Supplementary Information (SI) for Environmental Science: Processes & Impacts.
This journal is © The Royal Society of Chemistry 2025

Supplementary Information for

Ice-water distribution of antibiotics and antiviral drugs during freezing-thawing process: Influencing factors and related mechanisms

Wenbin Wei, Linke Ge*, Siyuan Wang, Xuanyan Li, Peng Zhang, Jiahong Wang

School of Environmental Science and Engineering, Shaanxi University of Science & Technology, Xi'an 710021, P. R. China

* Corresponding author.

E-mail address: gelinke@sust.edu.cn

Table S1 The occurrence of antibiotics and antiviral drugs (ATVs) in surface waters of cold regions

Regions (Sampling time)	Mean concentration (ng L^{-1}) (Number of target compounds)								References
	TCs	MLs	SAs	QNs	CPs	β-Ls	LMs	ATVs	
Lake Päijänne, Finland (Sep. 2015 and Mar. 2016)	nd [1] (2)		32.5 (2)	81 (2)		nd (1)		6 (3)	[1]
The Vistula River, Poland (April 2013 ~ Dec. 2014)		324.2 (3)	219.63 (7)	44.42 (8)		51.43 (5)	65.33 (2)	20.19 (1)	[2]
The Songhua River, North China (Dec. 2018 ~ Mar. 2019)	17.8 (1)	6.1 (2)	55.6 (4)	39.6 (3)	150.3 (2)	46.1 (1)	6.8 (1)		[3]
Fenhe River, North China (Aug. 2019 and Nov. 2019)	34.3 (4)	85.85 (4)	211 (10)	86.8 (5)	48.2 (3)				[4]
Nine rivers in Germany (July 2014 and June 2015)								390.56 [2] (6)	[5]
Khatoritsa River, Russia (March 2021)								13 (1)	[6]

[1] nd is non-detected. [2] The total mean concentration of the target ATVs and their transformation products.

TCs, MLs, SAs, QNs, CPs, β-Ls and LMs are the abbreviations for tetracyclines, macrolides, quinolones, chloramphenicols, β-lactams and lincomycins, respectively.

Table S2 Relevant information on the model compounds

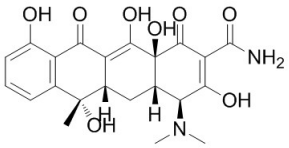
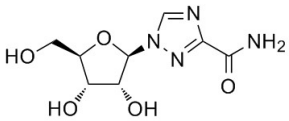
Compounds	Abbreviation	CAS No.	Chemical Structure	Molecular weight
Tetracycline	TC	60-54-8		444.435
Ribavirin	RBV	36791-04-5		244.205

Table S3 Ice-water distribution of tetracycline (TC) at different freezing temperatures

Freezing temperature (℃)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
-10	4.26	24.06	0.1770
-15	2.54	29.59	0.0857
-20	1.38	29.95	0.0460
-25	1.48	32.30	0.0457

Table S4 Ice-water distribution of ribavirin (RBV) at different freezing temperatures

Freezing temperature (℃)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
-10	2.89	23.55	0.1229
-15	2.24	27.94	0.0801
-20	1.93	32.89	0.0587
-25	1.54	35.18	0.0436

Table S5 Ice-water distribution of tetracycline (TC) at different freezing time

Freezing time (h)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
12	2.54	24.06	0.1054
24	4.09	28.36	0.1443
36	0.95	42.27	0.0224
48	1.01	73.73	0.0137
54	2.14	83.89	0.0255

Table S6 Ice-water distribution of ribavirin (RBV) at different freezing time

Freezing time (h)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
12	2.89	23.55	0.1229
24	2.37	26.32	0.0900
36	1.10	30.35	0.0361
48	0.39	72.63	0.0054
54	4.43	118.42	0.0374

Table S7 Ice-water distribution of tetracycline (TC) at different initial concentrations

Initial concentration (μM)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
5	0.68	5.78	0.1180
10	1.34	11.25	0.1196
20	2.54	24.06	0.1054
40	2.47	45.85	0.0539

Table S8 Ice-water distribution of ribavirin (RBV) at different initial concentrations

Initial concentration (μM)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
5	0.70	6.01	0.1168
10	2.37	11.40	0.2077
20	2.89	23.55	0.1229
40	2.94	45.26	0.0649

Table S9 Ice-water distribution of tetracycline (TC) with different NaCl contents

NaCl (M)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
0	2.54	24.06	0.1054
0.1	10.48	21.97	0.4771
0.25	10.52	21.48	0.4897
0.5	12.93	20.88	0.6194
0.68	16.77	20.12	0.8338

Table S10 Ice-water distribution of ribavirin (RBV) with different NaCl contents

NaCl (M)	Average concentration in ice (μM)	Average concentration in water (μM)	K_{IW}
0	2.89	23.55	0.1229
0.1	3.82	22.76	0.1676
0.25	5.70	22.68	0.2515
0.5	8.16	21.71	0.3758
0.68	9.43	20.70	0.4555

Table S11 Release of two model compounds during thawing processes

Melt water	Concentration of TC (μM)	Concentration of RBV (μM)
A	3.79	6.27
B	1.74	5.61
C	2.77	3.11
D	0.91	0.79

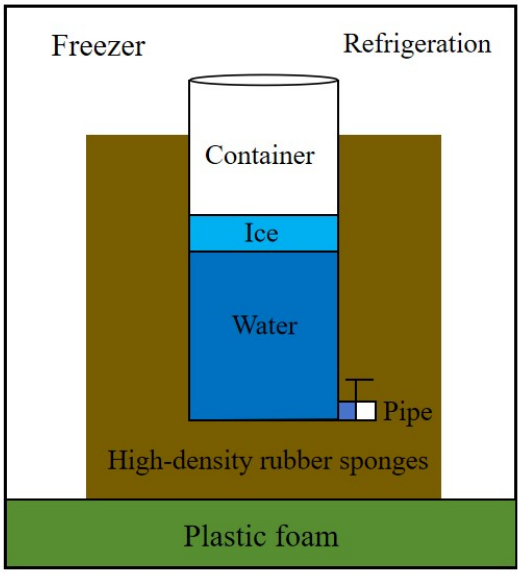


Fig. S1 Schematic diagram of the experimental setup

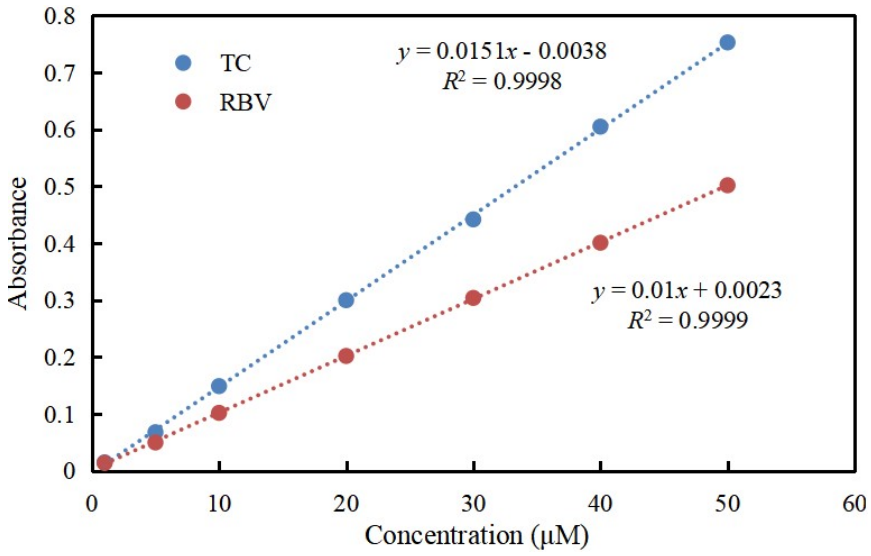


Fig. S2 Calibration curves for tetracycline (TC) and ribavirin (RBV)

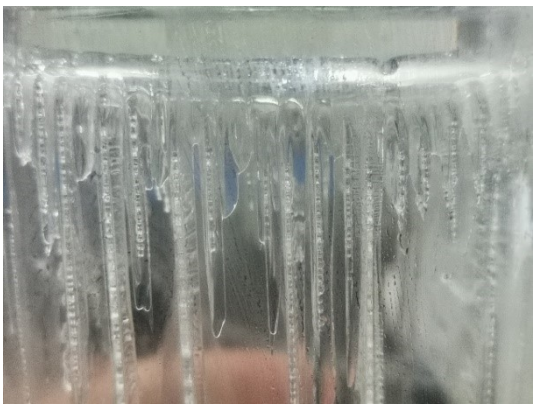


Fig. S3 Dendritic ice formed when frozen at -25 ℃ for 12 h

References

1. E. Ngumba, P. Kosunen and A. Gachanja, A multiresidue analytical method for trace level determination of antibiotics and antiretroviral drugs in wastewater and surface water using SPE-LC-MS/MS and matrix-matched standards, *Anal. Methods*, 2016, **8**(37), 6720-6729, **DOI: 10.1039/C6AY01695B.**

2. G. Joanna, T. Stefan, W. Renata, G. Wanda, Z. Tomasz, D. Agata, W. Piotr and N.-J. Grzegorz, Occurrence of antimicrobial agents, drug-resistant bacteria, and genes in the sewage-impacted Vistula River (Poland), *Environ. Sci. Pollut. Res.*, 2018, **25**(6), 5788-5807, **DOI: 10.1007/s11356-017-0861-x.**

3. L. Zhang, S. Du, X. Zhang, G. Lyu, D. Dong, X. Hua, W. Zhang and Z. Guo, Occurrence, distribution, and ecological risk of pharmaceuticals in a seasonally ice-sealed river: From ice formation to melting, *J. Hazard. Mater.*, 2020, **389**, 122083, **DOI: 10.1016/j.jhazmat.2020.122083.**
4. L. Wang, H. Li, J. Dang, H. Guo, Y. Zhu and W. Han, Occurrence, distribution, and partitioning of antibiotics in surface water and sediment in a typical tributary of Yellow River, China, *Environ. Sci. Pollut. Res.*, 2021, **28**(22), 28207-28221, **DOI: 10.1007/s11356-021-12634-1.**
5. J. Funke, C. Prasse and T. A. Ternes, Identification of transformation products of antiviral drugs formed during biological wastewater treatment and their occurrence in the urban water cycle, *Water Res.*, 2016, **98**, 75-83, **DOI: 10.1016/j.watres.2016.03.045.**
6. N. V. Ul'yanovskii, D. S. Kosyakov, S. A. Sypalov, I. S. Varsegov, I. S. Shavrina and A. T. Lebedev, Antiviral drug umifenovir (arbidol) in municipal wastewater during the COVID-19 pandemic: Estimated levels and transformation, *Sci. Total Environ.*, 2022, **805**, 150380, **DOI: 10.1016/j.scitotenv.2021.150380.**