono facial and bi-facial passivated emitter rear contact (PERC) solar cells (Jia et al., 2021). For PERC with electronic grade silicon (PERC-EGS) and tandem luminescent solar concentrator - silicon (LSC-Si) solar cells, Lunardi et al. (2019) pointed out that the manufacturing stages of electronic grade silicon and mono c-Si contributed up to 70 % of the total life cycle GHG emissions.

The GHG emissions during the manufacturing stage may either come from material production (energy embodied in the materials) or the manufacturing process itself. In both cases, it obviously connects to the electricity consumption and the emission intensity of the consumed electricity. It was identified that electricity consumption has great impacts on all generations of solar cells, including crystalline silicon, thin film and organic cells. For crystalline silicon solar cells, the manufacturing and treatment of crystalline silicon are energy intensive processes (Muteri et al., 2020). For thin film and organic solar cells, though the manufacturing process requires less energy than silicon treatment, the energy embodied in the materials is the largest source of GHG emissions. Specifically, Li et al. (2022) identified that 80 % of the energy consumption of both perovskite and organic solar cells, originated from graphene transparent electrodes (GTE). Correspondingly, GHG emissions of GTE accounted for 90 % to 91 % of the GWP of both cells (Li et al., 2022).

It is the same situation for toxicity impact indicators, such as human toxicity and ecotoxicity. According to Zhang et al., the manufacturing stage accounted for 99 % to 100 % of the whole life cycle human toxicity potential of PSC (Zhang et al., 2017). Among different processes during the manufacturing stage, there is a difference in sources of human toxicity among reviewed case studies. For silicon based solar cells, both cancer and non-cancer human toxicity impacts were equally shared among the production of EGS, mono c-Si, PERC cell, module fabrication and installation (Lunardi et al., 2019). However, the study of Jia et al. indicated that the most significant human cancer impact originated from aluminium frames, followed by silicon wafers (Jia et al., 2021). The manufacturing of aluminium frames accounted for 45 % of mono facial and 34 % for bi-facial silicon based solar cells. The large difference is due to the fact that bi-facial cells used 70 % of aluminium alloys of mono facial ones. While the human cancer toxicity of aluminium frames originated from the disposal of red mud from bauxite digestion in the supply chain of primary aluminium (Zhang et al., 2017), that of silicon wafers came from the electricity consumption of coal fired power (Jia et al., 2021).

Regarding ecotoxicity impacts, the manufacturing stage contributed more than 60 % of the total life cycle impact, regardless of the type of solar cells. Specifically, manufacturing stage accounted for 97 % to 100 % of the whole life cycle of PSC (Zhang et al., 2017). For silicon solar cells, PERC and module fabrication accounted for up to 70 % of the total life cycle freshwater toxicity impacts (Lunardi et al., 2019), and silicon wafers contributed to about 60 %–70 % of the total life cycle freshwater toxicity impact, mainly due to the monocrystalline silicon ingot manufacturing (Jia et al., 2021).

For abiotic depletion, the manufacturing stage is the hotspot during the life cycle of SSC. According to Lunardi et al. (2019), the highest impact originates from module fabrication, followed by PERC cells, Si wafers, EGS and mono c-Si. This is due to the consumption of materials such as glass and aluminium used in the module manufacturing phase, and metals such as copper and silver used in the cell manufacturing phase. The authors pointed out that the most significant impact of ADP arises from silver-based metallization paste (Lunardi et al., 2019), which is the same result in the study of (Jia et al., 2021).

5. Conclusion

This review studied the life cycle environmental impacts of solar cells in the context of climate change and material shortage. It is identified that energy consumption and GHG emissions are indicators which attract the most attention. Other impact indicators such as material and metal depletion, ecotoxicity and human toxicity are also considered in many recent studies, due to the important role of raw materials in renewable energy technologies in general and solar PV technologies specifically.

It is observed that the manufacturing process is the hotspot for both SSC and PSC regarding all considered environmental impact indicators of energy consumption, GHG emissions, mineral and metal consumption. Energy embodied in materials of PSC accounts for up to 90 % of energy and GHG impacts, while 50 % of these impacts originate from energy consumption during the fabricating process of the SSC itself. These results indicate the crucial role of eco-design in reducing the energy consumption and GHG emissions of the solar cells over their life

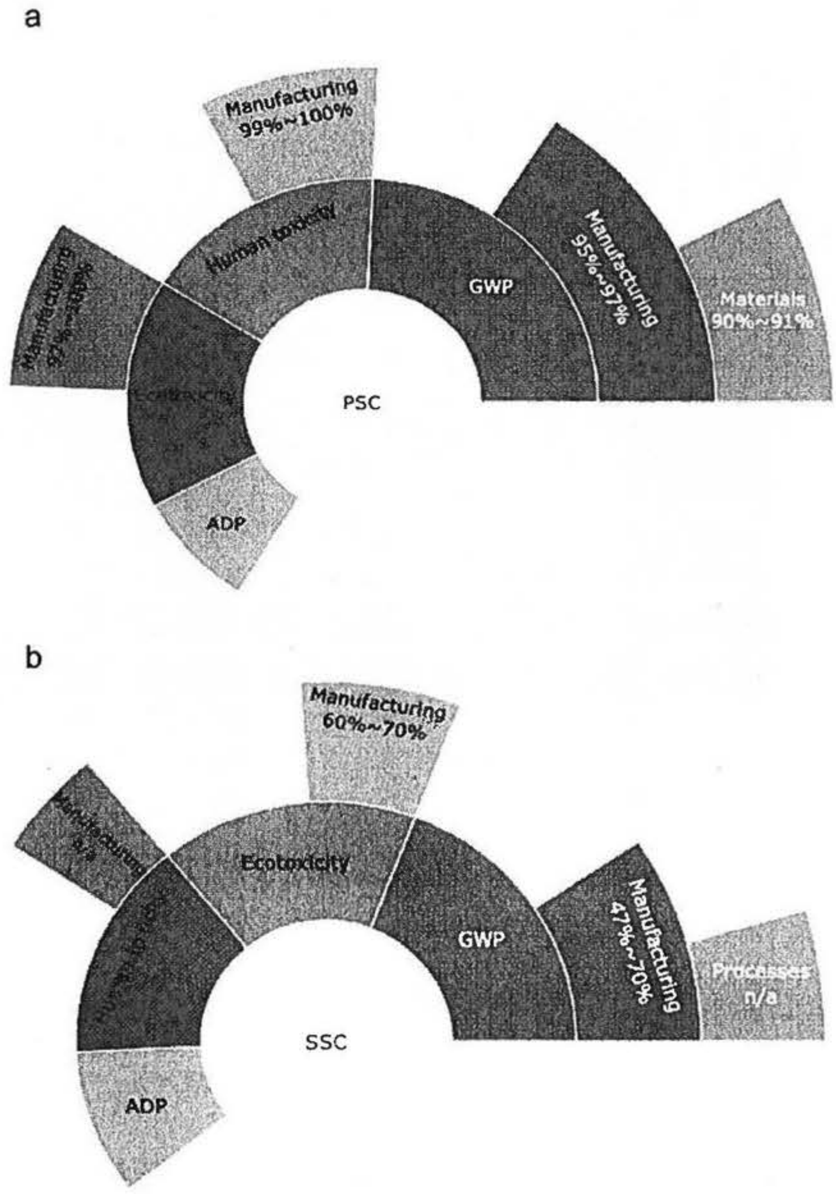


Fig. 8. a. Contribution of manufacturing stage to the life cycle environmental impacts of PSC.
b. Contribution of manufacturing stage to the life cycle environmental impacts of SSC.

cycle. The eco-design of solar cells covers different aspects such as the choice of materials, the structure or architecture of the cells, the manufacturing processes of the cells, the end of life treatment of the cells, the recovery or recycle of the materials. It helps to minimize the energy consumption during the material extraction, the cell manufacture, the waste treatment and the cell recycle, consequently, GHG emissions from those activities. At the same time, the better choice of material suggests the potential of converting into materials which are less critical and less toxic than those used in the existing technologies. All of these will support the sustainable energy and material transition.

There is a large range in the energy consumption and carbon footprints of both conventional solar cells such as SSCs, CdTe and CIGS, as well as emerging solar cells such as PSCs and tandem. This is due to the differences in methodological aspects of LCA such as system boundary, FUs and environmental indicators. Besides, the production scale of PCS and other emerging solar cells is currently at lab-scale, which makes the quantified and estimated results in some studies higher than they should be. It is expected that considering the same production scale, system boundary and FU, energy consumption and corresponding carbon footprint of emerging solar cells will be lower than those of conventional solar cells.

Regarding the material and metal consumption of solar cells, it is likely that the ADP of emerging solar cells will be lower than conventional cells. The existing literature concerned on the material and metal consumption in general, without any concentration on the links between critical raw materials and emerging solar cells. In the context of material shortage, future LCA studies should be applicable to the requirement of critical raw materials for solar PV. Besides, emerging solar cells with new materials such as perovskite and tandem cells may use some toxic materials, while the conventional SSCs use the abundant, cheap and non-toxic material of silicon. It is, consequently, recommended that the toxicity of emerging solar cells, both ecotoxicity and human toxicity should be taken into account during the design of emerging solar cells.

This review limits in the most common impact indicators of solar cells such as energy consumption, GHG emissions, material and metal depletion, ecotoxicity and human toxicity. In fact, the life cycle impacts

and CdTe-panels. Energy 138, 1099–1111. https://doi.org/10.1016/j.energy.2017.07.031.

Vodapally, S.N., Ali, M.H., 2022. A comprehensive review of solar photovoltaic (PV) technologies, architecture, and its applications to improved efficiency. Energies 16, 319. https://doi.org/10.3390/en16010319.

Zhang, J., Gao, X., Deng, Y., Zha, Y., Yuan, C., 2017. Comparison of life cycle environmental impacts of different perovskite solar cell systems. Sol. Energy Mater. Sol. Cells 166, 9–17. https://doi.org/10.1016/j.solmat.2017.03.008.