## Solvent bar micro-extraction of heavy metals from natural water samples using 3-hydroxy-2-naphthoatebased ionic liquids

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|               |     |               |   |     |                           |   |     |                           |    |                            | Extra  | action ef                  | ficacy ± | SD            | (%) |                           |     |                           |   |     |      |   |     |
|---------------|-----|---------------|---|-----|---------------------------|---|-----|---------------------------|----|----------------------------|--------|----------------------------|----------|---------------|-----|---------------------------|-----|---------------------------|---|-----|------|---|-----|
|               |     | Cu            |   |     |                           |   |     |                           | Ag |                            | Cd     |                            | Pb       |               |     |                           |     |                           |   |     |      |   |     |
|               |     | [P66614][HNA] |   |     | [P <sub>1888</sub> ][HNA] |   |     | [N <sub>1888</sub> ][HNA] |    | [P <sub>66614</sub> ][HNA] |        | [P <sub>66614</sub> ][HNA] |          | [P66614][HNA] |     | [P <sub>1888</sub> ][HNA] |     | [N <sub>1888</sub> ][HNA] |   |     |      |   |     |
| Dodecan-1-ol  | 90  | n/a           |   |     | 45.6                      | ± | 1.3 | 29.5                      | ±  | 1.6                        | n/a    |                            | n/a      |               |     | n/a                       |     | 28.1                      | ± | 1.7 | 12.9 | ± | 0.8 |
| (wt%)         | 75  | <5            |   |     | 70.4                      | ± | 4.7 | 40.0                      | ±  | 7.0                        | 35.2 ± | 2.9                        | 5.5      | ±             | 0.9 | <5                        |     | 40.8                      | ± | 2.8 | 37.7 | ± | 8.3 |
|               | 60  | n/a           |   |     | 83.7                      | ± | 2.5 | 80.3                      | ±  | 1.4                        | n/a    |                            | n/a      |               |     | n/a                       |     | 47.6                      | ± | 0.8 | 47.3 | ± | 6.8 |
|               | 50  | <5            |   |     | 87.4                      | ± | 0.8 | 90.1                      | ±  | 1.7                        | 73.8 ± | 2.5                        | 4.4      | ±             | 0.4 | 20.9 ±                    | 6.7 | 50.4                      | ± | 2.1 | 69.1 | ± | 2.7 |
|               | 25  | 30.6          | ± | 2.8 | n/a                       |   |     | n/a                       |    |                            | 74.8 ± | 2.6                        | 9.1      | ±             | 3.0 | 54.3 ±                    | 3.0 | n/a                       |   |     | n/a  |   |     |
|               | 0   | 55.5          | ± | 3.7 | n/a                       |   |     | n/a                       |    |                            | 80.2 ± | 1.2                        | 27.9     | ±             | 3.2 | 70.1 ±                    | 3.4 | n/a                       |   |     | n/a  |   |     |
| рН            | 2   | <5            |   |     | <5                        |   |     | <5                        |    |                            | 76.9 ± | 0.9                        | <5       |               |     | <5                        |     | <5                        |   |     | <5   |   |     |
|               | 4   | 33.8          | ± | 2.1 | <5                        |   |     | <5                        |    |                            | 83.2 ± | 1.0                        | 11.4     | ±             | 1.6 | 55.8 ±                    | 2.8 | 16.8                      | ± | 1.9 | <5   |   |     |
|               | 6   | 54.0          | ± | 3.4 | 37.6                      | ± | 3.6 | 56.1                      | ±  | 1.0                        | 82.4 ± | 1.3                        | 18.9     | ±             | 1.2 | 64.7 ±                    | 3.5 | 15.5                      | ± | 2.4 | 32.5 | ± | 3.3 |
|               | 8   | 55.5          | ± | 3.7 | 87.4                      | ± | 0.8 | 90.1                      | ±  | 1.7                        | 80.2 ± | 1.2                        | 27.9     | ±             | 3.2 | 70.1 ±                    | 3.4 | 50.4                      | ± | 2.1 | 69.1 | ± | 2.7 |
| Stirring rate | 0   | 17.3          | ± | 0.6 | 15.5                      | ± | 4.7 | 28.2                      | ±  | 2.9                        | 39.5 ± | 0.7                        | 15.4     | ±             | 0.3 | 11.6 ±                    | 1.4 | 19.1                      | ± | 2.2 | 16.1 | ± | 1.2 |
| (rpm)         | 100 | 42.4          | ± | 1.1 | 59.4                      | ± | 0.8 | 61.0                      | ±  | 0.9                        | 53.3 ± | 1.8                        | 23.2     | ±             | 0.4 | 48.6 ±                    | 1.6 | 32.6                      | ± | 1.3 | 35.0 | ± | 1.7 |
|               | 300 | 56.8          | ± | 1.0 | 75.1                      | ± | 0.1 | 85.6                      | ±  | 1.8                        | 73.5 ± | 0.4                        | 29.4     | ±             | 0.4 | 56.4 ±                    | 2.0 | 44.9                      | ± | 2.0 | 73.3 | ± | 3.1 |
|               | 600 | 55.5          | ± | 3.7 | 87.4                      | ± | 0.8 | 90.1                      | ±  | 1.7                        | 80.2 ± | 1.2                        | 27.9     | ±             | 3.2 | 70.1 ±                    | 3.4 | 50.4                      | ± | 2.1 | 69.1 | ± | 2.7 |
|               | 800 | 63.1          | ± | 0.0 | 74.1                      | ± | 4.3 | 87.8                      | ±  | 3.5                        | 81.4 ± | 1.4                        | 27.2     | ±             | 0.2 | 70.7 ±                    | 3.6 | 57.5                      | ± | 3.0 | 68.0 | ± | 4.4 |
| Fiber length  | 10  | 45.7          | ± | 0.2 | 72.3                      | ± | 3.8 | 75.7                      | ±  | 0.8                        | 70.9 ± | 1.1                        | 14.5     | ±             | 2.5 | 62.2 ±                    | 1.6 | 29.9                      | ± | 1.7 | 54.7 | ± | 2.1 |
| (cm)          | 15  | 55.5          | ± | 3.7 | 87.4                      | ± | 0.8 | 90.1                      | ±  | 1.7                        | 80.2 ± | 1.2                        | 27.9     | ±             | 3.2 | 70.1 ±                    | 3.4 | 50.4                      | ± | 2.1 | 69.1 | ± | 2.7 |
|               | 20  | 57.4          | ± | 0.9 | 88.7                      | ± | 1.4 | 82.7                      | ±  | 1.5                        | 81.8 ± | 0.6                        | 27.1     | ±             | 2.8 | 65.3 ±                    | 2.0 | 39.5                      | ± | 3.2 | 61.3 | ± | 0.9 |
| NaCl          | 0   | 55.5          | ± | 3.7 | 87.4                      | ± | 0.8 | 90.1                      | ±  | 1.7                        | 80.2 ± | 1.2                        | 27.9     | ±             | 3.2 | 70.1 ±                    | 3.4 | 50.4                      | ± | 2.1 | 69.1 | ± | 2.7 |
| (g L⁻¹)       | 5   | 54.2          | ± | 2.3 | 77.9                      | ± | 3.7 | 50.1                      | ±  | 1.9                        | 72.3 ± | 0.8                        | 41.4     | ±             | 1.2 | 64.5 ±                    | 2.9 | 31.6                      | ± | 1.9 | 19.3 | ± | 2.3 |
|               | 10  | 59.1          | ± | 1.1 | 79.7                      | ± | 3.7 | 53.3                      | ±  | 1.5                        | 74.2 ± | 0.7                        | 66.5     | ±             | 2.6 | 73.1 ±                    | 3.2 | 39.7                      | ± | 2.6 | 18.4 | ± | 1.4 |
|               | 15  | 53.7          | ± | 1.5 | 60.7                      | ± | 3.7 | 56.3                      | ±  | 2.0                        | 60.3 ± | 2.6                        | 72.3     | ±             | 0.9 | 38.6 ±                    | 1.6 | 21.6                      | ± | 2.8 | 26.4 | ± | 0.6 |
|               | 30  | 53.8          | ± | 2.3 | 77.2                      | ± | 1.5 | 47.2                      | ±  | 1.4                        | 63.9 ± | 1.2                        | 78.0     | ±             | 1.6 | 29.9 ±                    | 4.2 | <5                        |   |     | 8.8  | ± | 0.6 |
|               | 60  | 46.6          | ± | 2.2 | 36.4                      | ± | 2.0 | 40.6                      | ±  | 2.0                        | 55.2 ± | 1.8                        | 86.5     | ±             | 1.9 | 22.1 ±                    | 3.1 | <5                        |   |     | 9.9  | ± | 1.5 |

Table S1: Summarized results for the optimization of extraction efficacy. Considered were all metals that showed an extraction efficacy >40% after the time dependent experiments for each setup respectively.

n/a= not applicable.

|                |       | Leaching $\pm$ SD (mg L <sup>-1</sup> DOC) |       |      |                   |       |       |      |                        |     |  |  |
|----------------|-------|--|-------|------|-------------------|-------|-------|------|------------------------|-----|--|--|
|                |       | [P6661                                     | ۱][4] | HNA] | [P <sub>188</sub> | 8][⊦  | INA]  |      | [N <sub>1888</sub> ][H | NA] |  |  |
| Dodecan-1-ol   | 90    | n/a  |       |      | 14.9              | ±     | 1.4   | 6.2  | ±                      | 0.9 |  |  |
| (wt%)          | 75    | 11.6                                       | ±     | 0.6  | 19.3              | ±     | 0.9   | 9.0  | ±                      | 0.2 |  |  |
|                | 60    | n/a  |       |      | 21.1              | ±     | 1.1   | 15.6 | ±                      | 0.8 |  |  |
|                | 50    | 13.9                                       | ±     | 0.1  | 20.6              | ±     | 0.2   | 19.4 | ±                      | 0.6 |  |  |
|                | 25    | 12.8                                       | ±     | 0.1  | n/a               |       |       | n/a  |                        |     |  |  |
|                | 0     | 11.3                                       | ±     | 0.7  | n/a               |       |       | n/a  |                        |     |  |  |
| рН             | 2     | 2.9  | ±     | 0.2  | 12.6              | ±     | 0.3   | 8.0  | ±                      | 0.3 |  |  |
|                | 4     | 7.6  | ±     | 0.5  | 16.6              | ±     | 0.9   | 13.2 | ±                      | 0.2 |  |  |
|                | 6     | 10.1                                       | ±     | 0.5  | 18.2              | ±     | 0.6   | 15.1 | ±                      | 0.9 |  |  |
|                | 8     | 11.3                                       | ±     | 0.7  | 20.6              | ±     | 0.2   | 19.4 | ±                      | 0.6 |  |  |
| Stirring rate  | 0     | 7.9  | ±     | 0.3  | 16.2              | ±     | 0.9   | 13.3 | ±                      | 0.5 |  |  |
| (rpm)          | 100   | 10.9                                       | ±     | 0.6  | 22.8              | ±     | 1.2   | 18.3 | ±                      | 1.0 |  |  |
|                | 300   | 11.4                                       | ±     | 0.4  | 21.7              | ±     | 1.8   | 18.7 | ±                      | 0.3 |  |  |
|                | 600   | 11.3                                       | ±     | 0.7  | 20.6              | ±     | 0.2   | 19.4 | ±                      | 0.6 |  |  |
|                | 800   | 11.7                                       | ±     | 0.4  | 24.8              | ±     | 2.2   | 19.9 | ±                      | 0.6 |  |  |
| Fiber length   | 10    | 7.0  | ±     | 0.9  | 17.5              | ±     | 1.2   | 14.9 | ±                      | 0.2 |  |  |
| (cm)           | 15    | 11.3                                       | ±     | 0.7  | 20.6              | ±     | 0.2   | 19.4 | ±                      | 0.6 |  |  |
|                | 20    | 19.5                                       | ±     | 1.8  | 24.5              | ±     | 0.9   | 21.0 | ±                      | 0.5 |  |  |
| NaCl           | 0     | 11.3                                       | ±     | 0.7  | 20.6              | ±     | 0.2   | 19.4 | ±                      | 0.6 |  |  |
| (g L⁻¹)        | 5     | 13.9                                       | ±     | 0.3  | 19.2              | ±     | 0.9   | 12.3 | ±                      | 0.5 |  |  |
|                | 10    | 16.1                                       | ±     | 0.5  | 21.6              | ±     | 0.9   | 14.5 | ±                      | 0.1 |  |  |
|                | 15    | 13.9                                       | ±     | 0.2  | 16.7              | ±     | 0.7   | 14.7 | ±                      | 0.1 |  |  |
|                | 30    | 10.2                                       | ±     | 0.1  | 23.4              | ±     | 1.9   | 11.2 | ±                      | 0.2 |  |  |
|                | 60    | 12.6                                       | ±     | 0.4  | 24.4              | ±     | 2.1   | 14.7 | ±                      | 0.2 |  |  |
| Drinking water |       | 16   | .2    | ± 1. | 3 24              | .5    | ± 2.0 | 19.4 | ±                      | 0.5 |  |  |
| WWTP effl      | 3.8   |  | ± 0.  | 3 25 | .4                | ± 0.4 | 19.3  | ±    | 0.2                    |     |  |  |
| Sea wate       | 12.2  |  | ± 0.  | 3 29 | .7                | ± 0.1 | 26.1  | ±    | 2.7                    |     |  |  |
| Hypersaline    | water | 11   | .3    | ± 0. | 9 27              | .0    | ± 0.0 | 24.6 | ±                      | 0.5 |  |  |

**T**able S2: Summarized results for leaching during extraction. WWTP = wastewater treatment plant, DOC = dissolved organic carbon.

n/a= not applicable.

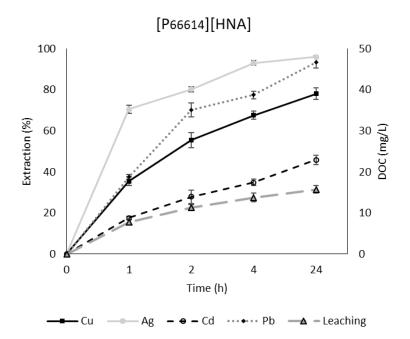


Figure S1: Time dependency of extraction and leaching using pure [P<sub>66614</sub>][HNA], pH = 8.0 (n=3, error bars =  $\pm$  SD).