Supplementary Information

On Biosafety of Sn-containing Halide Perovskites

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Key words: perovskite; toxicity evaluation; tin based; lead free.

Experimental design:

Since surface properties[1-5] play an important role for the toxicity evaluation of chemicals, to eliminate the effect of surface ligands of perovskite, the intake method utilized by Li *et al*[6] has been adopted with slight modification. They[6] employed the perovskite precursors (PbI_2 & MAI for $MAPbI_3$ and SnI_2 & MAI for $MASnI_3$) to represent the perovskite, thus the influence of surface ligand can be avoid. This method is reasonable as the existence of water and moisture can accelerate the decomposition of perovskite towards the precursors. To mimic the practical application condition where the perovskites $MASnI_3$ ($MAPbI_3$) are released from the solar cell and dissolved into the rainwater, we dissolved the MAI and SnI_2 (PbI_2) or SnI_2 powder directly into water and the resulted solution were intraperitoneally injected into the BALB/c mice very day for 30 days.

Accumulation analysis of tin and lead in the mice body:

Since the heavy metal can accumulate in the body over prolonged periods of time, we analyze the accumulation effect for both lead and tin-based halide perovskite.

As the appearance of accumulation effect is related to the intake concentration, we carried out our examination under different ingestion concentration (daily intake of 2 mg/kg and 0.1 mg/kg) for both Pb and Sn. We observed obvious accumulation when the mice are treated with 2 mg/kg of Pb from lead containing halide perovskite per day (30 days), as revealed by the organ pictures and H&E staining. Specifically, the lead is accumulated in the liver, as seen in Figure S 2 and S 5. While the accumulation become not apparent when the daily ingestion of lead (from lead-based halide perovskite) decreased to 0.1 mg/kg (30 days), as presented in Figure S 4 and R 6. Instead, for Sn intake, neither 2 mg/kg nor 0.1 mg/kg of daily injection (30 day) from tin containing halide perovskite will cause obvious accumulation in the body, as exhibited in Figure S 1, S 3, S 5, and S 6.

Even under a very high injection dose (2 mg/kg per day, 30 days) of Sn from tin-based perovskite, we still do not observe obvious accumulation in the body, therefore it is reasonable to conclude that under 0.1 mg/kg (much lower injection concentration) of Sn daily intake do not cause apparent accumulation in the body even over prolonged periods of time. On the contrary, in the condition of Pb intake, we recognized Pb accumulation in liver under daily intake of 2 mg/kg. Thus, we have reason to speculate that the disappearance of Pb accumulation in liver under daily ingestion of 0.1 mg/kg is due to the treatment time (*e.g.,*30 days) is not long enough to observe the accumulation. In the future, longer term observation (*e.g.,* several years) of Pb and Sn accumulation will need to be considered and performed.

Altogether, our results indicate that Sn is eliminated from the body, while Pb is accumulated in the body. They have different behaviors.

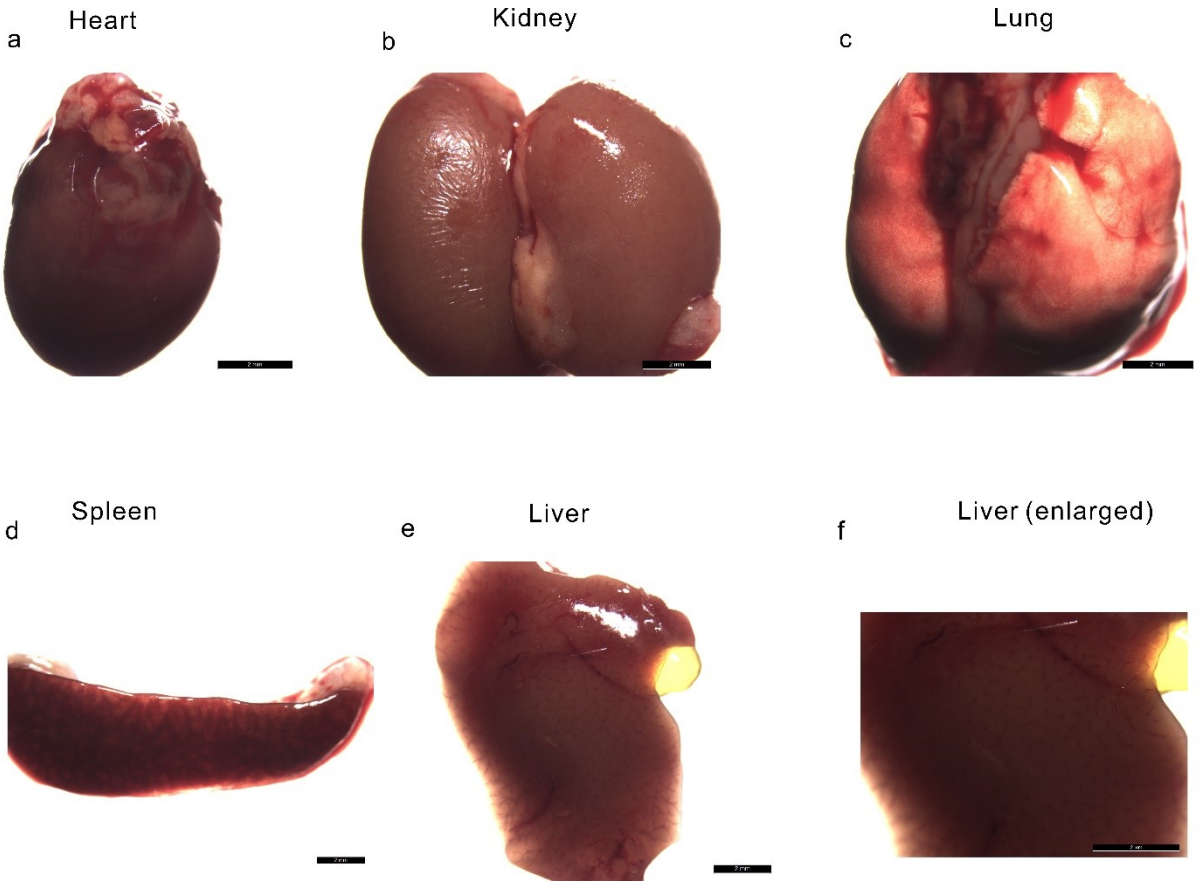


Figure S1 Main organ (heart, kidney, lung, spleen, and liver) pictures of the mice after treated with Sn (from tin-based halide perovskite $MASnI_3$) with a daily injection of 2 mg/kg (30 days). We do not observe obvious accumulation of tin in the main organs. Scale bar: 2 mm, (n=4 mice/per group)

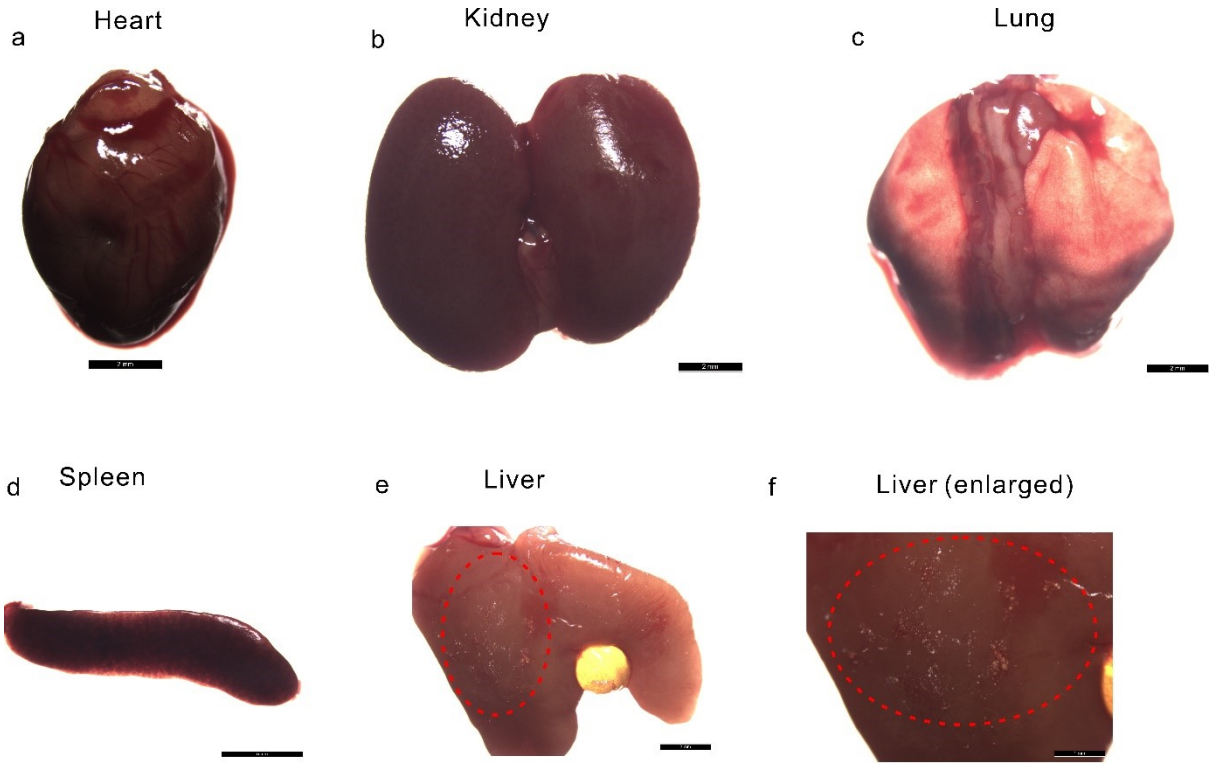


Figure S2 Main organ (heart, kidney, lung, spleen, and liver) pictures of the mice after treated with Pb (from lead-based halide perovskite $MAPbI_3$) with a daily injection of 2 mg/kg (30 days). The accumulation of Pb in the liver can be clearly seen (Figure e and f, highlighted by the red dashed line). Scale bar: 2 mm for a, b, c, e; 5 mm for d; 1 mm for f (n=4 mice/per group)

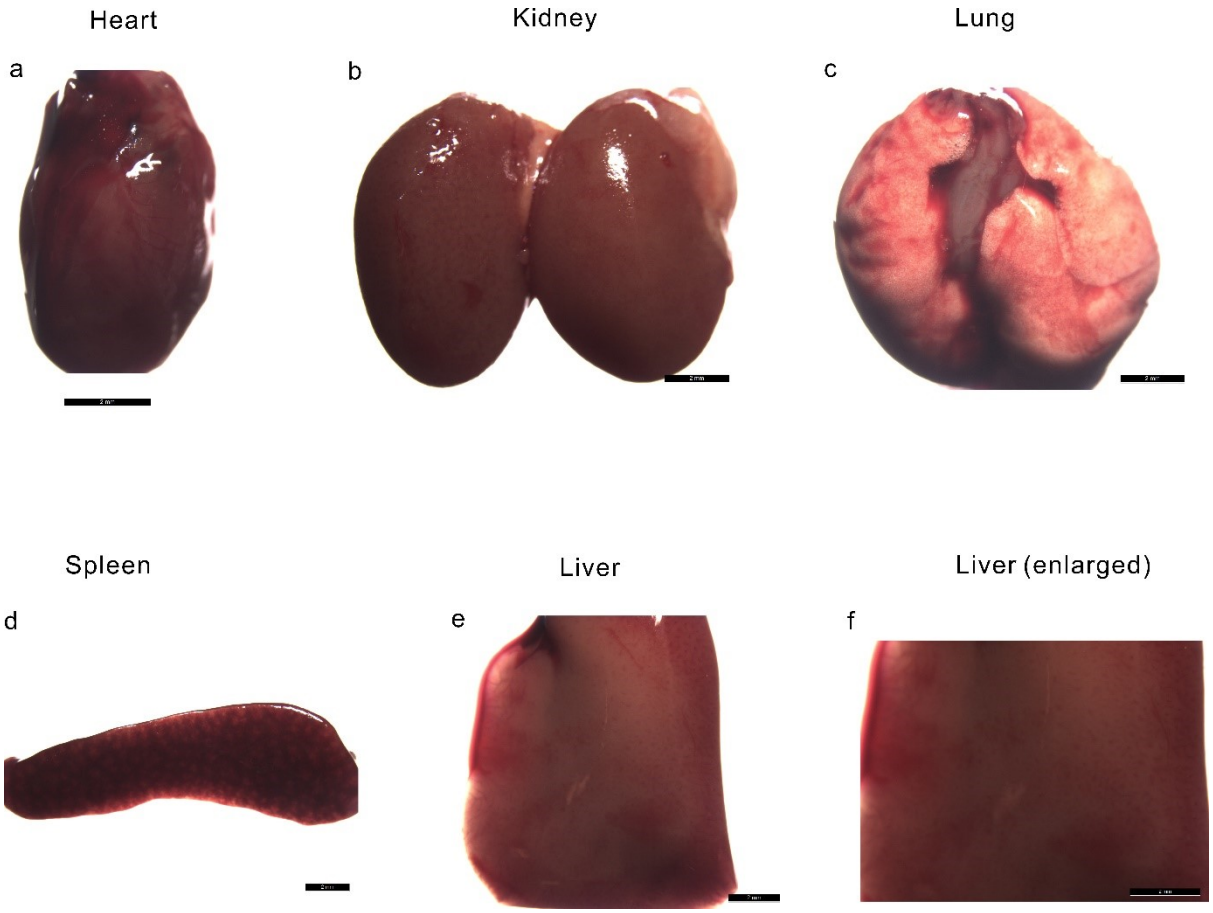


Figure S3 Main organ (heart, kidney, lung, spleen, and liver) pictures of the mice after treated with Sn (from tin-based halide perovskite $MASnI_3$) with a daily injection of 0.1 mg/kg (30 days). We do not observe obvious accumulation of tin in the main organs. Scale bar: 2 mm, (n=4 mice/per group)

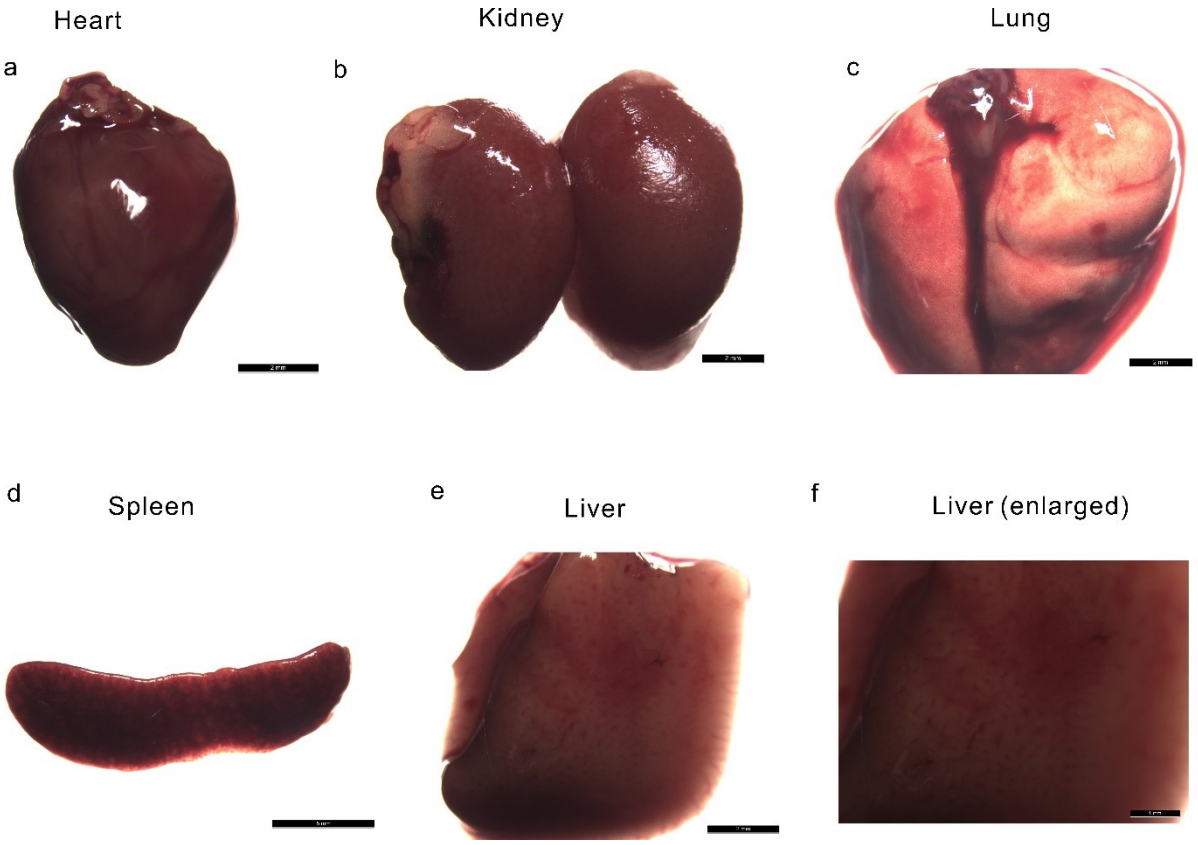


Figure S4 Main organ (heart, kidney, lung, spleen, and liver) pictures of the mice after treated with Pb (from lead-based halide perovskite $MAPbI_3$) with a daily injection of 0.1 mg/kg (30 days). We do not observe obvious accumulation of lead in the main organs. Scale bar: 2 mm for a, b, c, e; 5 mm for d; 1 mm for f (n=4 mice/per group).

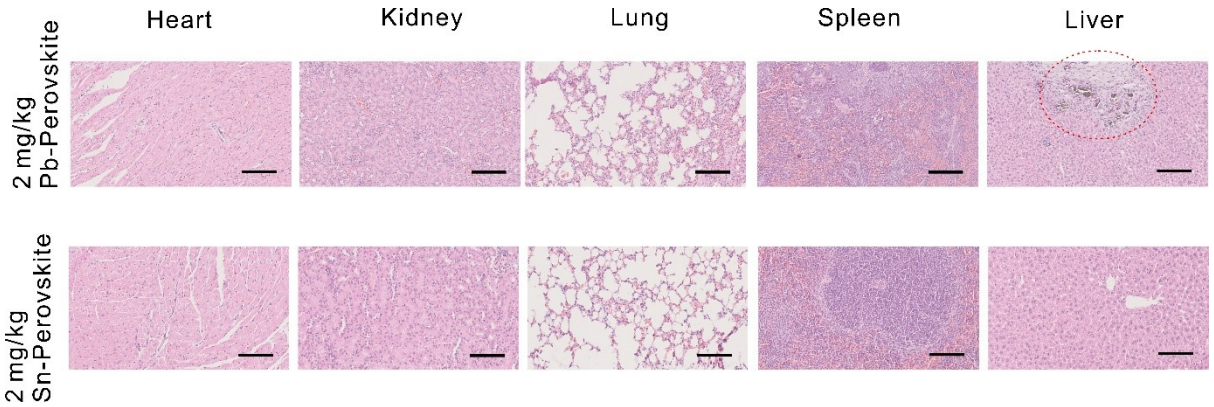


Figure S5 H&E stained tissue slices (heart, kidney, spleen, lung, and liver) of mice treated with Pb-based perovskite (daily injection: 2 mg/kg of Pb from halide perovskite, 30 days) and Sn-based perovskite (daily injection: 2 mg/kg of Sn from halide perovskite, 30 days). The Pb based halide perovskite injection result in the Pb accumulation in the mice liver, as highlighted by the red dashed line. Instead, we do not observe the obvious accumulation in the main organs from the Sn based halide perovskite treatment group. Scale bar: 100 μm. (n=4 mice/per group)

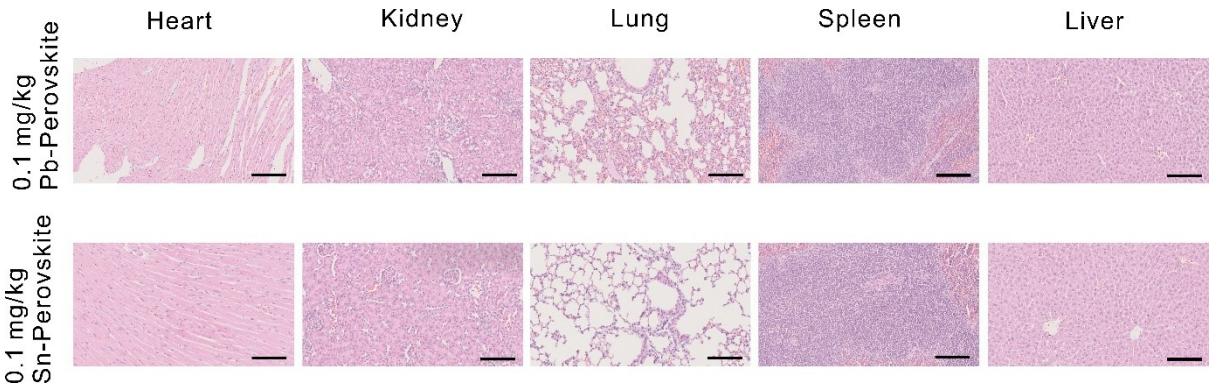
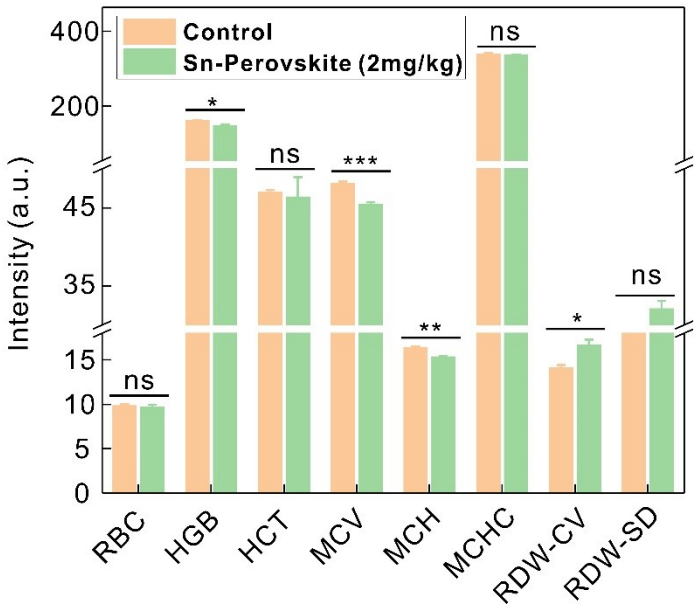


Figure S6 H&E stained tissue slices (heart, kidney, spleen, lung, and liver) of mice treated with Pb-based halide perovskite (daily injection: 0.1 mg/kg of Pb from perovskite, 30 days) and Sn-based halide perovskite (daily injection: 0.1 mg/kg of Sn from perovskite, 30 days). Scale bar: 100 μm. (n=4 mice/per group)

The Sn impact on the red blood cell

To explore the impact of Sn on red blood cell, the parameters of red blood cell including count of red blood cell (RBC), hemoglobin (HGB), hematocrit (HCT), mean corpuscular volume (MCV), mean corpuscular hemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), red cell distribution width - coefficient of variation (RDW-CV), & red cell distribution width- standard deviation (RDW-SD) have been tested. And the results are displayed in Figure S 7 and 8. It can be clearly seen (Figure S 7) that a daily intake of 2 mg/kg of tin (30 days) from tin-based halide perovskite led to significant decrease of MCV and MCH, which indicate the microcytic anemia and iron deficiency. The competition between Sn and iron in heme contribute to the iron deficiency and decreased MCV & MCH. Besides, the body's capability to generate red blood cell is also declined by the tin ingestion (daily intake: 2 mg/kg, 30 days) as uncovered by the decreased HGB and increased RDW-CV. Altogether, daily ingestion of 2 mg/kg of Sn from tin-based halide perovskite could cause the microcytic anemia, iron deficiency, and diminished red blood cell generation ability. While Figure S 8 show that all the above-mentioned injuries to red blood cell disappear when the Sn ingestion decreased to 0.1 mg/kg per day (30 days).

a

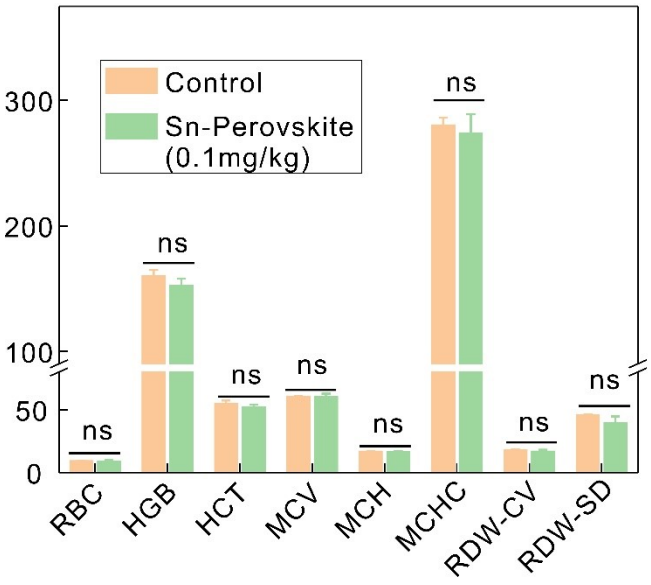


b

Indicator	P value
RBC (10^{12}/L)	0.297
HGB (g/L)	***0.042***
HCT (%)	0.418
MCV (fL)	***0.0006***
MCH (pg)	***0.0029***
MCHC (g/L)	0.171
RDW-CV (%)	***0.018***
RDW-SD (fL)	0.062

Figure S7 The impact of Sn perovskite on the red blood cell. Indicators of red blood cells: count of red blood cell (RBC), hemoglobin (HGB), hematocrit (HCT), mean corpuscular volume (MCV), mean corpuscular hemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), red cell distribution width - coefficient of variation (RDW-CV), & red cell distribution width- standard deviation (RDW-SD). Daily intake: 2 mg/kg of tin from halide perovskite. For plots a, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:P<0.05, **: P≤0.01, ***: P≤0.001, ****: P≤0.0001. ns: no significant difference.

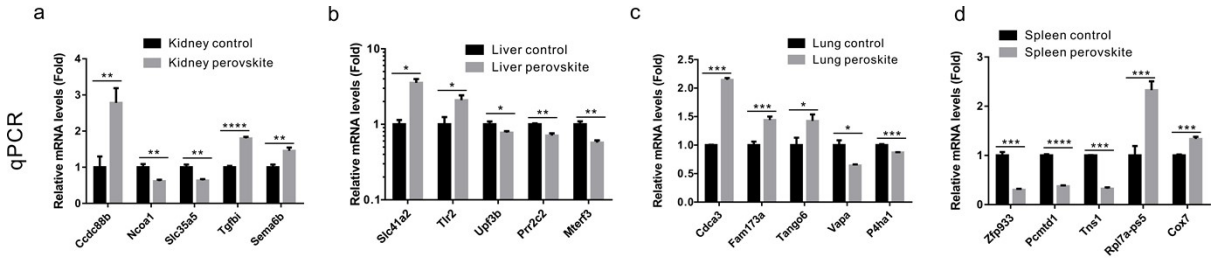
a



b

Indicator	P value
RBC (10^{12}/L)	0.405
HGB (g/L)	0.168
HCT (%)	0.196
MCV (fL)	0.483
MCH (pg)	0.202
MCHC (g/L)	0.356
RDW-CV (%)	0.217
RDW-SD (fL)	0.175

Figure S8 The impact of Sn perovskite on the red blood cell. Indicators of red blood cells: count of red blood cell (RBC), hemoglobin (HGB), hematocrit (HCT), mean corpuscular volume (MCV), mean corpuscular hemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), red cell distribution width - coefficient of variation (RDW-CV), & red cell distribution width- standard deviation (RDW-SD). Daily intake: 0.1 mg/kg of tin from halide perovskite. For plots a, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:P<0.05, **: P≤0.01, ***: P≤0.001, ****: P≤0.0001. ns: no significant difference.



qPCR

RNA seq

e Kidney

Gene ID	log2Fold Change	padj
Ccdc88b	2.33	0.000128 213
Ncoa1	−0.99	0.002448 17
Slc35a5	−1.14	0.004110 463
Tgfbi	1.68	0.000512 189
Sema6b	1.12	0.005852 759

f Liver

Gene ID	log2Fold Change	padj
Slc41a2	2.33	0.000004 89
Tlr2	1.93	0.000706 76
Upf3b	−1.34	0.004071 163
Prrc2c	−1.04	0.007394 242
Mterf3	−1.23	0.002027 589

g Lung

Gene ID	log2Fold Change	padj
Cdca3	1.21	0.002411 43
Fam173a	0.69	0.006997 619
Tango6	0.83	0.009887 443
Vapa	−0.93	0.000877 601
P4ha1	−0.88	0.004637 417

h Spleen

Gene ID	log2Fold Change	padj
Zfp933	−1.65	0.001610 632
Pcmtd1	−1.46	0.000565 277
Tns1	−0.99	0.003474 704
Rpl7a-ps5	1.26	0.006127 191
Cox7c	1.53	0.000001 39

i Kidney

Gene ID	RNA Seq	qPCR
Ccdc88b	↑	↑
Ncoa1	↓	↓
Slc35a5	↓	↓
Tgfbi	↑	↑
Sema6b	↑	↑

j Liver

Gene ID	RNA Seq	qPCR
Slc41a2	↑	↑
Tlr2	↑	↑
Upf3b	↓	↓
Prrc2c	↓	↓
Mterf3	↓	↓

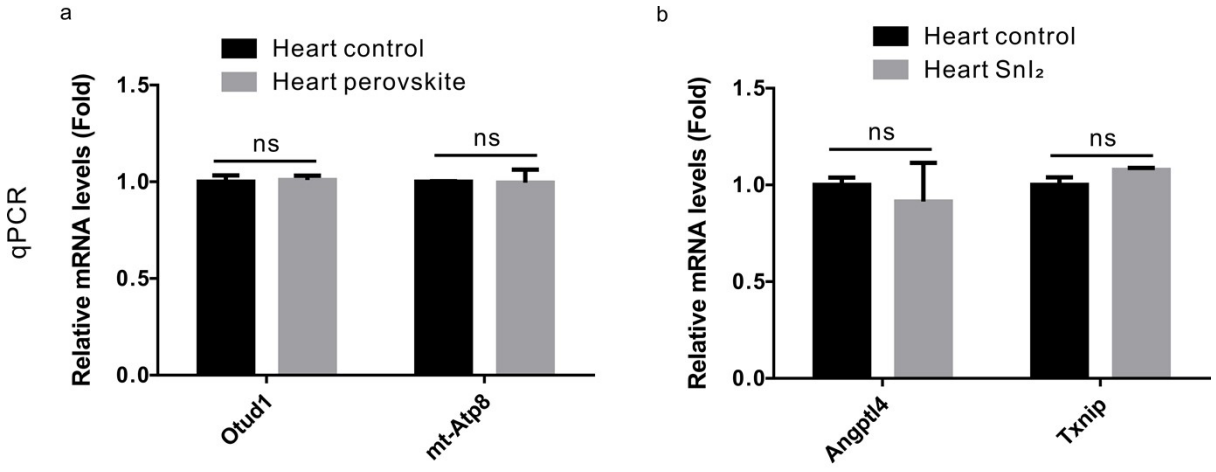
k Lung

Gene ID	RNA Seq	qPCR
Cdca3	↑	↑
Fam173a	↑	↑
Tango6	↑	↑
Vapa	↓	↓
P4ha1	↓	↓

l Spleen

Gene ID	RNA Seq	qPCR
Zfp933	↓	↓
Pcmtd1	↓	↓
Tns1	↓	↓
Rpl7a-ps5	↑	↑
Cox7c	↑	↑

Figure S9 5 differentially expressed genes are selected randomly to validate the reliability of RNA Sequencing results. **a – d**: gene expression changes of kidney, liver, lung, and spleen determined by qPCR. **e – h**: differentially expressed genes of kidney, liver, lung, and spleen obtained from RNA sequencing. As display in **i – l**, RNA sequencing results are consistent with the qPCR results, thus implying the reliability of the RNA seq results. ↑: upregulated, ↓: down regulated. Daily intake: 2 mg/kg of tin from perovskite ($MASnI_3$). For plots a-d, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:P<0.05, **: P≤0.01, ***: P≤0.001, ****: P≤0.0001. ns: no significant difference.



qPCR

RNA Seq

c Perovskite

Gene ID	log2FoldChange	padj
Otud1	−1.86	5.33E-06
mt-Atp8	2.27	4.38E-06

d SnI_2

Gene ID	log2FoldChange	padj
Angptl4	3.32	1.09E-24
Txnip	1.30	0.0018

e Perovskite

Gene ID	RNA Seq	qPCR
Otud1	↓	ns
mt-Atp8	↑	ns

f SnI_2

Gene ID	RNA Seq	qPCR
Angptl4	↑	ns
Txnip	↑	ns

Figure S10 The obtained gene changes of heart from RNA sequencing is generated by measurement error. The top two changed genes (from RNA sequencing) of heart are selected for the verification. **a, b**: The qPCR results for these two genes, **c, d**: RNA sequencing results for the top two changed genes. **e, f**: comparison between the RNA sequencing and qPCR results. The qPCR results show that both the genes do not display any significant difference, indicating the differentially expressed genes obtained from the RNA sequencing is generated by the measurement error. ↑: upregulated, ↓: down regulated. Daily intake: 2 mg/kg of tin from perovskite ($MASnI_3$). For plots a - b, Statistical analysis was performed using a one-sided Student's T-test. *:$P<0.05$, **: $P\leq0.01$, ***: $P\leq0.001$, ns: no significant difference.

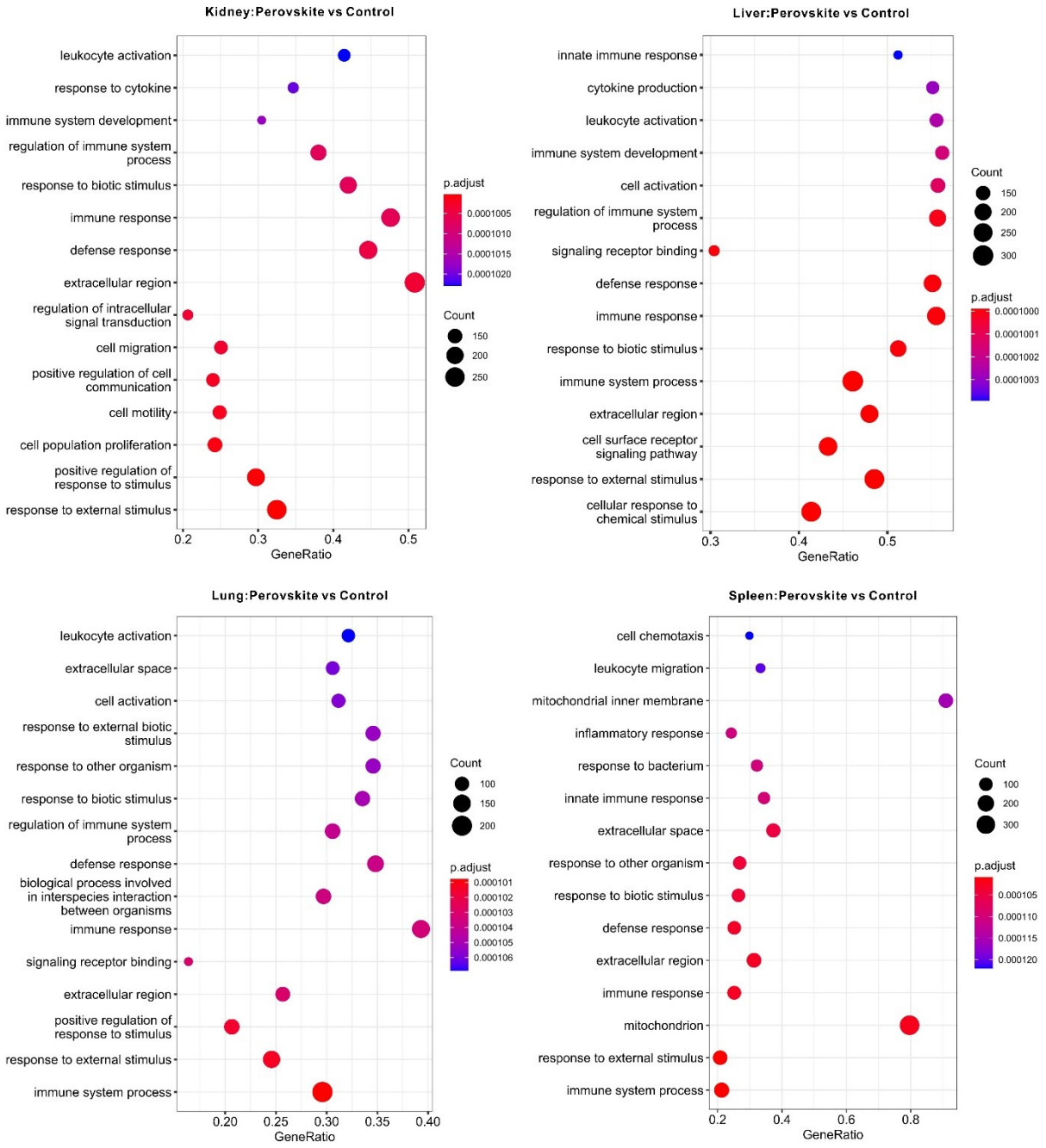


Figure S11 Dot heatmaps of top activated pathways of kidney, liver, lung, and spleen. Perovskite ($MASnI_3$) (2 mg/kg of Sn) vs Control by DEseq2 (v1.34.0) analysis.

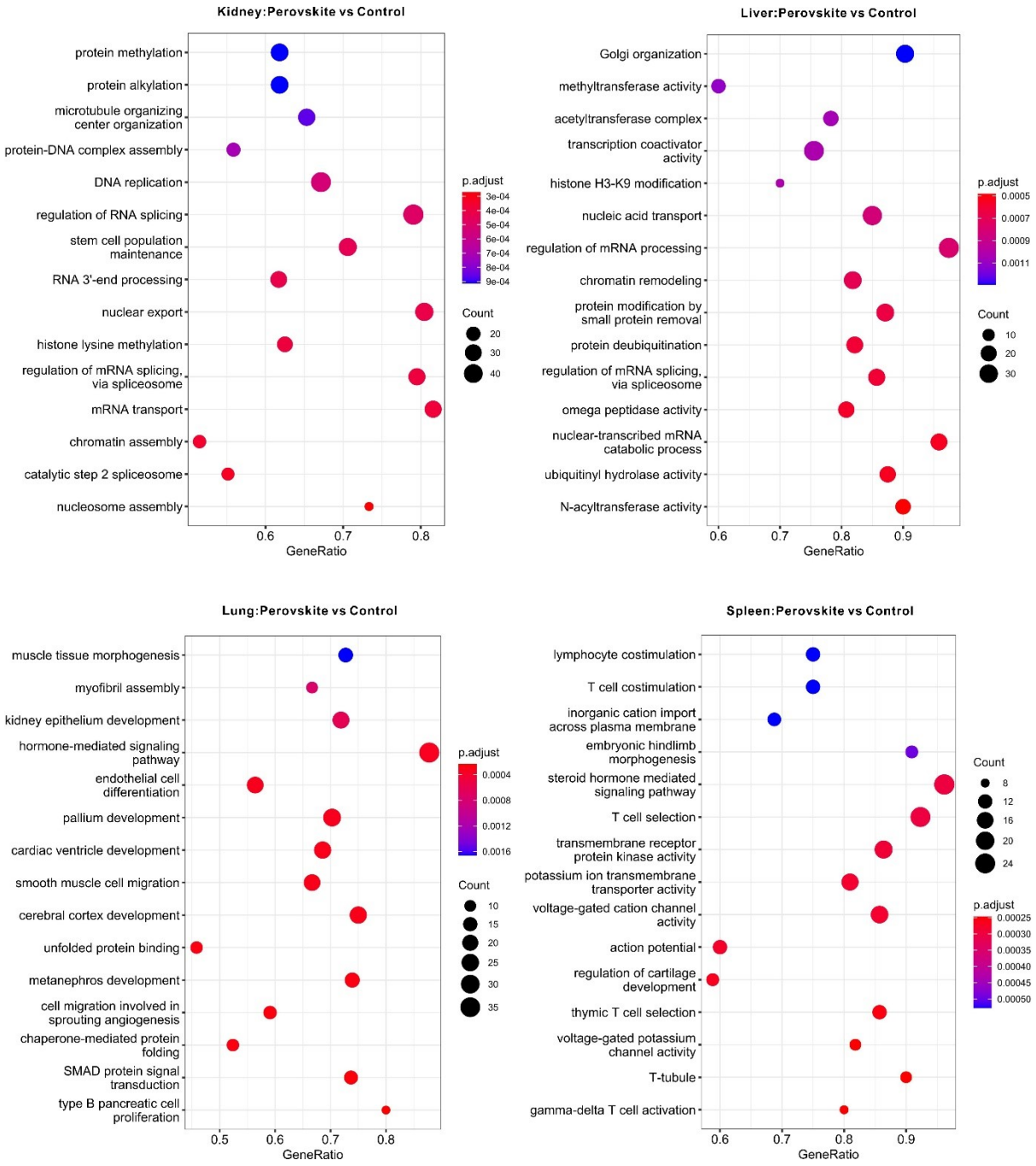
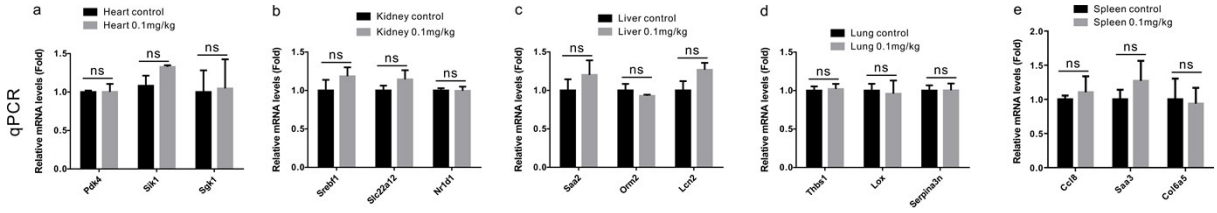


Figure S12 Dot heatmaps of top suppressed pathway of kidney, liver, lung, and spleen. Perovskite ($MASnI_3$) (2 mg/kg of Sn) vs Control by DEseq2 (v1.34.0) analysis.



RNA Seq

f Heart

Gene ID	log2Fold Change	padj
Pdk4	1.46	7.34E-05
Sik1	1.35	0.00077
Sgk1	1.04	7.34E-05

g Kidney

Gene ID	log2Fold Change	padj
Srebf1	0.62	2.4E-06
Slc22a12	-0.53	7.45E-07
Nr1d1	-0.71	7.06E-07

h Liver

Gene ID	log2Fold Change	padj
Saa2	6.40	0
Orm2	2.55	3.85E-53
Lcn2	2.66	8.91E-54

i Lung

Gene ID	log2Fold Change	padj
Thbs1	1.45	0.016
Lox	1.07	0.02
Serpina3n	0.94	0.02

j Spleen

Gene ID	log2Fold Change	padj
Ccl8	5.00	6.46E-22
Saa3	5.97	3.34E-12
Col6a5	2.65	8.06E-10

k Heart

Gene ID	RNA Seq	qPCR
Pdk4	↑	ns
Sik1	↑	ns
Sgk1	↑	ns

l Kidney

Gene ID	RNA Seq	qPCR
Srebf1	↑	ns
Slc22a12	↓	ns
Nr1d1	↓	ns

m Liver

Gene ID	RNA Seq	qPCR
Saa2	↑	ns
Orm2	↑	ns
Lcn2	↑	ns

n Lung

Gene ID	RNA Seq	qPCR
Thbs1	↑	ns
Lox	↑	ns
Serpina3n	↑	ns

j Spleen

Gene ID	RNA Seq	qPCR
Ccl8	↑	ns
Saa3	↑	ns
Col6a5	↑	ns

Figure S13 RNA sequencing results verification for 0.1 mg/kg of tin ingestion from perovskite. The obtained differentially expressed genes from RNA sequencing are generated by measurement error. The top three differentially expressed genes (from RNA sequencing) are selected for the verification. **a - e**: The qPCR results of heart, kidney, liver, lung, and spleen for these three genes, **f - j**: top three differentially expressed genes of heart, kidney, liver, lung, and spleen determined by RNA sequencing. **k - j**: comparison between the RNA sequencing and qPCR results. The qPCR results show that all the genes do not display any significant difference, indicating the differentially expressed genes obtained from RNA sequencing is generated by the measure error. ↑: upregulated, ↓: down regulated. Daily intake: 0.1 mg/kg of tin from perovskite ($MASnI_3$). For plots a - e, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:$P<0.05$, **: $P\leq0.01$, ***: $P\leq0.001$, ****: $P\leq0.0001$. ns: no significant difference.

Toxicity evaluation of Pb-based halide perovskites (daily injection: 0.1 mg/kg of lead from lead-based halide perovskite):

Mice (BALB/c, 6 mice each group) were intraperitoneally injected with 0.1 mg/kg of lead from halide perovskite ($MAPbI_3$) every day. After 30 days, the mice were sacrificed, and main organs and blood samples were collected for the analysis. Our data demonstrated that daily intake of 0.1 mg/kg of lead from lead-based halide perovskite indeed cause toxicity to mice. The detailed results are shown below:

1. the mice body weight and organ weight index (organ weight/mice weight) of main organs (heart, kidney, liver, lung, and spleen) from lead-based halide perovskite do not manifest significant difference compared to control group (Figure S 14).
2. blood biochemistry test implied that lead based halide perovskite **cause injury to the liver and kidney** even though their organ weight index does not manifest a significant difference compared to control group, as presented in Figure S 15.
3. blood hematology measurements showed that lead based perovskite do not result in obvious damage to the white blood cell (Figure S 16).
4. RNA sequencing analysis signified that lead based halide perovskite **cause apparent gene expression changes of kidney and liver**, thus indicating the toxicity, as exhibited in Figure S 17.

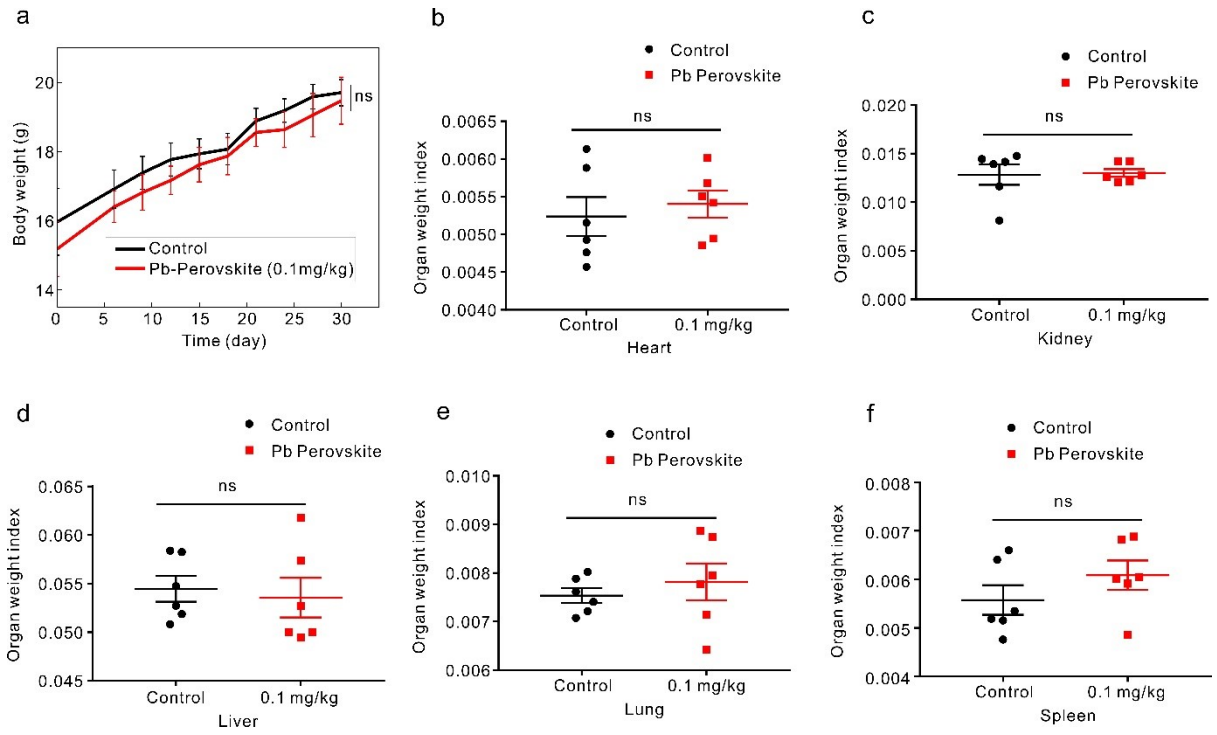
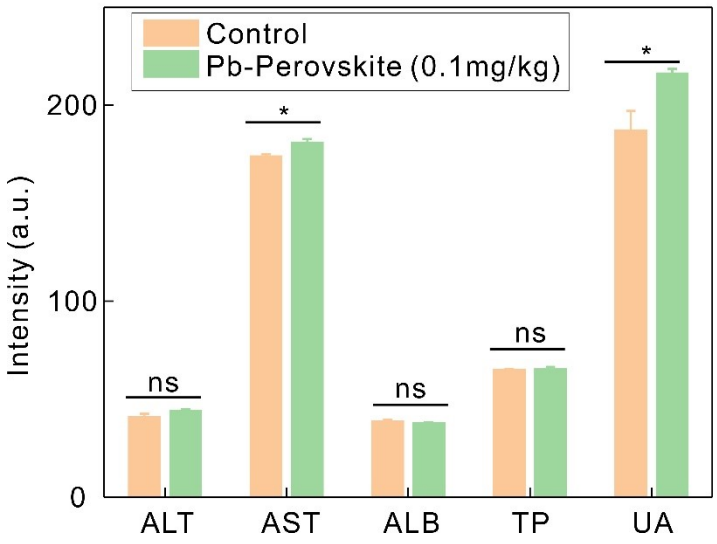


Figure S14 a. mice body weight, b – f: organ weight index (organ weight/mice weight) for heart, kidney, liver, lung, and spleen. Daily intake: 0.1 mg/kg of lead from Pb based perovskite. For plots a - f, Statistical analysis was performed using a one-sided Student's T-test. *:P<0.05, **: P≤0.01, ***: P≤0.001, ns: no significant difference.

a

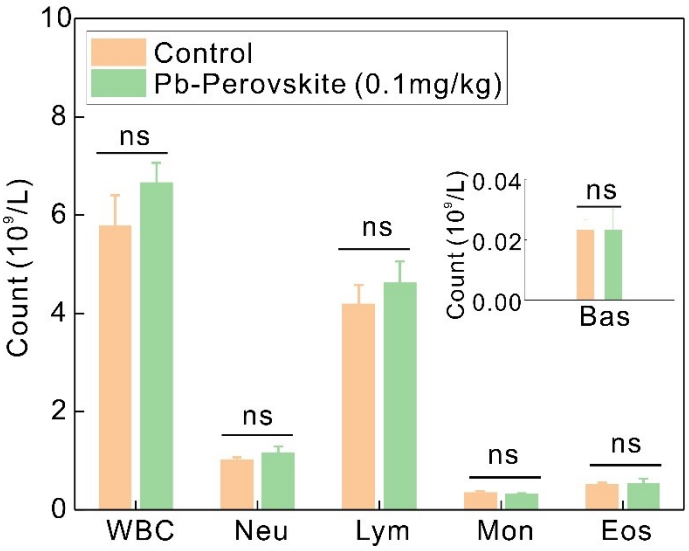


b

Indicator	P value
ALT	0.083
AST	***0.017***
ALB	0.249
TP	0.393
UA	***0.043***

Figure S15 Blood biochemistry analysis. ALT: alanine aminotransferase, AST: aspartate aminotransferase, ALB: albumin blood, TB: total protein, UA: uric acid. Liver indicators: ALT, AST, ALB, TP. Kidney indicator: UA. For plots a, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:P<0.05, **: P≤0.01, ***: P≤0.001, ****: P≤0.0001. ns: no significant difference. Daily intake: 0.1 mg/kg of lead from Pb based perovskite.

a



b

Indicator	P value
WBC	0.156
Neu	0.203
Lym	0.253
Mon	0.259
Eos	0.479
Bas	0.5

Figure S16 Hematology analysis. WBC: white blood cells, Neu: neutrophils, Lym: lymphocytes, Mon: monocytes, Eos: eosinophils, Bas: basophils. Daily intake: 0.1 mg/kg of lead from Pb based perovskite. For plots a, Error bars show mean ± SEM and the one-side Student's T-test was used to calculate significance. *:P<0.05, **: P≤0.01, ***: P≤0.001, ****: P≤0.0001. ns: no significant difference.

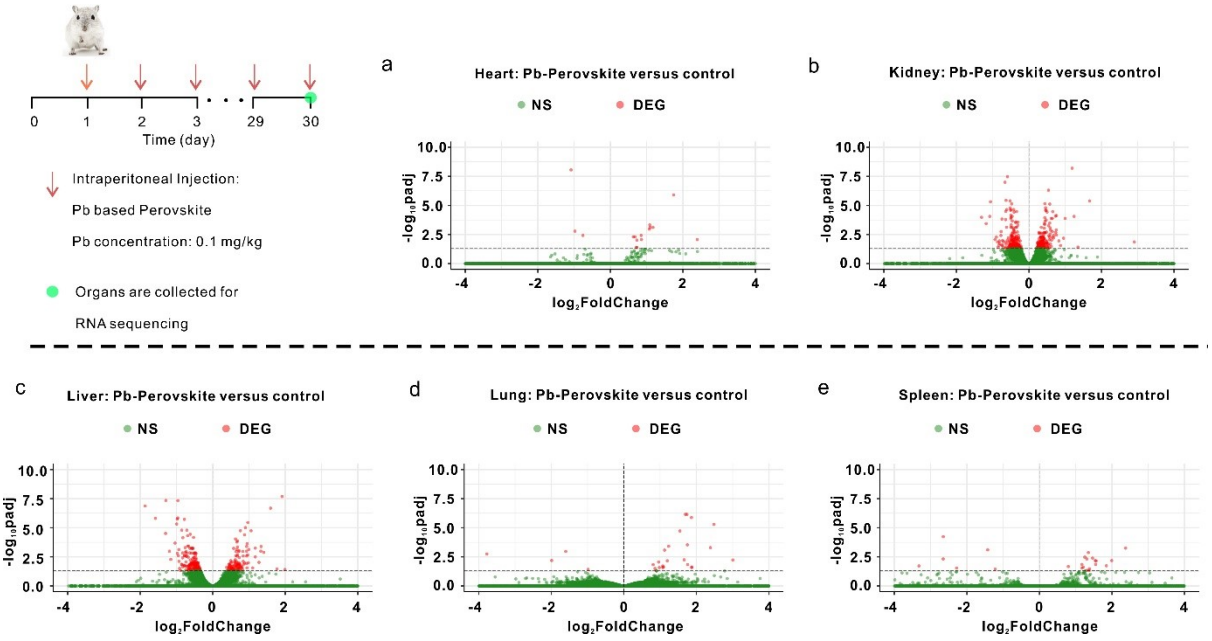


Figure S17 RNA sequencing results for the mice injected with Pb based perovskite with 0.1 mg/kg lead per day. Differentially expressed genes (DEG) analysis for heart, kidney, liver, lung, and spleen under 0.1 mg/kg of lead injection (from lead-based halide perovskite) by DEseq2 (v1.34.0) analysis.

Taken together, our results demonstrate that daily intake of 0.1 mg/kg of lead from lead-based halide perovskite will **cause injure to the kidney and liver**. Instead, daily intake of 0.1 mg/kg of tin from tin-based halide perovskite is bio safe. Therefore, we conclude that lead based halide perovskite is more toxic than tin based one.

Table S2 primers utilized in this work

	F (5‘-3’)	R (5‘-3’)
Ccdc88b	CCGAGGAGGACTTCGAATGG	AGCTGTAGCTCCTCCTGGTA
Tgfbi	AACCGACCACAAGAACGAGG	TGATAGACAGGGGCAAGTCG

Alg6	CTCTCAGTTCCTACTCAGGTGC	ATAGGCCGTAAGAGGTGGGTA
Ncoa1	ACAGACTAGAGGAGCTCTACAGG	CCAGGCTGGTTCAGGTAAGG
Slc35a5	TCCCTGAGCGACTGAGGTCT	GGAATGTGTACAGCGTTGGTG
Sema6b	AGACACAAGGTCAGGGGTAGG	GATGACCACAGATGACACCAGAAA
Slc41a2	GGCTGACGGAGCGATTGAA	CTTCCAAAAGCACAGCGGAA
Tcaim	CGCAGATAGCGGGGCAATTA	GAAGCCAATGAGGGAGGACC
Tlr2	TGCGGACTGTTTCCTTCTGA	TCCTCTGAGATTTGACGCTTTGT
Mterf3	CCTCGCGGCTTGACTAAAAT	GCAGAGCGTTTGGTGACTTG
Upf3b	CAGGGACCGATTTGATGGCT	TTCTGTATTCTGGATCATCCTCG
Prrc2c	GTAACAAGCAAGGTGGGCAAG	AGCAAGCAACATTTGGAGGG
Vapa	TGGGTAAAACTCCACCAGGG	TGCTAGGTTCCATATCATTCTCTT
Cdca3	GGAAGCCAAACAATCCGCAG	TGCTGCGCTTAGAACCTGAG
P4ha1	CTGTCTGGCTACGAAGACCC	ATCCGGCTCATCTTTCCTTGC
Fam173a	CTCGGGATTGGCCGTCTAT	GCCGCCAGCACGATCC
Tango6	CCGTGGTTCATGAGGTGACA	GAAGCAGCAGCACAACTACG
Igsf9	TGATGCTCTCTGGGATTGCC	AGGCTTTCTTCGACCGTCAG
Cox7c	GAGTATCCGGAGGTTCACGAC	CGCCACTTGTTTTCCACTGA
Oscp1	GCCTCCAGGCTGCTAAATCA	TGTCGTTCAGAACTTTGCGG
Pcmtd1	TCTTCTGCGCCTTCGGTTTAAT	CAGCTCCTCCCATGACAGTAT
Zfp933	GATGCAAGCTCTCCACCTTGA	TCGAGACTTAGGACCTTGCC
Tns1	TCTCCACAACAAGGGAAACCG	CTTCATTGCAAACCGGTCCAG
Rpl7a-ps5	CACCACCTTGGTGGAGAACA	GCAGTAGGGCATCTTTCGAC
s100a8	TCAAGACATCGTTTGAAAGGAAA	TCTGCACAAACTGAGGACACT
s100a9	ATGGAGCGCAGCATAACCA	AAAGGTTGCCAACTGTGCTTC
s100a6	GGCTGGGATGTTCGTTTGC	CTAGAAGAAGCGCACGGT
Pdk4	CAGCTGGTGAAGAGCTGGTAT	TGCCTTGAGCCATTGTAGGG
Sgk1	ATGCAGTAAACCAAGCCGGT	CTTGATCCATCTTCGTACCCGT
Sik1	ATCATGTCGGAGTTCAGTGC	CAATTATTTTTATTGCAACCTGC

		GT
Srebf1	GTTTCCGGGGAACTTTTCCT	GAGCTGGAGCATGTCTTCGAT
Nr1d1	TCAGGCTTCCACTATGGAGT	CCAAAACGCACAGCATCTCTA
Slc22a12	CTCCATGCTGTGCTGGTTTG	CACAATCCCGATGAGTGCCT
Saa2	GCTGGCTGGAAAGATGGAGAC	GCTCTCTCTTGCATCACTGATTTT
Lcn2	CAATGTCACCTCCATCCTGGT	GTACCTGAGGATACCTGTGCAT
Orm2	ATTGGTGCGGCTGTCCTAAA	ACACAGTGGTCATCTATGGTGT
Serpina3n	ATTCTCTGAAACCCAGGATGATAG	GCCCAGCTTTGAAAGGACATC
Lox	GTAACTGCAAACTGCCACGTC	CTGCCCGTTGTTCTCCCATT
Ccl8	CCATGGAAGCTGTGGTTTTCCAG	GGAGAACTTCCAGCTTTGGCT
Saa3	GGATGAAGCCTTCCATTGCCA	CCACATGTCTCTAGACCCTTGAC
Col6a5	CCACGTTGATAAGACAGTTCCCT	TGTGGTCCCCACTGACTCAT
mt-Atp8	CACTGGCACCTTCACCAAAAT	ATTGTTGGGGTAATGAATGAGGCA
Otud1	TGGGAGAACCACACGAACTC	GCGGCTCTGAGAGGACATTC
Angptl4	ACCCACTTACACAGGCCGC	GTTGAAGTCCACAGAGCCGT
Txnip	TTACCCGAGTCAAAGCCGTC	CGTTCTCACCTGCTGTAGGC

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