# Supporting information

## Impact of inorganic and organic pollutants from a Belgian wastewater treatment plant on adjacent surface and groundwaters

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## 1.1 Acid digestion of suspended particulate matter (SPM)

The filters containing SPM were stored in petri dishes (Sigma-Aldrich, polystyrene) and dried for 24 h under a clean laminar flow hood in a clean laboratory room. The dried filters were weighted again to obtain the mass of the particulate phase, used for the metal concentration determinations, and transferred into acid-cleaned and Milli-Q water-rinsed teflon vessels. A total digestion procedure was applied by adding 3 mL HCl, 1 mL $HNO_3$ and 3 mL HF to the tubes containing the filters. The vessels were placed in the oven at 70 °C for 24 h and cooled down afterwards. Twenty mL $H_3BO_3$ was added to the teflon tubes to complex the remaining HF and the acid solutions were reheated overnight at 70 °C. After cooling down, the digested samples were transferred into 50 mL PP tubes, stored at 4 °C and diluted 10 times with Milli-Q water prior to analysis.

## 1.2 Labile metal measurement by DGT in waters

All the tweezers, cutters, glass plates and spacers used for gel preparation were soaked in 10 % $HNO_3$ and were rinsed thoroughly by Milli-Q water prior to use. The employed materials, including the DGT piston caps and bases (DGT Research Ltd.), were pre-cleaned in 10 % $HNO_3$ solution for at least 24 h and rinsed with Milli-Q water. Gel preparation and DGT assembly were prepared under a laminar flow hood in a clean laboratory room according to the method reported by Zhang and Davison (1995).

### 1.2.1 Preparation of diffusive gel

Standard gel solution used to polymerize diffusive gel and binding gel was made of the mixture of 15% acrylamide solution and 0.3% cross-linker (DGT Research Ltd., UK). For one polyacrylamide diffusive gel (0.8 mm thickness), 5 mL gel solution, 35 µL of a 10 % freshly prepared ammonia persulfate (APS, Merck, Belgium) solution, and 12.5 µL N, N, N, N-tetraethylenediamine (TEMED, Merck, Belgium) was introduced into a 15 mL PP tube in order and mixed well. After that the solution is quickly cast between 2 glass plates separated by a Teflon spacer (0.5 mm thickness). Then the glass assemblage is placed upright in the oven at 45 °C for 45 min to serve the polymerization. After the heating process, the formed diffusive gel is peeled off from the glass plate and immersed in Milli-Q water for 24 h to allow hydration and expansion of the gel. During the hydration, the gel is washed carefully to remove the remained chemicals from the polymerization (7 times at least). Afterwards, the hydrated diffusive gel is stored in a 10 mM NaCl solution at 4 °C prior to use.

### 1.2.2 Preparation of binding gel (Chelex®-100 gel, CH)

CH binding gel was applied for the determination of metal cations (Fe, Mn, Cd, Pb, Cr, Co, Cu, and Ni). The preparation of CH is based on the procedure reported by (Zhang and Davison, 1995). To obtain one CH gel, 0.8 g Chelex®-100 resin is well mixed with 2 mL gel solution. After that, 12 µl of 10% fresh prepared APS, and 3 µl TEMED are added sequentially into the mixture. The well mixed solution is cast into the interspace between two glass plates, which is created by the 0.25 mm Teflon spacer sandwiched between, after that the assembly is placed horizontally in the oven at 45 °C for 45 min to serve the polymerization. Afterwards, the same procedure of treating the diffusive gel is applied here for the binding gel.

### 1.2.3 Diffusive boundary layer (DBL) calculation

The DBL is a region in flowing water solution, close to the surface of DGT, where the transport of analytes undergoes a rapid transition from advective to diffusive control (Zhang and Davison, 2015; Warnken et al., 2006). The thickness of DBL is impacted by the velocity of the flow, as the DBL becomes thinner with fast flowing waters. When the thickness of DBL is far less compared to the thickness of the diffusion layer, the DBL is negligible in the calculations, otherwise the DBL thickness must be measured and considered. The DBL can be calculated by plotting reciprocal of accumulated mass on the binding gel (1/M) versus thickness of diffusion layer (Δg) according to Warnken et al (2006). To obtain DBL, additional DGT devices with different thickness of diffusion layer (0.4 mm and 1.2 mm) were also deployed in parallel, except for the 6 DGT pistons (0.8 mm) deployed in each station.

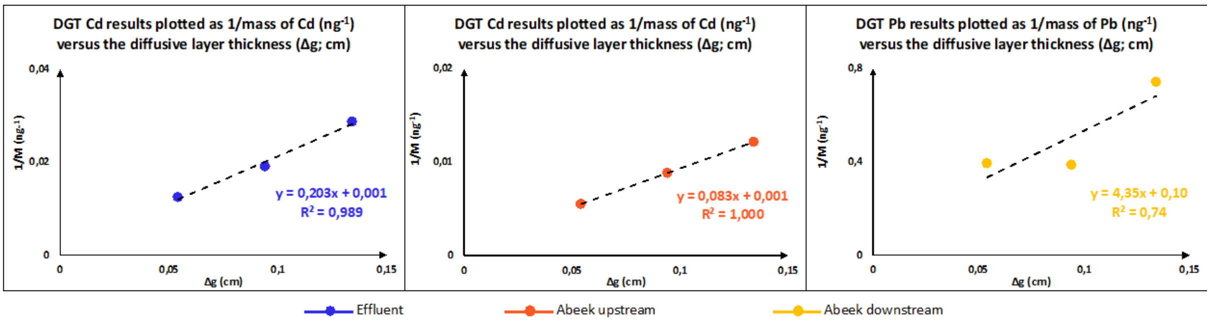

Figure S 1 Plot of 1/M in function of the diffusive layer thickness (Δg) for the DBL thickness calculations in the WWTP effluent, Abeek upstream and Abeek downstream.

Based on the plots above, the DBL thickness (δ) can be obtained by the formula performed with slope and intercept of the plots (Warnken et al., 2006). The equations are shown below:

$$\frac{1}{\mathrm{M}} = \frac{\Delta \mathrm{g}}{\mathrm{C_w AtD_{gel}}} + \frac{\delta}{\mathrm{C_w AtD_w}} \qquad \text{Equation. S1}$$

$$\frac{\mathrm{Intercept}}{\mathrm{Slope}} = \delta \frac{\mathrm{D_{gel}}}{\mathrm{D_w}} \qquad \text{Equation. S2}$$

where δ represents the DBL thickness, $C_w$ is the concentration of the analyte in the water measured by DGT, $D_{gel}$ and $D_w$ are the diffusion coefficients of the analyte in the gel and water respectively and A and t are the exposure window area and deployment time as described in section 2.3.1. According to Warnken et al. (2006), the values of $D_{gel}$ equate to ~0.85 $D_w$. Thus, DBL thickness in our sampling stations are:

$\mathrm{DBL_{WWTP\ effluent}} = \frac{0.001}{0.203} * \frac{1}{0.85} = 0.0058$ (neglectable)

$\mathrm{DBL_{Abeek\ upstream}} = \frac{0.001}{0.083} * \frac{1}{0.85} = 0.014\ \mathrm{cm}$

$\mathrm{DBL_{Abeek\ downstream}} = \frac{0.01}{4.35} * \frac{1}{0.85} = 0.027\ \mathrm{cm}$

### 1.3 Recovery of certified reference material

Table S1 recovery of reference materials for the measurement of particulate trace metals (ERM-CC144; sewage sludge, European Reference Materials) and for the analysis of trace metals by HR-ICP-MS (SLRS-6; river water, National Research Council Canada).

| | | **Cd** | **Pb** | **Cr** | **Ni** | **Cu** | **As** |
|---|---|---|---|---|---|---|---|
| **Dissolved frations** | measured (µg $L^{-1}$) | 0.0085 | 0.17 | 0.217 | 0.749 | 25.698 | 0.695 |
| | certified (µg $L^{-1}$) | 0.0063 | 0.17 | 0.252 | 0.616 | 23.9 | 0.57 |
| | recovery (%) | 135 | 100 | 86 | 122 | 108 | 122 |
| **SPM fractions** | measured (mg $kg^{-1}$) | 13.8 | 131 | 141 | 79 | 293 | 6.9 |
| | certified (mg $kg^{-1}$) | 14.5 | 157 | 168 | 91 | 348 | 7.7 |
| | recovery (%) | 95 | 84 | 84 | 87 | 84 | 89 |

## 1.4 Comparison of metal concentrations in Kinrooi waters with other literature studies

Table S2 comparison of dissolved metal concentrations in Kinrooi waters with literature studies

| **Element** | **Station** | **Min-Max** µg L$^{-1}$ | **Median** µg L$^{-1}$ | **Average** µg L$^{-1}$ | **Zenne** (average)* µg L$^{-1}$ | **Garonne** (average)** µg L$^{-1}$ | **Deûle** (average)*** µg L$^{-1}$ | **BC**[1] µg L$^{-1}$ | **EQS dissolved** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | AA µg L$^{-1}$ | MAC µg L$^{-1}$ |
| Cd | Effluent | 0.01-0.04 | 0.01 | 0.01 | 0.03 | 0.02 | 0.25 | 0.08 | 0.2[2] | 0.45[2] |
| | Abeek upstream | 0.01-0.11 | 0.02 | 0.03 | | | | | | |
| | Abeek downstream | 0.01-0.08 | 0.03 | 0.03 | | | | | | |
| | PB01A | 0.002-0.15 | 0.01 | 0.03 | | | | | | |
| | PB03A | 0.002-0.04 | 0.01 | 0.01 | | | | | | |
| Pb | Effluent | 0.04-0.32 | 0.19 | 0.17 | 0.38 | 0.06 | 14.1 | 0.2 | 1.2[2] | 14[2] |
| | Abeek upstream | 0.01-0.16 | 0.09 | 0.1 | | | | | | |
| | Abeek downstream | 0.04-0.33 | 0.09 | 0.15 | | | | | | |
| | PB01A | 0.005-0.29 | 0.01 | 0.08 | | | | | | |
| | PB03A | 0.002-0.07 | 0.02 | 0.03 | | | | | | |
| Cr | Effluent | 0.07-0.45 | 0.33 | 0.32 | 1.7 | 0.7 | 0.2 | 0.2 | / | 100[3] |
| | Abeek upstream | 0.14-0.52 | 0.24 | 0.28 | | | | | | |
| | Abeek downstream | 0.18-0.45 | 0.22 | 0.28 | | | | | | |
| | PB01A | 0.09-0.25 | 0.12 | 0.14 | | | | | | |
| | PB03A | 2.4-4.3 | 3.4 | 3.5 | | | | | | |
| Ni | Effluent | 0.08-6.6 | 2.6 | 3.0 | 3.6 | 0.4 | 3.4 | 3.3 | 4[2] | 34[2] |
| | Abeek upstream | 6.4-13 | 9.8 | 9.6 | | | | | | |
| | Abeek downstream | 5.3-15 | 6.8 | 8.5 | | | | | | |
| | PB01A | 1.08-6.1 | 1.9 | 2.7 | | | | | | |
| | PB03A | 0.63-10 | 1.7 | 3 | | | | | | |
| Cu | Effluent | 0.16-2.6 | 0.60 | 0.64 | 1.8 | 1.3 | 3 | 0.4 | / | 8.2[4] |
| | Abeek upstream | 0.08-1.6 | 0.81 | 0.79 | | | | | | |
| | Abeek downstream | 0.002-1.4 | 0.58 | 0.56 | | | | | | |
| | PB01A | 0.002-2.1 | 0.34 | 0.69 | | | | | | |
| | PB03A | 0.02-1.7 | 0.11 | 0.61 | | | | | | |
| As | Effluent | 0.04-0.98 | 0.39 | 0.47 | / | 2.3 | 2 | 0.8 | / | 10[5] |
| | Abeek upstream | 0.01-1.3 | 0.84 | 0.83 | | | | | | |
| | Abeek downstream | 0.49-1.1 | 0.7 | 0.73 | | | | | | |
| | PB01A | 0.97-3.1 | 1.9 | 2 | | | | | | |
| | PB03A | 1.9-3.3 | 2.2 | 2.3 | | | | | | |

* Ma et al., 2023 ; ** Deycard et al., 2014 ; *** Lesven et al., 2009.

[1] Natural background concentrations (BC) used in Dutch water policy (Osté et al., 2011).

[2] DIRECTIVE 2013/39/EU.

[3] Current Chromium Drinking Water Standard according to the Safe Drinking Water Act, United States Environmental Protection Agency (EPA)

[4] DIRECTIVE 2000/60/EC.

[5] Guideline value for arsenic in drinking-water, World Health Organization (WHO)

Table S3 comparison of particulate metal concentrations with other literature studies

| **Element** | **Station** | **Min-Max** µg g$^{-1}$ | **Median** µg g$^{-1}$ | **Average** µg g$^{-1}$ | **Zenne** (average)[*] µg g$^{-1}$ | **Garonne** (average)[**] µg g$^{-1}$ | **Deûle** (average)[***] µg g$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Cd | Effluent | 0.14-10 | 1.1 | 3.4 | 4 | 0.81 | 83 |
| | Abeek upstream | 2.9-16 | 12 | 11 | | | |
| | Abeek downstream | 0.7-12 | 8.2 | 7.6 | | | |
| Pb | Effluent | 23-117 | 40 | 53 | 203 | 60 | 2 |
| | Abeek upstream | 17-285 | 97 | 121 | | | |
| | Abeek downstream | 38-418 | 118 | 179 | | | |
| Cr | Effluent | 3-344 | 83 | 124 | 247 | 100 | 85 |
| | Abeek upstream | 17-232 | 75 | 87 | | | |
| | Abeek downstream | 7-194 | 111 | 98 | | | |
| Ni | Effluent | 0.5-140 | 23 | 35 | 51 | 56 | 40 |
| | Abeek upstream | 37-238 | 146 | 138 | | | |
| | Abeek downstream | 13-140 | 103 | 93 | | | |
| Cu | Effluent | 0.001-221 | 119 | 120 | 294 | 40 | 127 |
| | Abeek upstream | 0.001-182 | 78 | 73 | | | |
| | Abeek downstream | 16-83 | 62 | 49 | | | |
| As | Effluent | 0.08-533 | 42 | 121 | / | 23 | / |
| | Abeek upstream | 17-242 | 73 | 102 | | | |
| | Abeek downstream | 18-304 | 63 | 121 | | | |

[*] Ma et al., 2023.

[**] Deycard et al., 2014.

[***] Lesven et al., 2009.

## 1.5 Seasonal variations of metal partition coefficients (Log $K_d$) for particulate trace element concentrations to dissolved trace element concentrations.

Figure S2 Seasonal variations of metal partition coefficients (Log $K_d$) for particulate trace element concentrations to dissolved trace element concentrations. According to the literature data for suspended matter in water column, Log $K_d$ profile is distributed into three areas: grey area (■) represents the average values with the standard deviation; light red area (🟥) represents the range between the minimum and maximum values; and no background area represents the values out of literature ranges.

Table S4 Comparison of partitioning coefficients (Log $K_d$) in WWTP and receiving rivers in Belgium.

| | Log $K_d$ | | | | | | SPM |
|---|---|---|---|---|---|---|---|
| | Pb | Cr | Cd | Cu | As | Ni | (mg/L) |
| Effluent WWTP (Kinrooi) | 5.52 | 5.26 | 5.12 | 5.28 | 4.88 | 3.94 | 4 |
| Abeek upstream | 6.04 | 5.46 | 5.55 | 4.91 | 5.09 | 4.13 | 9 |
| Abeek downstream | 6.08 | 5.49 | 5.39 | 4.68 | 5.09 | 3.99 | 18 |
| Effluent WWTP (Brussels) | 5.41 | 5.05 | 4.49 | 4.65 | 3.75 | 3.7 | 14 |
| Zenne downstream | 5.86 | 5.37 | 5.46 | 5.24 | 4.1 | 3.86 | 29 |

Results for Zenne downstream and the effluent of WWTP are unpublished results.

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