Major and trace element concentrations in hydrological Critical Zone compartments in the Conventwald (Black Forest, Germany)

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1. Licence

2. Citation

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3. Data Description

This dataset contains element concentrations of six different hydrological compartments sampled on a daily basis over the course of one year in two neighboured first order headwater catchments located in the Conventwald (Black Forest, Germany). Critical Zone water compartments include above-canopy precipitation (bulk precipitation including rainwater, snow and fog water), below-canopy precipitation (throughfall), subsurface flow from three distinct soil layers (organic layer, upper mineral soil, deep mineral soil), groundwater, creek water and spring water. Element concentrations include major elements (Ca, K, Mg, Na, Si, S), trace elements (Al, Ba, Cr, Cu, Fe, Li, Mn, P, Sr, Zn), anion (Cl), and dissolved organic elements (DOC, DON).

The data were used to explore concentration (C) - discharge (Q) relationships and to calculate short-term element-specific chemical weathering fluxes, which were compared with previously published long-term element-specific chemical weathering fluxes. The ratio of both weathering fluxes, described by the so-called "Dissolved Export Efficiency" (DEE) metric revealed deficits in the stream dissolved load. These deficits were attributed to colloid-bound export and either storage in re-growing forest biomass or export in biogenic particulate form.

Tables supplementary to the article, including data quality control, are provided in .pdf and .xlsx formats. In addition, data measured in the course of the study are also provided as machine readable ASCII files.

3.1. Sampling

Time series of water samples were taken over the course of one year from 01.03.2015 to 25.02.2016. Groundwater, creek water, and spring water were sampled at a daily resolution. Subsurface flow was only sampled on days that were preceded by precipitation events. Sampling was carried out at midnight by automatic samplers (self-construction, University of Freiburg, Hydrology). At a bi-weekly resolution, bulk precipitation and throughfall were sampled in precipitation collectors. Field samples were collected every three to four days, acidified after filtration through 0.8 µm membranes, shipped to GFZ-Potsdam and stored at 4° C prior to analyses.

3.2. Analytical methods

Analytical procedures were mainly carried out at the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES). Briefly, concentrations of major elements (Ca, K, Mg, Na, S, Si) and trace elements (Al, Ba, Cr, Cu, Li, Fe, Sr, Zn) were measured with an inductively coupled plasma optical spectrometer (ICP-OES, Varian 720ES) by external calibration with matrix-matched calibration standards. Analytical uncertainties were obtained from repeat analyses of four standard reference materials (National Research Council of Canada (SLRS-5), National Institute of Standards and Technology (SRM 1640a), and U.S. Geological Survey (M-212, T187)). Relative uncertainties were better than 5% for major and better than 10% for trace elements.

Phosphorus concentrations (previously published in Sohrt et al. (2019)) were measured without dilution by inductively coupled plasma mass spectrometry (ICP-MS, Element2, Thermo Fischer Scientific) in medium resolution ($m/mz \approx 4000$) and with external calibration. Accuracy and precision were assessed using two standard reference materials (SLRS-5 and M212) and are better than 10%.

Concentrations of total dissolved carbon (C), dissolved inorganic carbon (DIC), dissolved organic nitrogen (DON), and chloride (Cl) were also previously published in Sohrt et al. (2019). Concentrations of C, DIC, and DON were measured with a Shimadzu Vcpn analyzer. Given that all concentrations of DIC were below the limit of detection of 50 $\mu g\ l^{-1}$, total dissolved carbon corresponds to dissolved organic carbon (DOC). Chloride was measured with an ion chromatograph (790 Personal IC, Metrohm) at the Chair of Soil Ecology, University of Freiburg.

The relative proportions of different water compartments contributing to discharge were disentangled using an end member mixing analysis (EMMA). The EMMA was described in detail in Sohrt et al. (2019) and used solute concentrations presented in this study as input parameters from three end members: Groundwater, subsurface flow from the top layer (SF1) and from the combined intermediate and basal layer (SF2 & SF3). Annual average element concentrations of Ca, Cl, DOC, K, Mg, Na, S and Si from all water compartments were processed with the software package EMMAgeo in the R Environment (Dietze & Dietze, 2013). Then, the model was calibrated to time series data using element concentrations of spring water. Data from the basal layer SF3 was combined with data from the intermediate layer SF2 because of the limited number of samples from SF3.

4. File description

Supplementary tables to Uhlig et al. (2023) are provided in .pdf and .xlsx formats. In addition, analytical data are provided as tab separated ASCII files. The first three rows in the ASCII files begin with "#" and contain licence and citation. In all files, values that were not measured or which were below the limit of detection were marked with "NA".

4.1. File inventory

- **Table S1** Element concentrations in bulk precipitation (BP)
- **Table S2** Element concentrations in throughfall (TF)
- **Table S3** Element concentrations in subsurface flow (SF1, SF2, SF3)
- **Table S4** Element concentrations in creek water (CW) and relative contributions of groundwater (f_{GW}) and subsurface flow (f_{SF1}, $f_{SF2 \& SF3}$) to creek water
- **Table S5** Element concentrations in spring water (SW) and relative contributions of groundwater (f_{GW}) and subsurface flow (f_{SF1}, $f_{SF2 \& SF3}$) to spring water
- **Table S6** Element concentrations in groundwater (GW)
- **Table S7** Data quality control

4.2. 2023-020_Uhlig Table S1 Element concentrations in bulk precipitation (BP)

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling period	dimensionless	Date at the beginning and ending of sampling period (day, month, year)
precipitation min.	$l\ d^{-1}$	Minimum rainfall
precipitation max.	$l\ d^{-1}$	Maximum rainfall
Ca	$mg\ l^{-1}$	[a] Concentration of calcium
K	$mg\ l^{-1}$	[a] Concentration of potassium
Mg	$mg\ l^{-1}$	[a] Concentration of magnesium
Na	$mg\ l^{-1}$	[a] Concentration of sodium
Si	$mg\ l^{-1}$	[a] Concentration of silicon
S	$mg\ l^{-1}$	[a] Concentration of sulphur
Al	$\mu g\ l^{-1}$	[b] Concentration of aluminium
Ba	$\mu g\ l^{-1}$	[b] Concentration of barium
Cr	$\mu g\ l^{-1}$	[b] Concentration of chromium
Cu	$\mu g\ l^{-1}$	[b] Concentration of copper
Fe	$\mu g\ l^{-1}$	[b] Concentration of iron
Li	$\mu g\ l^{-1}$	[b] Concentration of lithium
Mn	$\mu g\ l^{-1}$	[b] Concentration of manganese
Sr	$\mu g\ l^{-1}$	[b] Concentration of strontium
Zn	$\mu g\ l^{-1}$	[b] Concentration of zinc
P	$\mu g\ l^{-1}$	[c] Concentration of phosphorus
Cl	$mg\ l^{-1}$	[d] Concentration of chlorine
DOC	$mg\ l^{-1}$	[d] Concentration of dissolved organic carbon
DON	$mg\ l^{-1}$	[d] Concentration of dissolved organic nitrogen

[a] major element, measured with ICP-OES

[b] trace element, measured with ICP-OES

[c] trace element, measured with ICP-MS

[d] anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)

4.3. 2023-020_Uhlig Table S2 Element concentrations in throughfall (TF)

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling period	dimensionless	Date at the beginning and ending of sampling period (day, month, year)
precipitation min.	$l\ d^{-1}$	Minimum rainfall
precipitation max.	$l\ d^{-1}$	Maximum rainfall
Ca	$mg\ l^{-1}$	[a] Concentration of calcium
K	$mg\ l^{-1}$	[a] Concentration of potassium
Mg	$mg\ l^{-1}$	[a] Concentration of magnesium
Na	$mg\ l^{-1}$	[a] Concentration of sodium
Si	$mg\ l^{-1}$	[a] Concentration of silicon
S	$mg\ l^{-1}$	[a] Concentration of sulphur
Al	$\mu g\ l^{-1}$	[b] Concentration of aluminium
Ba	$\mu g\ l^{-1}$	[b] Concentration of barium
Cr	$\mu g\ l^{-1}$	[b] Concentration of chromium
Cu	$\mu g\ l^{-1}$	[b] Concentration of copper
Fe	$\mu g\ l^{-1}$	[b] Concentration of iron
Li	$\mu g\ l^{-1}$	[b] Concentration of lithium
Mn	$\mu g\ l^{-1}$	[b] Concentration of manganese
Sr	$\mu g\ l^{-1}$	[b] Concentration of strontium
Zn	$\mu g\ l^{-1}$	[b] Concentration of zinc
P	$\mu g\ l^{-1}$	[c] Concentration of phosphorus
Cl	$mg\ l^{-1}$	[d] Concentration of chlorine
DOC	$mg\ l^{-1}$	[d] Concentration of dissolved organic carbon
DON	$mg\ l^{-1}$	[d] Concentration of dissolved organic nitrogen

[a] *major element, measured with ICP-OES*

[b] *trace element, measured with ICP-OES*

[c] *trace element, measured with ICP-MS*

[d] *anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)*

4.4. 2023-020_Uhlig Table S3 Element concentrations in subsurface flow (SF1, SF2, SF3)

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling date	dimensionless	Date of sampling (day, month, year)
Subsurface flow compartment	dimensionless	[a] Description of subsurface flow compartment
Ca	mg l^{-1}	[b] Concentration of calcium
K	mg l^{-1}	[b] Concentration of potassium
Mg	mg l^{-1}	[b] Concentration of magnesium
Na	mg l^{-1}	[b] Concentration of sodium
Si	mg l^{-1}	[b] Concentration of silicon
S	mg l^{-1}	[b] Concentration of sulphur
Al	µg l^{-1}	[c] Concentration of aluminium
Ba	µg l^{-1}	[c] Concentration of barium
Cr	µg l^{-1}	[c] Concentration of chromium
Cu	µg l^{-1}	[c] Concentration of copper
Fe	µg l^{-1}	[c] Concentration of iron
Li	µg l^{-1}	[c] Concentration of lithium
Mn	µg l^{-1}	[c] Concentration of manganese
Sr	µg l^{-1}	[c] Concentration of strontium
Zn	µg l^{-1}	[c] Concentration of zinc
P	µg l^{-1}	[d] Concentration of phosphorus
Cl	mg l^{-1}	[e] Concentration of chlorine
DOC	mg l^{-1}	[e] Concentration of dissolved organic carbon
DON	mg l^{-1}	[e] Concentration of dissolved organic nitrogen

[a] SF1 (0-15 cm) refers to the organic layer, SF2 (15-150 cm) refers to the upper mineral soil, SF3 (150 – 320 cm) refers to the deep mineral soil

[b] major element, measured with ICP-OES

[c] trace element, measured with ICP-OES

[d] trace element, measured with ICP-MS

[e] anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)

4.5. 2023-020_Uhlig Table S4 Element concentrations in creek water (CW) and relative contributions of groundwater (f_{GW}) and subsurface flow (f_{SF1}, $f_{SF2\ \&\ SF3}$) to creek water

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling date	dimensionless	Date of sampling (day, month, year)
discharge	$l\ s^{-1}$	streamflow
T	°C	water temperature
Ca	$mg\ l^{-1}$	[a] Concentration of calcium
K	$mg\ l^{-1}$	[a] Concentration of potassium
Mg	$mg\ l^{-1}$	[a] Concentration of magnesium
Na	$mg\ l^{-1}$	[a] Concentration of sodium
Si	$mg\ l^{-1}$	[a] Concentration of silicon
S	$mg\ l^{-1}$	[a] Concentration of sulphur
Al	$\mu g\ l^{-1}$	[b] Concentration of aluminium
Ba	$\mu g\ l^{-1}$	[b] Concentration of barium
Cr	$\mu g\ l^{-1}$	[b] Concentration of chromium
Cu	$\mu g\ l^{-1}$	[b] Concentration of copper
Fe	$\mu g\ l^{-1}$	[b] Concentration of iron
Li	$\mu g\ l^{-1}$	[b] Concentration of lithium
Mn	$\mu g\ l^{-1}$	[b] Concentration of manganese
Sr	$\mu g\ l^{-1}$	[b] Concentration of strontium
Zn	$\mu g\ l^{-1}$	[b] Concentration of zinc
P	$\mu g\ l^{-1}$	[c] Concentration of phosphorus
Cl	$mg\ l^{-1}$	[d] Concentration of chlorine
DOC	$mg\ l^{-1}$	[d] Concentration of dissolved organic carbon
DON	$mg\ l^{-1}$	[d] Concentration of dissolved organic nitrogen
f_GW	dimensionless	Relative contribution of groundwater to creek water
f_SF1	dimensionless	Relative contribution of subsurface water from top layer to creek water
f_SF2 & SF3	dimensionless	Relative contribution of subsurface water from intermediate and basal layer to creek water

[a] major element, measured with ICP-OES
[b] trace element, measured with ICP-OES
[c] trace element, measured with ICP-MS
[d] anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)

4.6. 2023-020_Uhlig Table S5 Element concentrations in spring water (SW) and relative contributions of groundwater (f_{GW}) and subsurface flow (f_{SF1}, $f_{SF2\ \&\ SF3}$) to spring water

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling date	dimensionless	Date of sampling (day, month, year)
discharge	$l\ s^{-1}$	streamflow
T	°C	water temperature
Ca	$mg\ l^{-1}$	[a] Concentration of calcium
K	$mg\ l^{-1}$	[a] Concentration of potassium
Mg	$mg\ l^{-1}$	[a] Concentration of magnesium
Na	$mg\ l^{-1}$	[a] Concentration of sodium
Si	$mg\ l^{-1}$	[a] Concentration of silicon
S	$mg\ l^{-1}$	[a] Concentration of sulphur
Al	$\mu g\ l^{-1}$	[b] Concentration of aluminium
Ba	$\mu g\ l^{-1}$	[b] Concentration of barium
Cr	$\mu g\ l^{-1}$	[b] Concentration of chromium
Cu	$\mu g\ l^{-1}$	[b] Concentration of copper
Fe	$\mu g\ l^{-1}$	[b] Concentration of iron
Li	$\mu g\ l^{-1}$	[b] Concentration of lithium
Mn	$\mu g\ l^{-1}$	[b] Concentration of manganese
Sr	$\mu g\ l^{-1}$	[b] Concentration of strontium
Zn	$\mu g\ l^{-1}$	[b] Concentration of zinc
P	$\mu g\ l^{-1}$	[c] Concentration of phosphorus
Cl	$mg\ l^{-1}$	[d] Concentration of chlorine
DOC	$mg\ l^{-1}$	[d] Concentration of dissolved organic carbon
DON	$mg\ l^{-1}$	[d] Concentration of dissolved organic nitrogen
f_GW	dimensionless	Relative contribution of groundwater to spring water
f_SF1	dimensionless	Relative contribution of subsurface water from top layer to spring water
f_SF2 & SF3	dimensionless	Relative contribution of subsurface water from intermediate and basal layer to spring water

[a] major element, measured with ICP-OES
[b] trace element, measured with ICP-OES
[c] trace element, measured with ICP-MS
[d] anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)

4.7. 2023-020_Uhlig Table S6 Element concentrations in groundwater (GW)

Column header	unit	Description
sample ID	dimensionless	Sample identifier used in this study
sampling date	dimensionless	Date of sampling (day, month, year)
T	°C	water temperature
Ca	mg l^{-1}	[a] Concentration of calcium
K	mg l^{-1}	[a] Concentration of potassium
Mg	mg l^{-1}	[a] Concentration of magnesium
Na	mg l^{-1}	[a] Concentration of sodium
Si	mg l^{-1}	[a] Concentration of silicon
S	mg l^{-1}	[a] Concentration of sulphur
Al	µg l^{-1}	[b] Concentration of aluminium
Ba	µg l^{-1}	[b] Concentration of barium
Cr	µg l^{-1}	[b] Concentration of chromium
Cu	µg l^{-1}	[b] Concentration of copper
Fe	µg l^{-1}	[b] Concentration of iron
Li	µg l^{-1}	[b] Concentration of lithium
Mn	µg l^{-1}	[b] Concentration of manganese
Sr	µg l^{-1}	[b] Concentration of strontium
Zn	µg l^{-1}	[b] Concentration of zinc
P	µg l^{-1}	[c] Concentration of phosphorus
Cl	mg l^{-1}	[d] Concentration of chlorine
DOC	mg l^{-1}	[d] Concentration of dissolved organic carbon
DON	mg l^{-1}	[d] Concentration of dissolved organic nitrogen

[a] major element, measured with ICP-OES
[b] trace element, measured with ICP-OES
[c] trace element, measured with ICP-MS
[d] anion and dissolved organic elements taken from Supplementary Material published in Sohrt et al. (2019)

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