**Supporting Information**

# What control the chemical speciation of abundant heavy metals during wastewater treatment: Insights from combined spectroscopic and modeling analyses

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Table S1. Summary of Fe speciation data using synchrotron X-ray absorption spectroscopy.

| **Label** | **Sludge source** | **Chemical species** | | | | | | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| | | Pyrite | Siderite | Vivianite | Strengite | FeO(OH) | Fe-Org | |
| Wang(2020) | Mixed primary and WAS | - | 23.5 | - | 16.8 | 26.2 | 33.5 | 1 |
| | Lab-scale AD | - | - | 73.3 | 12.2 | 14.5 | - | |
| Huang(2021) | WAS | - | - | 7.5 | 28.3 | 13 | 51.2 | 2 |
| | Full-scale AD | 2.6 | 40.3 | 19.6 | 37.4 | - | - | |
| Li(2018)[a] | WAS from an aerobic MBR with Fe dosing | - | - | - | 18.1 | 81.9 | - | 3 |
| | Lab anaerobic fermenter | - | - | 65.6 | - | 34.4 | - | |
| Li(2020) | WAS with Fe-dosed sludge | - | - | - | 31.5 | 68.5 | - | 4 |
| Wu(2015)[b] | WAS from an MBR with Fe dosing | - | - | - | 50 | 50 | - | 5 |
| Wilfert (2016)[c] | WAS from WWTP#1 | 34 | - | 34 | - | 5 | - | 6 |
| | WAS from WWTP#2 | 8 | - | 87 | - | 5 | - | |
| Wilfert (2016)[d] | AD sludge#1 | 27 | - | 58 | - | 15 | - | |
| | AD sludge#2 | 15 | - | 81 | - | 4 | - | |

*Note*: (a) The FeO(OH) phase includes ferrihydrite and goethite, (b) The FeO(OH) phase includes ferrihydrite and lepidocrocite; (c) the species were identified with Mossbauer spectroscopy, WWTP#1 has 26% of unidentified $Fe^{2+}$ species. (d) the species were identified with Mossbauer spectroscopy.

Table S2. Summary of Zn speciation data using synchrotron X-ray absorption spectroscopy.

| Label | Sludge source | Chemical species | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Zn-Cys | Zn-S[(a)] | (Zn,Fe)-S[(b)] | Zn-Fe[(c)] | Zn-PO4 | Zn-Org | |
| Donner (2011) | Mixed primary and WAS | - | - | 54 | 17 | 29 | - | 7 |
| | AD of mixed sludges | - | - | 53 | 29 | 19 | - | |
| | AD of mixed sludges | - | - | 40 | 20 | 40 | - | |
| | Composting | 24 | - | - | 22 | 54 | - | |
| Lombi (2012) | Mixed primary and WAS | 15 | - | 80 | | 5 | - | 8 |
| | Lab AD of mixed sludges | 15 | - | - | 48 | 38 | - | |
| Donner (2013) | Lab AD of mixed sludges | - | - | 69.5 | 30.5 | - | - | 9 |
| | 3-month Aged | - | - | 28.3 | 48.2 | 23.6 | - | |
| Ma (2014) | Air-dried (oxic) | - | - | 23 | 55 | 21 | - | 10 |
| | 7d anaerobic aged | - | - | 62 | 16 | 23 | - | |
| Legros (2017) | WAS from experimental WWTP | - | 25 | - | 22 | 53 | - | 11 |
| | AD | - | 30 | - | 13 | 57 | - | |
| Le Bars (2018) | Raw sludge | 10 | - | 49 | - | 41 | - | 12 |
| | Raw sludge | - | - | 90 | - | 10 | - | |
| | AD | - | - | 81 | 19 | - | - | |
| | AD | - | - | 92 | - | 8 | - | |
| | Composting | - | - | 10 | 35 | 40 | 15 | |
| | Composting | - | - | - | | 100 | - | |
| Huang (2018) | Mixed primary and WAS | - | - | 39 | 35 | 26 | - | 13 |
| | AD of mixed sludges | - | - | 67 | 20 | 13 | - | |

*Note:* (a)This included amorphous or nano-zinc sulfides ;(b) This is either sphalerite or wurtzite that were used in spectral fitting; (c) This included Fe (hydro)oxides-adsorbed or substituted Zn species.

Table S3. Summary of Cu speciation data using synchrotron X-ray absorption spectroscopy.

| Label | Sludge source | Chemical species | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Cu(I)-Cys | $Cu(I)_2S$ | Cu(II)S | Cu-Fe-S[(c)] | Cu(II)-Org | Cu-PO4 | |
| Donner (2011) | Mixed primary and WAS | - | 41 | - | 38 | 21 | - | 7 |
| | AD of mixed sludges | - | 60 | - | 32 | 8 | - | |
| | AD of mixed sludges | - | 31 | - | 43 | 26 | - | |
| | Composting | - | - | 9 | | 62 | 29 | |
| Donner (2013) [(a)] | Lab AD of mixed sludges | - | - | 86.4 | 8.4 | 5.2 | - | 9 |
| | 3-month Aged | - | - | 67.6 | - | 32.4 | - | |
| Legros (2017) [(b)] | WAS from experimental WWTP | - | 42 | - | - | 58 | - | 11 |
| | AD | - | 51 | - | - | 49 | - | |
| Huang (2018) | Mixed primary and WAS | 16 | 37 | - | 40 | 8 | - | 13 |
| | AD of mixed sludges | 24 | 39 | - | 33 | 4.6 | - | |

*Note:* (a) the Cu(II)S species was fitted by covellite(b) The $Cu(I)_2S$ was fitted by Cu(I)methionine and the Cu(II)-Org was fitted by Cu(II)galacturonic; (c) Cu-Fe-S include cubanite and chalcopyrite.

Table S4. Summary of P speciation data using NMR and P K-edge XANES.

| Sludge source | $^{31}P$ NMR[(a)] | | P K-edge XANES [(b)] | | | Ref. |
|---|---|---|---|---|---|---|
| | Ortho-P | Others | Vivianite | Strengite | Others | |
| WAS | 63.5 | 36.5 | - | - | - | 14 |
| AD | 95.1 | 4.9 | - | - | - | |
| WAS | 52.8 | 47.1 | - | - | - | 15 |
| AD | 100 | 0 | - | - | - | |
| WAS | - | - | - | 24.3 | - | 3 |
| AD | - | - | 42.3 | - | - | |
| WAS | - | - | - | 23 | - | 1 |
| AD | - | - | 55.8 | 7.2 | - | |

Note: Only studies comparing sludges before and after AD were selected. (a) $^{31}P$ liquid NMR of liquid extracts of sludge samples, Others are organophosphorus and polyphosphates. (b) Others of the XANES data are species other than iron phosphates.

Figure S1. PHREEQC inputs for the simulation of variable pe (pe was varied from +5 to -6, while other parameters were maintained the same)

```
SOLUTION 1
    temp      25
    pH        7.6
    pe        5
    redox     pe
    units     mmol/kgw
    density   1
    Alkalinity 5
    Ca        4
    Cl        5
    Cu        0.05
    Fe        0.5
    K         0.5
    Mg        2
    Na        6.5
    P         0.5
    S         1.75
    Zn        0.1
    -water    1 # kg
```

```
EQUILIBRIUM_PHASES 1
    Calcite    0 0
    Chalcocite 0 0
    Chalcopyrite 0 0
    Covellite 0 0
    Cu(OH)2    0 0
    Cu3(PO4)2 0 0
    Ferrihydrite 0 0
    Gypsum     0 0
    Mackinawite 0 0
    Pyrite     0 0
    Siderite   0 0
    Smithsonite 0 0
    Sphalerite 0 0
    Strengite 0 0
    Vivianite 0 0
    Wurtzite   0 0
    Zn3(PO4)2:4H2O 0 0
    Zn(OH)2(am)  0 0
```

Figure S2. An example of PHREEQC simulation output for variable pe (initial pe = 5)

```
--------------------------------Phase assemblage---------------------------------

                                                        Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

Calcite            0.00    -8.48     -8.48  0.000e+000  1.214e-004  1.214e-004
Chalcocite       -31.62   -66.54    -34.92  0.000e+000           0  0.000e+000
Chalcopyrite     -85.36  -120.63    -35.27  0.000e+000           0  0.000e+000
Covellite        -36.84   -59.14    -22.30  0.000e+000           0  0.000e+000
Cu(OH)2           -0.55     8.12      8.67  0.000e+000           0  0.000e+000
Cu3(PO4)2          0.00   -36.85    -36.85  0.000e+000  1.181e-005  1.181e-005
Ferrihydrite      -0.00     3.19      3.19  0.000e+000  5.000e-004  5.000e-004
Gypsum            -1.25    -5.86     -4.61  0.000e+000           0  0.000e+000
Mackinawite      -57.89   -61.49     -3.60  0.000e+000           0  0.000e+000
Pyrite           -89.33  -107.84    -18.51  0.000e+000           0  0.000e+000
Siderite          -3.90   -14.14    -10.24  0.000e+000           0  0.000e+000
Smithsonite       -1.31   -11.31    -10.00  0.000e+000           0  0.000e+000
Sphalerite       -47.21   -58.66    -11.45  0.000e+000           0  0.000e+000
Strengite         -1.01   -27.41    -26.40  0.000e+000           0  0.000e+000
Vivianite         -7.90   -43.90    -36.00  0.000e+000           0  0.000e+000
Wurtzite         -49.71   -58.66     -8.95  0.000e+000           0  0.000e+000
Zn(OH)2(am)       -3.88     8.60     12.47  0.000e+000           0  0.000e+000
Zn3(PO4)2:4H2O     0.00   -35.42    -35.42  0.000e+000  3.130e-005  3.130e-005
-----------------------------Solution composition------------------------------

     Elements           Molality       Moles

     C                 4.375e-003  4.375e-003
     Ca                3.879e-003  3.879e-003
     Cl                5.000e-003  5.000e-003
     Cu                1.456e-005  1.456e-005
     Fe                1.514e-008  1.514e-008
     K                 5.000e-004  5.000e-004
     Mg                2.000e-003  2.000e-003
     Na                6.500e-003  6.500e-003
     P                 4.138e-004  4.138e-004
     S                 1.750e-003  1.750e-003
     Zn                6.108e-006  6.108e-006

----------------------------Description of solution----------------------------

                                       pH  =   7.074      Charge balance
                                       pe  =   3.380      Adjusted to redox equilibrium
                        Activity of water  =   1.000
                           Ionic strength  =  2.104e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.080e-003
                       Total CO2 (mol/kg)  =  4.375e-003
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  5.802e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  20.02
                               Iterations  =   9
                                  Total H  = 1.110182e+002
                                  Total O  = 5.552813e+001
```

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