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Aquatic Toxicology 237 (2021) 105900

Contents lists available at ScienceDirect

Aquatic Toxicology

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

Comparative toxicity of potential leachates from perovskite and silicon solar cells in aquatic ecosystems

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ARTICLE INFO

Keywords:
Perovskite solar cell
Ecotoxicity
Leachate
Si-based solar cell

ABSTRACT

Globally, perovskite solar cells (PSCs) represent a third-generation photovoltaic technology that is being increasingly implemented and commercialized. However, the biological impacts of leachates from PSCs are poorly understood. Therefore, the aim of this study was to investigate the ecotoxicity of PSC leachates compared with that of commercial Si-based solar cell (SBSC) leachates. We performed leaching assessments and aquatic bioassays using internationally recommended test species and measured and compared the ecotoxicity of PSC and SBSC leachates. As a result of the leaching analyses, Si, Pb, and Al were found to be the most leached elements from broken PSCs and SBSCs. The bioassays indicated that polycrystalline SBSC (p-Si) and monocrystalline SBSC (m-Si) leachates were more toxic to fish embryos than the PSC leachates and that water fleas were sensitive to m-Si leachates, but less sensitive to PSC and p-Si leachates. In addition, principle component analyses indicated that the ecotoxicity of solar cell leachates was related to either the Pb or Si content. This is the first comparative study of the potential ecotoxicity of PSC and SBSC leachates in aquatic ecosystems, and the results of which can be used in the environmentally safe commercialization of solar cells.

1. Introduction

Solar photovoltaic technology provides renewable energy and is an important tool in sustainable development. However, environmental concerns regarding the safety of solar cells exist because solar cells contain harmful materials. Solar cells have been installed on mountains, in fields, and even on the water as floating solar power plants (Power-Technology, 2021). In this context, it is critical that the field of ecotoxicological research recognizes the aquatic toxicities of compounds that can be leached from solar cells.

Perovskites are emergent and promising materials for photovoltaic technology (Nature, 2013; Science, 2013) because their power conversion efficiency is 25.6% (Jeong et al., 2021), which exceeds those of commercial Si and Cu–In–Ga–Se^{2-} solar cells (Ke and Kanatzidis, 2019). However, the potential toxicity of leachates from perovskite solar cells (PSCs) remains unclear (Kwak et al., 2020) despite studies that have raised concerns surrounding the toxicity of perovskite (Babayigit et al., 2016b; Park et al., 2016). For example, PbI_2 can leach from Pb-based perovskite (Hailegnaw et al., 2015; Babayigit et al., 2016a; Park et al., 2016; Kwak et al., 2020; Panthi et al., 2021), which has prompted investigations into the toxicity of PbI_2 and perovskite (Babayigit et al., 2016a; Benmessaoud et al., 2016; Zhou et al., 2018; Bae et al., 2019; Li et al., 2020; Patsiou et al., 2020a; Kwak et al., 2021). Moreover, an understanding of the ecotoxicological effects of existing solar cell leachates, such as from Si-based or Cd/Te-based solar cells, is also lacking (Kwak et al., 2020) although Si-based solar cells (SBSCs) are most commonly used solar cells (Energy, 2021). For example, very limited ecotoxicological studies of the effects of Cd/Te-based solar cell leachates (Tammaro et al., 2016) and SBSC leachates (Tammaro et al., 2016; Zhi et al., 2018) on freshwater species (algae, water fleas, and microorganisms) have been reported.

Thus, to address this knowledge gap, the aim of this study was to investigate the potential aquatic ecotoxicity of PSC leachates and to compare perovskite and commercial SBSC leachates. Two types of PSCs were fabricated in the laboratory and two types of SBSCs were purchased. Subsequently, the ecotoxicity of the respective leachates was

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https://doi.org/10.1016/j.aquatox.2021.105900
Received 3 April 2021; Received in revised form 9 June 2021; Accepted 10 June 2021
Available online 16 June 2021
0166-445X/

Table 1
Pb^{2+}, Si^{2+}, Al^{3+}, Ni^{2+}, Cu^{2+}, NH_4^+, Cl^-, and Br^- concentrations (mg/L) of the studied solar cell types.

Chemical	Solar cell type			
	PSC 1	PSC 2	p-Si	m-Si
Pb^{2+}	0.28	1.36	4.37	0.69
Si^{2+}	0.99	0.28	0.30	3.72
Al^{3+}	0.01	0.22	0.15	182.80
Ni^{2+}	0.02	0.12	0.01	0.01
Cu^{2+}	0.05	0.03	0.06	0.01
NH_4^+	0.00	0.04	0.00	0.05
Cl^-	0.26	0.92	0.57	0.46
Br^-	0.00	0.00	0.00	0.00
Analytic replication	1	2–4	1	1

PSC: perovskite solar cell; p-Si: polycrystalline Si-based solar cell; m-Si: monocrystalline Si-based solar cell.

investigated via bioassays using fish embryos and water fleas under realistic environmental scenarios. To the best of our knowledge, this is the first comparative study of the potential ecotoxicity of PSC and SBSC leachates that elucidates the potential ecotoxicity of the former.

2. Experimental

2.1. PSC preparation

Test PSCs were fabricated in the laboratory using glass treated with F-doped SnO_2, NiO_2, perovskite, [6,6] phenyl-C_{60}-butyric acid methyl ester ($C_{72}H_{14}O_2$, PCBM), bathocuproine (BCP, $C_{26}H_{20}N_2$), and Au. Perovskite films consisted of methylammonium lead triiodide ($MAPbI_3$). NiO_2, PCBM, and BCP were used as the hole transport, electron transport, and buffer layers, respectively. F-doped SnO_2 and Au were used as electrodes. The fabricated solar cells were encapsulated with SiO_2 layers deposited by plasma-enhanced chemical vapor deposition processes and Al_2O_3 layers deposited by plasma-enhanced atomic layer deposition processes, followed by glass encapsulation with resin. PSC 1 and PSC 2 were fabricated using the same process but were encapsulated with 10 and 4 mm of resin, respectively. In addition, PSC 1 and PSC 2 had slightly different perovskite active areas. Figure S1 shows the appearances of PSC 1 and PSC 2. Two commercial SBSCs [polycrystalline SBSC (p-Si) and monocrystalline SBSC (m-Si)] were purchased from the Korean online market (fabricated in Taiwan and Korea, respectively) to compare with the PSCs (Table S1).

2.2. Solar cell leaching procedure and material analyses

To simulate an accident scenario, the solar cells were cut into 1.5 mm × 0.8 mm pieces using a glass knife. According to the United States Environmental Protection Agency's toxicity characteristic leaching procedure (USEPA, 1992), a leaching solution containing CH_3COOH and NaOH was prepared, with a pH of 4.9. The ratio of broken solar cells to the leaching solution was 1:20 (w:v). After an 18 h leaching period (USEPA, 1992), the leachates were filtered using 0.7-μm glass fiber filters and analyzed to determine their ecotoxicity. Pb^{2+}, Si^{2+}, Al^{3+}, Ni^{2+}, and Cu^{2+} contents were analyzed using inductively coupled plasma atomic emission spectrometry (iCAP7400DUO, Thermo Fisher Scientific, Waltham, MA, U.S.A.; Ultima Expert, Jobin Yvon, France) or inductively coupled plasma mass spectrometry (Agilent 7800, Agilent, Santa Clara, CA, U.S.A.). Cl^- and Br^- contents were determined using ion chromatography (ICS-1600, DX-600, Thermo Fisher Scientific, Waltham, MA, U.S.A.). NH_4^+ levels were analyzed using a Spectroquant system (Nova 60, Merk Milipore, Burlington, MA, U.S.A.).

2.3. Fish embryo assays

Zebrafish (*Danio rerio*) was selected as a model fish and tested according to the modified organisation for Economic Co-operation and Development (OECD) guidelines (OECD, 2013; Kwak et al., 2016). The fish embryo assay was conducted using leachates at 0% (control), 1%, 5%, 10%, 25%, and 50% concentrations in an embryonic rearing solution ($MgSO_4$, 0.163 g/L; $CaCl_2{\bullet}2H_2O$, 0.04 g/L; KCl, 0.03 g/L; NaCl, 1 g/L; and pH, 7.0). The embryonic rearing solution constituents were introduced equally into the test solution, after which the pH was adjusted to 7.0 ± 0.2 before embryo exposure. One embryo was exposed to 100 μL of the test solution in a 96-well plate at 4–5 h post fertilization. Test well plates were maintained at 28 °C under a 16:8 light:dark photoperiod. The hatching rate was recorded. Data on mortality, tail malformation, peritoneal edema, pericardial edema, hemostasis, abnormal eyes, airbladder development, and developmental stages were recorded seven days post fertilization under a stereomicroscope. Ten replicates were performed for each leachate concentration, and the assay for each concentration was repeated two to eight times.

2.4. Water flea assay

Water fleas (*Daphnia magna*, from the National Institute of Environmental Research, Incheon, South Korea), were selected as a model freshwater invertebrate and tested according to the guidelines of the OECD (OECD, 2004) and the Korean Ministry of Environment (MOE, 2017). The water flea assay was conducted at leachate concentrations of 0% (control), 6.25%, 12.5%, 25%, and 50% in modified moderate hard water ($MgSO_4$, 0.06 g/L; $CaSO_4{\bullet}0{\bullet}5H_2O$, 0.0788 g/L; KCl, 0.004 g/L; $NaHCO_3$, 0.096 g/L; vitamin B12, 1 μg/L; Na_2SeO_4, 4.3 μg/L; and pH, 8)

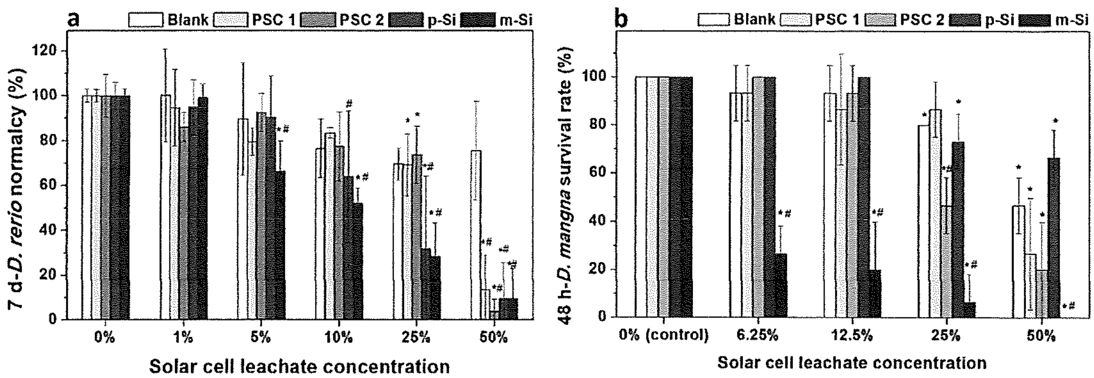

Fig. 1. Effects of the four solar cell leachates (perovskite solar cell (PSC) 1, PSC 2, monocrystalline Si-based solar cell (m-Si), and polycrystalline Si-based solar cell (p-Si)) on (a) zebrafish embryos (*Danio rerio*) and (b) water fleas (*Daphnia magna*). The control (0%) contained only the culture medium. Blank indicates a leaching solution that contained CH_3COOH and NaOH. # indicates a significant difference compared with the blank at the same concentration. * indicates a significant difference compared with the control group ($p < 0.05$).

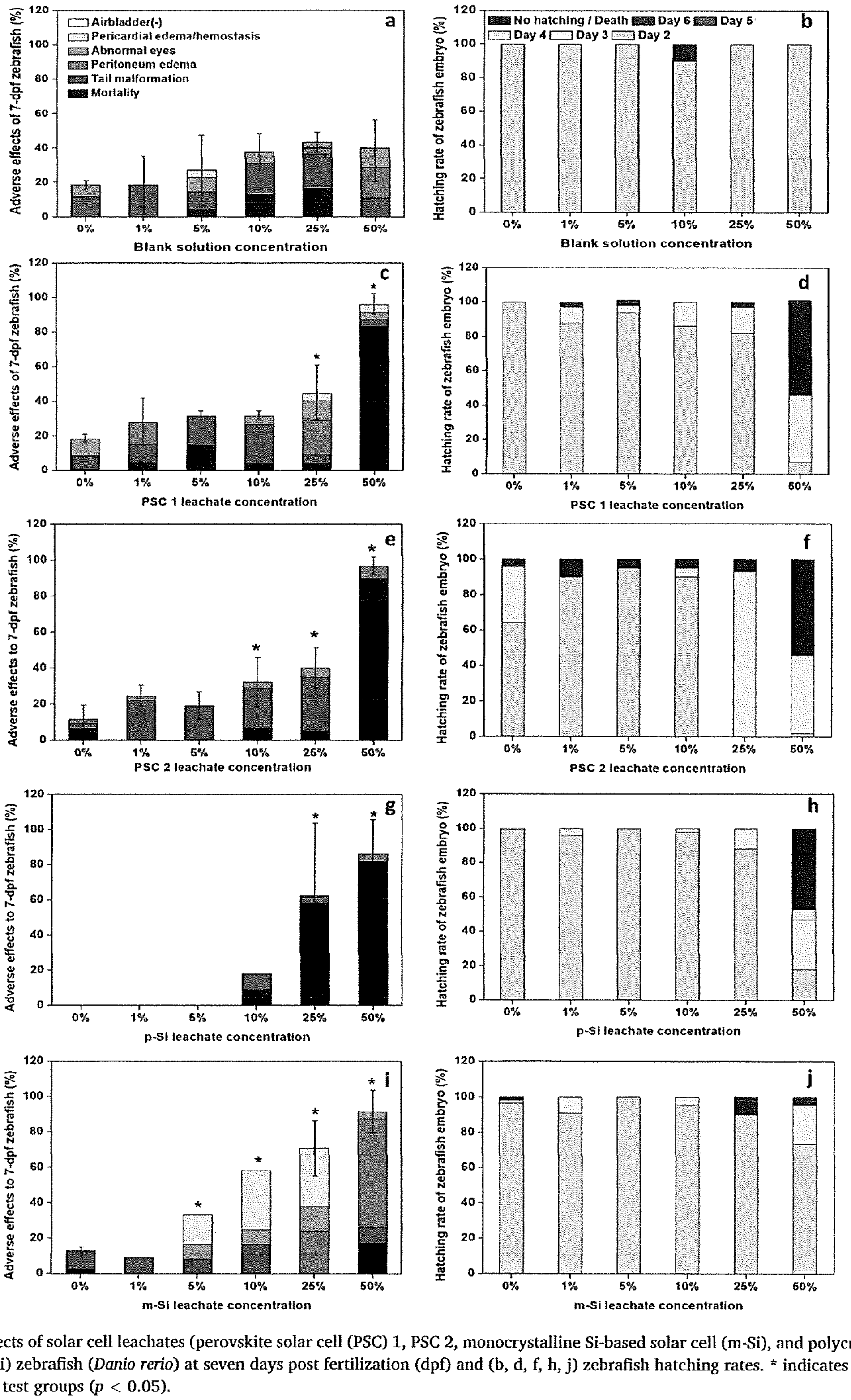

Fig. 2. Total adverse effects of solar cell leachates (perovskite solar cell (PSC) 1, PSC 2, monocrystalline Si-based solar cell (m-Si), and polycrystalline Si-based solar cell (p-Si)) on (a, c, e, g, i) zebrafish (*Danio rerio*) at seven days post fertilization (dpf) and (b, d, f, h, j) zebrafish hatching rates. * indicates a significant difference between the control and test groups ($p < 0.05$).

(USEPA, 2002). The pH of the test solution was adjusted to 8.0 before daphnid exposure. Five neonates (< 24 h old) were exposed to 10 mL of the test solution in a 35-mL glass vial. Test vessels were maintained at 21 °C under a 16:8 light:dark photoperiod. The survival rate was measured after 48 h. Three replicates were performed for each leachate concentration.

2.5. Data analyses

The effective concentration at 50% (EC_{50}) was estimated using the trimmed Spearman–Karber method (Hamilton et al., 1977; USEPA, 1999b) at a 95% significance level ($p < 0.05$). Means were compared using the Dunnett's method (USEPA, 1999a) based on a one-way analysis of variance ($p < 0.05$). The toxic unit (TU) was defined as 100

Table 2
Effective concentration at 50% (EC_{50}) and toxic unit (TU) values for leachates derived from the four solar cells, i.e., perovskite solar cell (PSC) 1, PSC 2, monocrystalline Si-based solar cell (m-Si), and polycrystalline Si-based solar cell (p-Si), in fish embryo (seven days post fertilization) and water flea (48 h) assays. Asterisks (*) indicate higher ecotoxicity to fish embryos or water fleas with values of $EC_{50} < 10\%$ or $TU > 16$.

Solar cell	EC_{50} (%)		TU	
	Fish embryo	Water flea	Fish embryo	Water flea
PSC 1	25.75 (21.82–30.38)	25.48 (22.39–29.01)	3.9	3.9
PSC 2	26.01 (22.93–29.50)	38.33 (35.74–41.11)	3.8	2.6
p-Si	15.20 (13.27–17.41)	> 50	6.6	3.3
m-Si	9.71 (8.07–11.68) *	< 6.25*	10.3*	> 16*

divided by the EC_{50} or the mortality multiplied by 0.02 when EC_{50} could not be obtained when the mortality was 10%–49% in the 100% test solutions (MOE, 2017). Chemical speciation of the test solution at the highest leachate concentration (50%) was estimated using a chemical equilibrium model (Visual MINTEQ ver. 3.1, KTH, Stockholm, Sweden). Input data for the chemical equilibrium model are described in Tables S1–S2. By applying the fish embryo TU, water flea TU, and chemical speciation of the leachates from three solar cell types (PSC1, PSC2, and p-Si), principal component analyses (PCAs) were performed using the SPSS software package (ver. 24, IBM) to determine the factors that affect the ecotoxicity of the solar cell leachates, except for m-Si, which had Al concentration outliers. Principle components of up to 60%–100% of the cumulative percentage were selected (Table S3).

3. Results

3.1. Chemical leakage from broken solar cells

We performed a toxicity characteristic leaching procedure to investigate the leakage of chemicals from four solar cell types (PSC 1, PSC 2, p-Si, and m-Si). Eight chemicals (Pb^{2+}, Si^{2+}, Al^{3+}, Ni^{2+}, Cu^{2+}, NH_4^+, Cl^-, and Br^-) were targeted, considering the inorganic components in the tested solar cells (Table 1). Most of the target chemicals were detected at concentrations ranging from micrograms to milligrams per liter, except for Br (Table 1). Pb and Si were the most leachable components in the PSC 1, PSC 2, and p-Si leachates, with concentrations of 0.28 mg/L Pb and 0.99 mg/L Si measured in the PSC 1 leachate, 1.36 mg/L Pb and 0.28 mg/L Si measured in the PSC 2 leachate, and 4.37 mg/L Pb and 0.30 mg/L Si measured in the p-Si leachate. In this context, we confirmed that the Pb originated from the perovskite in the PSC and from busbar in the SBSC. The m-Si leachate had a high Al concentration (182.8 mg/L) and Si and Pb concentrations of 3.72 and 0.69 mg/L, respectively. The Si in the PSC leachates originated from the glass and SiO_2 encapsulation, while the Pb in the SBSC leachates was associated with the busbar (Table S4 and Fig. 1). However, the source of Al in the leachates from the purchased m-Si was unclear. Subsequently, we found that 71 and 94 chemical species were present in the most concentrated leachate (50%) in the fish embryo test solution (Table S5) and water flea test solution (Table S6), respectively, based on the chemical equilibrium model analysis (Tables S1–S3).

3.2. Ecotoxicity of PCS and SBSC leachates

The ecotoxicity of the PCS and SBSC leachates was compared with that of the control (0%) or blank leaching solution because the 100% leaching solution contained 1480 mg/L Na^+ (USEPA, 1992). In the bioassays, *D. rerio* could tolerate the strongest leaching solution (50%), but the survival rate of *D. magna* decreased in the 25% and 50% leaching solutions (Fig. 1). *D. rerio* tolerated the blank leaching solution up to 50%; however, the survival rate of *D. magna* decreased in the 25% and 50% leaching solutions because of a high Na^+concentration in the 100% leaching solution (1480 mg/L). Therefore, we determined that the observed symptoms should be compared with the blank data.

The fish embryo assay revealed that neither PSC 1 nor PSC 2 affected the fish embryos at concentrations of up to 25%; however, at concentrations of 50%, the leachates caused mortality and severe deformities in the fish embryos at seven days post fertilization. Both of the SBSC leachates (p-Si and m-Si) were more ecotoxic than the PSC leachates (Figs. 1 and 2). Pericardial edema, hemostasis, peritoneum edema, tail malformation, and abnormal eyes developed in the zebrafish sac fry when they were exposed to 5% m-Si leachates, which was lower than the concentrations of the other leachates. Similarly, the m-Si leachates were significantly more toxic to *D. magna*, which could tolerate the PSC 1, PSC 2, and p-Si leachates.

EC_{50} was estimated based on the dose-response curve shown in Fig. 1, the data for which are listed in Table 2. The EC_{50} values of PSC 1, PSC 2, p-Si, and m-Si were 25.75%, 26.01%, 15.2%, and 9.71%, respectively, for fish embryos at seven days post fertilization, and 25.48%, 38.33%, > 50%, and 6.25%, respectively, for water fleas. The lowest EC_{50} and highest TU values were measured in the m-Si leachates for both test species. These results indicate that, among the test leachates, the m-Si leachates were most toxic to both the zebrafish embryos and the water fleas.

4. Discussion

PbI_2 is a well-known compound that is leachable from Pb-based perovskite (Hailegnaw et al., 2015; Babayigit et al., 2016a; Park et al., 2016; Zhu et al., 2016; Kwak et al., 2020, 2021). Previous studies have focused mostly on leachable compounds (Bae et al., 2019; Li et al., 2020), perovskite nanoparticles, or perovskite powders (Babayigit et al., 2016a; Benmessaoud et al., 2016; Zhou et al., 2018; Bae et al., 2019; Patsiou et al., 2020a; Zhai et al., 2020). As various chemical compounds (e.g., PbI_2 or SnI_2) and perovskite are not readily released into the environment under realistic exposure scenarios because commercialization has started from laboratories to the markets (Roy et al., 2020), the toxicity of PSC leachates has not been reported previously. This study emphasizes that the toxicity of PSC leachates should be investigated under environmentally relevant exposure scenarios, such as broken panels generated by fires or typhoon accidents (Physorg, 2013; Kwasinski et al., 2019). We performed leaching assessments and bioassays, measured the ecotoxicity of the PSC and SBSC leachates, and estimated the EC_{50} and TU values for fish embryos and water fleas (Table 2). Some countries, including France (Pandard and Römbke, 2013; INERIS, 2016), Germany (UBA, 2013), and Italy (ISPRA, 2012), have assessment protocols for evaluating the ecotoxicity of solid wastes using progressive aquatic bioassays (e.g., *Vibrio fischeri, Brachionus calyciflorus, Desmodesmus subspicatus, Pseudokirchneriella subcapitata, Daphnia magna, Ceriodaphnia dubia*, and *Poecilia reticulata*). These countries regard leachates with EC_{50} values less than 10% as ecotoxic (ISPRA, 2012; Pandard and Römbke, 2013; UBA, 2013; INERIS, 2016). In this study, we found solar cell leachates with EC_{50} values exceeding 10% or TU values of 10 (ISPRA, 2012; Pandard and Römbke, 2013; UBA, 2013; INERIS, 2016). Among the studied leachates, the m-Si leachates were the most ecotoxic to both the fish embryos and water fleas (Table 2). However, a comparison of the toxicity data between the commercial SBSCs and fabricated PSCs did not yield significant results.

Subsequently, to determine the chemicals relevant to the ecotoxicity of solar cell leachates, a PCA was conducted using the water flea and fish embryo TU values, as well as the Pb^{2+}, Si^{2+}, Al^{3+}, Ni^{2+}, Cu^{2+}, NH_4^+, and Cl^- concentrations. Fig. 3 shows the PCA loading plots of the ecotoxicity data (TU values) and the leachable and existing chemicals. Some Pb and Si species were positively correlated with the TU values of the test

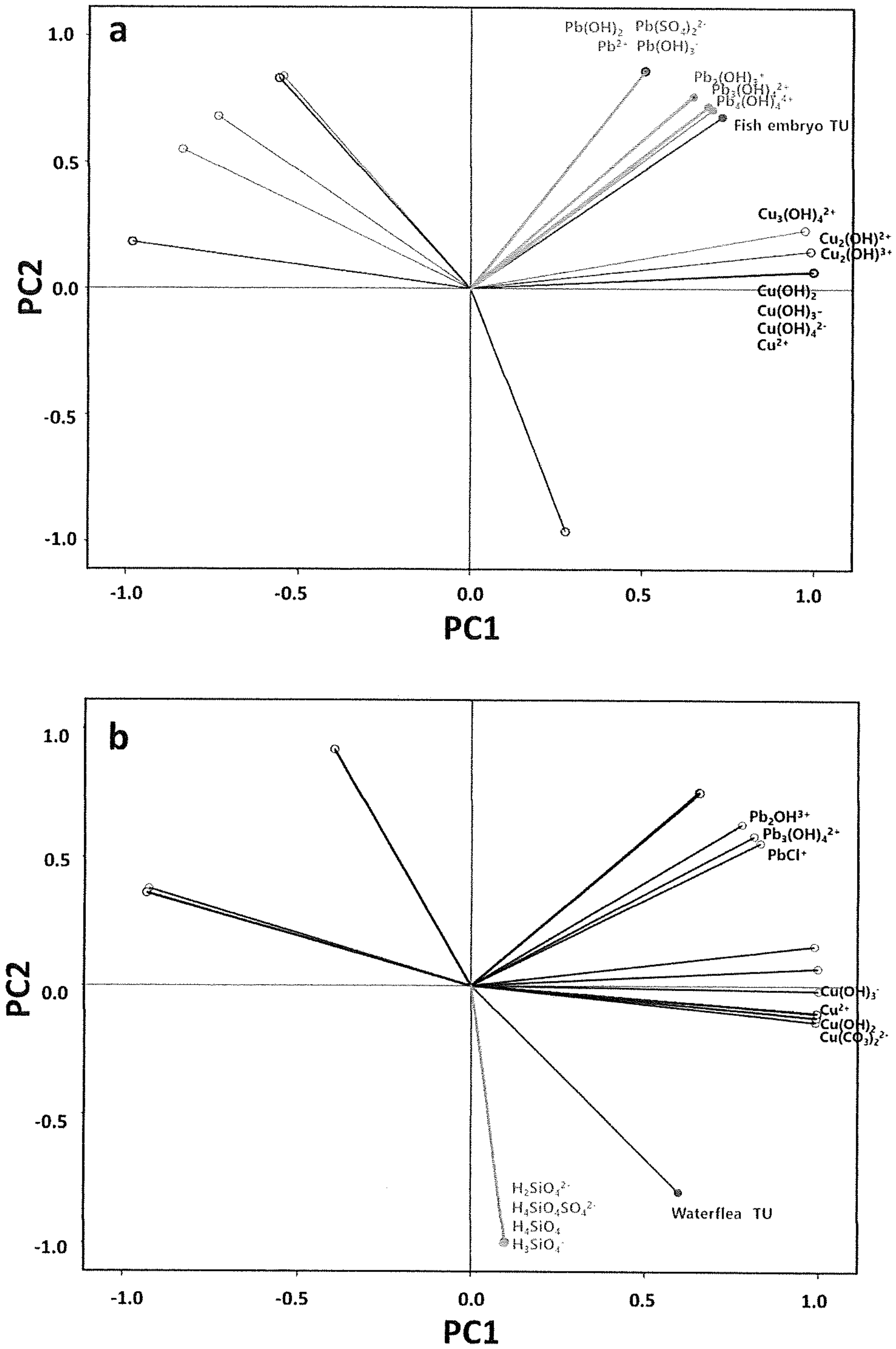

Fig. 3. Principal component analysis (PCA) loading plots of the (a) fish embryo toxic unit (TU) values and (b) water flea TU values based on three tested solar cells (PSC1, PSC2, and p-Si). Values in Tables S4 and S5 were used for the PCA in (a) and (b), respectively. PC 1: first principal component; PC 2: second principal component.

species, which indicates that these ions strongly influenced the ecotoxicity of the studied leachates (Fig. 3). As shown in Fig. 3a, Pb chemical species could be leached from perovskite and p-Si during fires or typhoon accidents (Physorg, 2013; Kwasinski et al., 2019); Pb species, such as $Pb(OH)_2$, $Pb(SO_4)_2^{2-}$, Pb^{2+}, $Pb(OH)_3^-$, $Pb_2(OH)^{3+}$, and $Pb_4(OH)_4^{4+}$, were positively correlated with fish embryonic toxicity. Similar to the correlation between fish embryonic and Pb chemical species, recent research (Kwak et al., 2021) has also reported that when fish embryos were exposed to PbI_2, deformity and growth inhibition in two fish embryos and sac fry (*D. rerio* and *Oryzias latipes*) were mostly related to Pb^{2+}, based on the chemical equilibrium model. In particular, evidence for the embryonic toxicity of Pb-based PSCs or PbI_2 on zebrafish *D. rerio* have been reported consistently (Bae et al., 2019; Patsiou et al., 2020b; Kwak et al., 2021). In the case of SBSCs, it has been determined that the Pb originating from the busbar contributed to fish embryonic toxicity.

For water flea toxicity, Si species, including $H_2SiO_4^{2-}$, $H_4SiO_4SO_4^{2-}$, H_4SiO_4, and H_3SiO^{4-}, exhibited positive correlations in this study. Si is known to be toxic to human health and that of aquatic ecosystems

(Wang et al., 2016; CDC, 2019). In contrast, Tammaro et al. (2016) observed that Pb, Al, and Cr were leached from Si-based thin film panels and caused toxicity in *D. magna*. The difference between the contributing toxic compounds to *D. magna* in this study (Si species) and previous studies (Pb, Al, and Cr) (Tammaro et al., 2016) might be because of the different types of tested solar cells. This study analyzed PSCs and SBSCs, while Tammaro et al. (2016) assessed amorphous silicon thin film panels.

5. Conclusions

In this study, we found that Si, Pb, and Al were the most leachable elements from broken PSCs and SBSCs. In particular, principle component analyses indicated that the ecotoxicity of solar cell leachates was related to either the Pb or Si content. Thus, this study reached several conclusions: 1) heavy metals can be emitted to the aquatic environment from perovskite or SBSCs in broken panel or rainfall scenarios; 2) Pb or Si ions are the key chemical species related to aquatic toxicity; and 3) measures to prevent Pb and Si release is necessary for the safe use of perovskites. Furthermore, this is the first comparative study of the potential ecotoxicity of PSC and SBSC leachates, and it provides new information on the potential ecotoxicity of the former. Therefore, despite the positive traits of PSCs, scientists and markets should consider the findings of this study to mitigate accidental spills of leachable components and to promote safe commercialization.

We demonstrated that the SBSC leachates were more toxic than the PSC leachates to fish embryos and water fleas. Nonetheless, this study had certain limitations, as only commercialized SBSCs and fabricated PSCs were compared. Future toxicological research using commercial PSCs should predict leachate spills from broken PSCs to prevent the occurrence of such accidents.

Author contribution statement

J.I. Kwak performed the experiments and drafted the first manuscript. L. Kim, T.-Y. Lee, G. Panthi, and S. Han performed the experiments. The project was planned and the manuscript was edited by Y.-J. An, S.-W. Jeong, and H. Chae. The project was supervised by Y.-J. An.

Funding

This study was supported by the National Research Foundation under the Ministry of Science and ICT, Korea [2016M3A6A7945504 and 2018M3A6A7074641].

Appendix A. Supporting information

Supplementary data associated with this article can be found at

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

We would like to thank the Korea Basic Science Institute (KBSI) for the ICP-AES analyses and Jieun Lee (Konkuk University) and Jiho Jang (Sungkyunkwan University) for their assistance during the experiments.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.aquatox.2021.105900.

References

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, 18721.
Babayigit, A., Ethirajan, A., Muller, M., Conings, B., 2016b. Toxicity of organometal halide perovskite solar cells. Nat. Mater. 15, 247.
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, 4242.
Benmessaoud, I.R., Mahul-Mellier, A.-L., Horváth, E., Maco, B., Spina, M., Lashuel, H.A., Forró, L., 2016. Health hazards of methylammonium lead iodide based perovskites: cytotoxicity studies. Toxicol. Res. 5, 407–419.
CDC, 2019. Evaluation of silica exposures during drywall sanding.
Energy, U.D.o., 2021. Crystalline silicon photovoltaics research. https://www.energy.gov/eere/solar/crystalline-silicon-photovoltaics-research (Last accessed 05-Jun-2021).
Hailegnaw, B., Kirmayer, S., Edri, E., Hodes, G., Cahen, D., 2015. Rain on methylammonium lead iodide based perovskites: possible environmental effects of perovskite solar cells. J. Phys. Chem. Lett. 6, 1543–1547.
Hamilton, M.A., Russo, R.C., Thurston, R.V., 1977. Trimmed Spearman-Karber method for estimating median lethal concentrations in toxicity bioassays. Environ. Sci. Technol. 11, 714–719.
INERIS, 2016. Classification réglementaire des déchets Guide d'application pour la caractérisation en dangerosité.
ISPRA, 2012. Atterie di test per la caratterizzazione ecotossicologica dei rifiuti: stato dell'arte.
Jeong, J., Kim, M., Seo, J., Lu, H., Ahlawat, P., Mishra, A., Yang, Y., Hope, M.A., Eickemeyer, F.T., Kim, M., Yoon, Y.J., Choi, I.W., Darwich, B.P., Choi, S.J., Jo, Y., Lee, J.H., Walker, B., Zakeeruddin, S.M., Emsley, L., Rothlisberger, U., Hagfeldt, A., Kim, D.S., Grätzel, M., Kim, J.Y., 2021. Pseudo-halide anion engineering for α-$FAPbI_3$ perovskite solar cells. Nature 592, 381–385.
Ke, W., Kanatzidis, M.G., 2019. Prospects for low-toxicity lead-free perovskite solar cells. Nat. Commun. 10, 965.
Kwak, J.I., Cui, R., Nam, S.-H., Kim, S.W., Chae, Y., An, Y.-J., 2016. Multispecies toxicity test for silver nanoparticles to derive hazardous concentration based on species sensitivity distribution for the protection of aquatic ecosystems. Nanotoxicology 10, 521–530.
Kwak, J.I., Kim, L., An, Y.-J., 2021. Sublethal toxicity of PbI_2 in perovskite solar cells to fish embryos (*Danio rerio* and *Oryzias latipes*): deformity and growth inhibition. Sci. Total Environ. 771, 145388.
Kwak, J.I., Nam, S.-H., Kim, L., An, Y.-J., 2020. Potential environmental risk of solar cells: current knowledge and future challenges. J. Hazard. Mater. 392, 122297.
Kwasinski, A., Andrade, F., Castro-Sitiriche, M.J., O'Neill-Carrillo, E., 2019. Hurricane maria effects on Puerto Rico electric power infrastructure. IEEE Power Energy Technol. Syst. J. 6, 85–94.
Li, J., Cao, H.-L., Jiao, W.-B., Wang, Q., Wei, M., Cantone, I., Lü, J., Abate, A., 2020. Biological impact of lead from halide perovskites reveals the risk of introducing a safe threshold. Nat. Commun. 11, 310.
MOE, S.K., 2017. Water quality pollution standard test method. acute toxicity test method of the *Daphnia magna* straus (Cladocera, Crustacea).
Nature, 2013. 365 days: nature's 10. Ten people who mattered this year. Nature 504, 357–365.
OECD, 2004. OECD TG No. 202 *Daphnia* sp. acute immobilisation test.
OECD, 2013. OECD TG No. 236 Fish, Fish embro acute toxicity (FET) test.
Pandard, P., Römbke, J., 2013. Proposal for a "Harmonized" strategy for the assessment of the HP 14 property. Integr. Environ. Assess. Manag. 9, 665–672.
Panthi, G., Bajagain, R., An, Y.-J., Jeong, S.-W., 2021. Leaching potential of chemical species from real perovskite and silicon solar cells. Process Saf. Environ. Protect. 149, 115–122.
Park, N.-G., Grätzel, M., Miyasaka, T., Zhu, K., Emery, K., 2016. Towards stable and commercially available perovskite solar cells. Nat. Energy 1, 16152.
Patsiou, D., del Rio-Cubilledo, C., Catarino, A.I., Summers, S., Fahmi, A.M., Boyle, D., Fernandes, T.F., Henry, T.B., 2020a. Exposure to Pb-halide perovskite nanoparticles can deliver bioavailable Pb but does not alter endogenous gut microbiota in zebrafish. Sci. Total Environ., 136941
Patsiou, D., del Rio-Cubilledo, C., Catarino, A.I., Summers, S., Mohd Fahmi, A., Boyle, D., Fernandes, T.F., Henry, T.B., 2020b. Exposure to Pb-halide perovskite nanoparticles can deliver bioavailable Pb but does not alter endogenous gut microbiota in zebrafish. Sci. Total Environ. 715, 136941.
Physorg, 2013. Dutch roof fire warning for 650,000 solar panels.
Power-Technology, 2021. World's biggest floating solar farms. https://www.power-technology.com/features/worlds-biggest-floating-solar-farms/ (Last update 23-Feb-2021).
Roy, P., Kumar Sinha, N., Tiwari, S., Khare, A., 2020. A review on perovskite solar cells: evolution of architecture, fabrication techniques, commercialization issues and status. Solar Energy 198, 665–688.
Science, 2013. Newcomer juices up the race to harness sunlight. Science 342, 1438–1439.
Tammaro, M., Salluzzo, A., Rimauro, J., Schiavo, S., Manzo, S., 2016. Experimental investigation to evaluate the potential environmental hazards of photovoltaic panels. J. Hazard. Mater. 306, 395–405.
UBA, 2013. Recommendations for the ecotoxicological characterization of wastes.
USEPA, 1992. SW-846 Test methods for evaluating solid wastes. physical/chemical methods, method 1311. Toxicity characteristic leaching procedure.

USEPA, 1999a. Dunnett program version 1.5 users' manual, in, U. S. EPA, environmental monitorign systems laboratory, Ecological monitoring research division, Cincinnati, Ohio.
USEPA, 1999b. Trimmed Spearman-Karber estimation of LC50 values users' manual, in, U. S. EPA, office of research and development, National exposure research laboratory-ecosystems research division, Center for exposure assessment modeling (CEAM), Athens, Georgia.
USEPA, 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. EPA 821/R-02/013. Washington, DC.
Wang, Y., Kalinina, A., Sun, T., Nowack, B., 2016. Probabilistic modeling of the flows and environmental risks of nano-silica. Sci. Total Environ. 545-546, 67–76.
Zhai, Y., Wang, Z., Wang, G., Peijnenburg, W.J.G.M., Vijver, M.G., 2020. The fate and toxicity of Pb-based perovskite nanoparticles on soil bacterial community: impacts of pH, humic acid, and divalent cations. Chemosphere 249, 126564.
Zhi, B., Mishra, S., Hudson-Smith, N.V., Kortshagen, U.R., Haynes, C.L., 2018. Toxicity evaluation of boron- and phosphorus-doped silicon nanocrystals toward *Shewanella oneidensis* MR-1. ACS Appl. Nano Mater. 1, 4884–4893.
Zhou, T., Fan, W., Liu, Y., Wang, X., 2018. Comparative assessment of the chronic effects of five nano-perovskites on *Daphnia magna*: a structure-based toxicity mechanism. Environ. Sci.: Nano 5, 708–719.
Zhu, Z., Hadjiev, V.G., Rong, Y., Guo, R., Cao, B., Tang, Z., Qin, F., Li, Y., Wang, Y., Hao, F., Venkatesan, S., Li, W., Baldelli, S., Guloy, A.M., Fang, H., Hu, Y., Yao, Y., Wang, Z., Bao, J., 2016. Interaction of organic cation with water molecule in perovskite $MAPbI_3$: from dynamic orientational disorder to hydrogen bonding. Chem. Mater. 28, 7385–7393.