

Motivation

Regarding the increasing number of technical applications using nanoparticles and reports of adverse effects of engineered nanoparticles, research on the occurrence and stability of particles in all compartments has to be intensified. Colloids in river water represent the geologic setting, environmental conditions, and the anthropogenic use in its catchment. The river not only acts as a sink for nanoparticles but also as the source term due to exchange in the hyporheic zone and in bank filtration setups.

The concentration, size distribution and elemental composition of particles in the River Inn were studied from the source in the Swiss Alps to the river mouth at Passau during a first sampling campaign in spring 2008. Other sampling campaigns were performed in autumn 2013 and late winter 2014 from the upper reaches of the River Inn to the city Kufstein, Austria. Samples were collected after each tributary from a sub-catchment as well as after expected sources of influence on the water chemistry or particle size.

Methods

- Four sampling campaigns were performed from 2008 to 2014. Samples were taken by submerging a sampling device holding a 1 L glass bottle, generally from a bridge to take water from the center of the river in a depth of about 0.2 -1 m.
- Temperature, pH, EC, redox potential, and alkalinity measured on site, cations, anions and metat concentrations of the bulk were analysed from water samples stored dark and cool.
- Filtration of samples started on site to avoid agglomeration and changes due to oxidation. Starting 2013 an on-site filtration unit was used, where the pressure to drive the water through the filter cascade is provided by N_2 , filter sizes were 10 nm to 10 µm.
- Quantification of the elemental composition of the particles retained on each filter stage wasperformed after two step microwave assisted acid digestion (HNO₃-HF) by ICP/MS. Blanks were measured and subtracted for each filter size.
- SEM/EDX was used to assist the identification of the different particles







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Results

- On site parameters (pH, EC, redox potential) of all four sampling campaigns showed a reproducible trend with increasing EC and increasing pH from the source to Kufstein. Against the trend, sampling site #10 always displayed lower pH, EC and redox potentials.
- While almost all elements were detected in the upper reaches of the River Inn, filtration results suggest that fine particles are aggregating with coarse particles further downstream and lost to the sediment.
- Sampling sites #1, #3, #6 and #9 show higher concentrations than the rest, especially with regard to metals. The particle size distribution shows that with increasing river run mostly particles $> 0.1 \mu m$ occur
- Zr, Ti, and K show maximum concentrations at sampling sites #3, #6, and #9. In #6 Mo and Na are enhanced.
- Co, Ba, Fe, Mg, Ni, and P are increasing after sampling site #9. Sb is detectable in #1, #3 and #9 while V is only found in #3, #6, #10, #12 and #14. P is found with small particles (10 and 50 nm) along the river run and with bigger particles at sampling sites #1 and #3. Ag was detected at sampling sites #2, #4 and #5 in the upper reach,
- Cr is only found in particles $> 0.1 \mu m$.
- Al is specially found in the upper reaches of the river and just sparsely after #11.

Conclusion

- The results from the sampling campaign show that particles in the upper, rural parts mainly reveal changes in the geological setting of the tributary catchments.
- SEM/EDX measurements show, not unexpectedly, that particles originating from crystalline rocks, were more stable than particles originating from calcareous rocks.
- A change of the size distribution and an increase of the number of organic particles indicates anthropogenic and industrial influences in the lower reaches of the river Inn.
- Interestingly, specific leisure activities in a subcatchment, like extensive downhill skiing, manifest itself in the particle composition.





