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1 **Elemental composition of natural nanoparticles and fine colloids in European forest**
2 **stream waters and their role as phosphorus carriers**

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89

90 **Key points:**

- 91 • Stream phosphorus is largely bound to natural nanoparticles and colloids
92 • The chemical composition of colloids varies systematically from Northern to Southern
93 European streams

95 Biogeochemical cycling of elements largely occurs in dissolved state, but many elements may
96 also be bound to natural nanoparticles (NNP, 1–100 nm) and fine colloids (100–450 nm). We
97 examined the hypothesis that the size and composition of stream water NNP and colloids vary
98 systematically across Europe. To test this hypothesis, 96 stream water samples were
99 simultaneously collected in 26 forested headwater catchments along two transects across
100 Europe. Three size fractions (~1–20 nm, >20–60 nm, >60 nm) of NNP and fine colloids were
101 identified with Field Flow Fractionation coupled to inductively coupled plasma mass-
102 spectrometry and an organic carbon detector. The results showed that NNP and fine colloids
103 constituted between $2 \pm 5\%$ (Si) and $53 \pm 21\%$ (Fe; mean \pm SD) of total element concentrations,
104 indicating a substantial contribution of particles to element transport in these European
105 streams, especially for P and Fe. The particulate contents of Fe, Al and organic C were
106 correlated to their total element concentrations, but those of particulate Si, Mn, P and Ca were
107 not. The fine colloidal fractions >60 nm were dominated by clay minerals across all sites. The
108 resulting element patterns of NNP <60 nm changed from North to South Europe from Fe- to
109 Ca-dominated particles, along with associated changes in acidity, forest type and dominant
110 lithology.

112 1. Introduction

113 Networks of small streams and large rivers transport mobile compounds over long distances
114 and drive their export from the continents to the oceans [Bishop *et al.*, 2008; Dynesius and
115 Nilsson, 1994]. Environmental water samples contain a wide variety of chemical species,
116 including simply hydrated ions, molecules, colloidal particles and coarser grains [Stumm and
117 Morgan, 1981]. The partitioning between these species controls elemental cycling, transport
118 and loss processes [Stolpe *et al.*, 2010]. Understanding the distribution of the elements
119 between different physicochemical binding forms is thus an important prerequisite for
120 understanding the mechanisms of aquatic and terrestrial ecosystem nutrition [Benedetti *et al.*,
121 1996; Hasseløev *et al.*, 1999; Tipping and Hurley, 1992; Wells and Goldberg, 1991]. This is
122 especially important for those nutrients that are frequently limiting like phosphorus (P)
123 [Jarvie *et al.*, 2012]. Indeed, the recent review by Bol *et al.* [2016] highlighted the
124 (unexpected) scarcity of data on colloidal P fluxes in temperate forest ecosystems, which
125 severely limits accurate quantification of forest P nutrition and losses.

126 Research on nutrient acquisition and cycling processes in stream waters and terrestrial
127 ecosystems has often focused on the ‘dissolved fraction’. This fraction is frequently
128 operationally defined as the aqueous phase that passes a $< 0.45 \mu\text{m}$ filter [Marschner and
129 Kalbitz, 2003 and references therein]. However, it is increasingly recognized that naturally
130 occurring nanoparticles (NNP, $d = 1\text{--}100 \text{ nm}$), and also larger particles belonging to the
131 overall term ‘colloids’ ($d = 1 \text{ nm--}1 \mu\text{m}$), can be substantial components within this
132 operational definition of elements present in the ‘dissolved fraction’. Colloids smaller than
133 $0.45 \mu\text{m}$ ($\approx 450 \text{ nm}$) are in the present study defined as fine colloids. In natural aqueous phases
134 up to 100% of the total elemental concentrations of metals, and also of specific nutrients like
135 P, can be associated with such particles [Gottselig *et al.*, 2014; Hart *et al.*, 1993; Hill and
136 Aplin, 2001; Jarvie *et al.*, 2012; Martin *et al.*, 1995]. Hence, identifying NNP and colloids in
137 water samples is necessary to better understand the cycling and transport of elements in
138 catchments and to determine their biological availability. Headwater catchments are
139 specifically interesting for this analysis because their input variables can be closely defined,
140 thereby facilitating data interpretation. However, it is unknown how the composition and size
141 distributions of NNP and fine colloids vary between headwater catchments on a continental
142 scale. Large-scale studies are advantageous in this context to identify more overarching and
143 broadly applicable principles of NNP and fine colloid composition, and their variations, in
144 natural waters.

145 Prior studies have performed pioneering investigations on particulate P pools in aqueous and
146 terrestrial systems [e.g. *Binkley et al.*, 2004; *Espinosa et al.*, 1999; *Sharpley et al.*, 1995], yet
147 through the applicability of modern particle analysis/fractionation techniques, these
148 functionally defined particulate fractions could be examined more closely and thus allow a
149 more accurate subcategorization of elements in the ‘particulate’ phase. Further, the focus of
150 dissolved elements as being ions of (hydr)oxidized elements in aqueous solution needs to be
151 reconsidered due to the presence of particles within the operationally defined dissolved range
152 [cf. e.g. *Gimbert et al.*, 2003; *Lyven et al.*, 2003; *Regelink et al.*, 2011]. In this regard, Field
153 Flow Fractionation [FFF; *Giddings et al.*, 1976] is a viable tool for these analyses, because it
154 is a nearly non-destructive technique for the fractionation of NNP and fine colloids, thus
155 eliminating the need for pretreatments which can alter the particle composition or size range.

156 The specific reactivity of nanoparticles is high, in comparison to larger sized colloids,
157 [*Hartland et al.*, 2013; *Qafoku*, 2010] rendering them potentially predominant carriers of
158 nutrients in ecosystems. It has already been shown that NNP can bind the majority of P
159 present in soil solutions [*Hens and Merckx*, 2001] and stream waters [*Gottselig et al.*, 2014;
160 *Gottselig et al.*, 2017], and that they can even support plant uptake of P from solution
161 [*Montalvo et al.*, 2015]. First results indicate that organic matter, Fe, and/or Al may be major
162 binding partners for P in NNP of an acidic forest river system and that the binding of P varies
163 depending on the stream water composition [*Baken et al.*, 2016b; *Gottselig et al.*, 2014].
164 Under the acidic conditions that characterize many natural settings (particularly many
165 coniferous forest soils), surfaces of metal (hydr)oxides are positively charged and thus act as
166 strong binding partners for negatively charged nutrients like P [*Hasseløev and von der*
167 *Kammer*, 2008; *Richardson*, 1985] and organic matter [*Celi et al.*, 2005]. Adsorbed P and
168 organic matter can even act as stabilizing agents for colloidal suspensions of particles
169 [*Ranville and Macalady*, 1997; *Six et al.*, 1999]. Organic matter associated with NNP and
170 larger colloids also contains P [*Darch et al.*, 2014]. Some authors even assume that in the
171 smaller size ranges, organophosphorus compounds can also act as the primary building blocks
172 of NNP [*Regelink et al.*, 2013], although these building blocks are more commonly thought to
173 be aluminosilicates, organic matter (org C), or oxides and/or hydroxides of iron (Fe),
174 aluminum (Al), and manganese (Mn) [*Baken et al.*, 2016b; *Hartland et al.*, 2013; *Lyven et al.*,
175 2003; *Regelink et al.*, 2011]. At elevated pH levels in stream water, calcium (Ca) is
176 increasingly present in the colloids and associated with P in the form of Ca phosphates. These
177 Ca phosphate colloids can either be in mineral form or associated on organic/organomineral
178 complexes or clays. In the case of Ca colloids, Ca is enriched in the colloidal phase in

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179 comparison to larger suspended matter [*Ran et al.*, 2000], especially when surface waters
180 drain carbonate-rich soils [*Hill and Aplin*, 2001]. This highlights that Ca may also be a
181 building block element of colloids [*Dahlqvist et al.*, 2004], depending on stream water
182 chemistry. The pH-dependent speciation of elements and their related affinity to particles give
183 rise to the hypothesis examined in our study, which states that the composition and size
184 distribution of NNP and fine colloids may not be uniform across large regions. If this is not
185 the case, at least the speciation of elements and their presence in particle fractions would be
186 expected to differ between acidic and alkaline stream waters.

187 Despite their important role in element binding, NNP and fine colloids were not considered as
188 a substantial contributor to nutrient cycling in the past [e.g. *Vitousek*, 1982] and are still often
189 neglected in pioneering studies on the analysis of influential factors on terrestrial nutrient
190 availability [e.g. *Fernández-Martínez et al.*, 2014]. Examining the significance of NNP and
191 fine colloids as well as their composition as a function of forest stream water pH on a
192 continental scale can provide insights into their ecological relevance, particularly if one can
193 use basic water quality parameters to estimate the total elemental concentrations that are
194 associated with NNP and colloids. Better information on the chemical form and reactivity of
195 elements in the putative "dissolved" fraction, in turn, can improve estimates of nutrient
196 availability to plants and microorganisms.

197 For this study, it was hypothesized that NNP and fine colloids are ubiquitous carriers for
198 elements in forested European river systems, but that their composition varies along
199 continental-scale gradients. The respective variations in climate, vegetation, soil and
200 freshwater characteristics (e.g. pH) substantially influence the physico-chemical forms of P
201 and other ecologically important constituents in forested freshwaters, thus, potentially
202 revealing systematic controlling effects on NNP and fine colloid concentrations and
203 composition. To test this hypothesis, 96 stream water samples from 26 forested sites from
204 across Europe were collected. These 26 sites cover a wide range of soil types and parent
205 materials, under deciduous or coniferous forests, over very differently sized catchments, and
206 spanning different elevations and topographic gradients (Table 1). FFF [*Giddings et al.*, 1976;
207 *Hasseløev et al.*, 1999; *Regelink et al.*, 2014], coupled online to high-precision elemental
208 detectors, was used for the fractionation of NNP and colloids. To untangle the importance of
209 single factors, a correlation matrix between all particulate elemental concentrations, total
210 elemental concentrations, and the basic site parameters such as MAT, MAP, forest coverage,
211 slope inclination, and runoff was also investigated.

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212 2. Materials and methods

213 2.1 Sampling

214 Twenty-six sites throughout Europe were selected along two transects, one from northern
215 Finland to Portugal and the other from Scotland to Greece (Figure 1, Table 1). Each site is a
216 forested headwater catchment with low-intensity forest management practices, high tree
217 coverage and without inflows from urban or agricultural settings (for site abbreviations, see
218 Table 1). Mean annual temperatures ranged between -1.4 °C (PA, Finland) and +15.9 °C (FR,
219 CO and PR, Italy) and mean annual precipitation ranged between 450 mm (BPC, Spain) and
220 2426 mm (LÜ, Switzerland) (Table 1). It was possible to assign a clear dominant forest type
221 for 25 of the 26 sites (either coniferous or broadleaf), while the BPC site had 50% coniferous
222 and 50% broadleaf tree species. Additionally, data on catchment size, average elevation,
223 average slope, percentage forest cover and mean annual runoff were collected where available
224 (Table 1). All data were provided by the current site operators. During sampling, the electrical
225 conductivity, pH and water temperature of the water samples ranged substantially from
226 13 µS/cm (SB) to 1775 µS/cm (BPC), from 4.2 (GS) to 9.5 (RS) and from 1.0 °C (PA) to
227 19.9 °C (RS) (for complete data of all main stream and tributary samples, see supplementary
228 material, Table S1). Up to six samples were taken per site in May 2015 in order to derive a
229 snapshot of NNP and fine colloid composition and their relevance for P transport across
230 Europe at a given time of the year. The sampling locations were defined in consultation with
231 the site operators to best reflect main and tributary streams of each catchment, similar to the
232 approach of *Gottselig et al.* [2014]. Sampling was conducted during base flow conditions. The
233 sampling resulted in a total of 96 samples taken in duplicates in pre-cleaned PE and glass
234 bottles and shipped cooled to the lab; analysis of NNP and fine colloids was completed within
235 1 week after sampling. Own unpublished data indicate that during one week there is no
236 significant alteration in the size distribution of NNP and fine colloids, despite selected risks of
237 minor particle re-aggregation in the larger size range. To minimize the risk of systematic
238 errors due to sampling storage and pretreatment, all samples were handled, treated and
239 analyzed in equal manner.

240 *Figure 1*

241 *Table 1*

242 2.2 Asymmetric Flow Field Flow Fractionation

243 Fractionation of the particles was performed with Asymmetric Flow Field Flow Fractionation
244 (AF⁴). Briefly, a 0.5 mm spacer, a 1 kDa polyether sulfone (PES) membrane and a 25 µM
245 NaCl eluent solution were applied. 5 mL of the PE bottled samples were injected into the AF⁴
246 system at 0.3 mL/min tip flow and 3 mL/min cross flow and focused for 30 min with
247 3.2 mL/min focus flow. Thereafter, a 30 min linear cross flow gradient down to 0 mL/min
248 with subsequent 40 min constant elution at a detector flow of 0.5 mL/min was applied.
249 Reference materials (Suwanee River NOM, Humic Acid Standard II and Fulvic Acid
250 Standard II, International Humic Substances Society, Denver, USA; Sulfate Latex Standards
251 8% w/v 21- 630 nm; Postnova Analytics, Landsberg, Germany) were used with the same AF⁴
252 conditions used for the samples for calibration of the particle diameters included in each size
253 fraction. No reference material exists that covers the diverse particle morphologies and
254 elemental concentrations of environmental samples. Therefore, the specified hydrodynamic
255 diameters of the particles are equivalent sizes based on the elution time of the reference
256 materials [c.f. *Neubauer et al.*, 2011; *Regelink et al.*, 2013; *Stolpe et al.*, 2010]. The lower size
257 range of the first fraction was estimated according to the molecular weight cut-off (MWCO)
258 of the membrane.

259 Online coupling of a UV detector (254 nm) served to initially determine peak elution and
260 turbidity of the particle fractions. A dynamic light scattering (DLS) device was coupled for
261 online size measurements of the largest size fraction. Blank runs inserted between sample
262 runs in the measurement sequence showed no pronounced peaks. A quadrupole inductively
263 coupled plasma mass-spectrometer (ICP-MS) with helium collision cell technology (Agilent
264 7500, Agilent Technologies, Japan) and for size-resolved detection of organic carbon an
265 Organic Carbon Detector (OCD; DOC Labor, Karlsruhe, Germany) were coupled online to
266 the AF⁴. The ICP-MS allowed size-resolved detection of Al, Si, P, Ca, Mn and Fe, and the
267 OCD allowed size-resolved detection of organic carbon. The ICP-MS system was calibrated
268 through a post-column [*Nischwitz and Goenaga-Infante*, 2012] multi-point linear calibration
269 injected via a T-junction between the AF⁴ and the ICP-MS at 0.5 mL/min AF⁴ injection flow
270 (= detector flow; no cross flow). The standard solutions (0 µg/L, 25 µg/L, 100 µg/L, 250 µg/L
271 and 500 µg/L) and the internal standards Rh and Y were dissolved in 0.5 mol/L HCl. This
272 calibration technique is more complex than injecting the calibration standards directly into the
273 AF⁴ system, but allows more precise correction of instrumental drift and calibration to higher
274 concentrations without potentially contaminating the following sample (because the standards

275 do not pass through the AF⁴). The variations of the ICP-MS peak areas for triplicate
276 measurements of a representative sample were calculated to be 5.9% for P, 7.6% for Al,
277 14.0% for Si, 5.3% for Mn and 15.6% for Fe. The limit of detection was 0.1 µg/L for P,
278 0.01 µg/L for Al, 3.3 µg/L for Si, 0.01 µg/L for Mn and 0.02 µg/L for Fe. Quantitative
279 atomization of the particles in the plasma has already been shown by *Schmitt et al.* [2002].

280 For the OCD coupling, 1 mL sample volume from the glass bottles was injected and focused
281 for 10 min; the remaining parameters were the same as for ICP-MS coupling. The OCD
282 system was calibrated using dilutions of Certipur® liquid TOC standard (EN 1484-H3/DIN
283 38409-H3, Potassium hydrogen phthalate in water, stabilized, 1000 mg/L; Merck Millipore
284 109017) in double-distilled water at concentrations of 0.05 mg/L, 0.1 mg/L, 0.5 mg/L,
285 1.0 mg/L, 3.0 mg/L and 5.0 mg/L. The same calibration standards were also used in
286 determining the total organic carbon in the stream water samples. For this determination, the
287 AF⁴ channel was bypassed by connecting the tip inflow tubing to the detector outlet tubing of
288 the channel. The runtime of the AF⁴ method for this data acquisition was 20 min at
289 0.5 mL/min tip flow. The relative standard deviation of the organic carbon concentration for
290 triplicate measurements of a representative sample was calculated to be 2.2%. The limit of
291 detection for organic C was 0.01 mg/L.

292 2.3 *Quality control*

293 First investigations on the stability of NNP and colloids were conducted prior to the sampling
294 campaign to elucidate which sampling, storage and transport procedures best reflect natural
295 conditions at the time of measurement. This resulted in a sampling of unprocessed stream
296 water with polypropylene containers; only samples for organic carbon analysis were taken
297 with pre-cleaned and pre-equilibrated glass vials. Samples were always taken in order moving
298 upstream, from the catchment outlet to the headwaters. Containers were preconditioned in
299 triplicates with stream water before the sample was taken from the center of the flowing
300 stream without disturbing the sediment. Larger-sized particulates (e.g., visible parts of leaves)
301 were not included in the water sample. For transport and storage, the samples were kept at a
302 cool to ambient temperature, but neither were they frozen nor did their temperature ever
303 exceed the stream temperature at sampling. Sample analysis was conducted as soon as
304 possible after sampling, especially for organic carbon analysis. The analyses were performed
305 in the order the samples arrived. For a more detailed discussion of circumstances affecting
306 colloidal stability, see Buffle and Leppard [1995].

307 Immediately prior to analysis, samples were homogenized through agitation, then filtered
308 through 5 µm cellulose nitrate filters (GE Healthcare, Munich, Germany) to avoid clogging of
309 the micrometer-sized AF⁴ tubing. No interference of cellulose and/or cellulose nitrate
310 compounds with the org C signal was expected because both are insoluble in water
311 [Hagedorn, 2006; Roth, 2011]. Still, the filters were pre-rinsed with 15 mL double-deionized
312 water to eliminate eventual bleeding compounds. Caking was prevented by filtering only
313 small sample volumes up to 15 mL. Additionally, more than one filter was available per
314 sample, but this was not needed due to the low turbidity of the samples. Filtration at 0.45 µm
315 was purposely not performed, to avoid the risk of excluding particles not specific to the given
316 size due to unknown morphological heterogeneity of the natural particles. Avoiding filtration
317 also avoided the risk of membrane clogging when filtering occurs close to target size ranges
318 of the analytes, which can result in a severe risk of underestimating NNP and fine colloidal
319 concentrations [Zirkler *et al.*, 2012].

320 The recovery of NNP and fine colloids fractionated by AF⁴ is greatly influenced by
321 interactions of the natural particles with the membrane, particularly during focus time and at
322 long and/or high cross flows. For natural samples, a portion of the sample was thus withdrawn
323 from the fractionation process and measured by independent ICP-MS analysis (cf. section
324 3.1), thereby allowing us to relate element yields after fractionation to those without AF⁴
325 treatment. This analysis showed that the different elements associated to NNP and fine
326 colloids ranged up to 99.5% of total elemental concentration, showing that generally there
327 was no major particle loss. A more in-depth investigation of the AF⁴ recoveries with synthetic
328 iron oxyhydroxide colloids revealed recoveries between 70 and 93% [Baken *et al.*, 2016a].
329 These results are encouraging also for natural samples due to the similarity of the particle
330 constituents.

331 2.4 Analysis of raw data

332 ICP-MS raw data were collected in counts per second (cps) using the MassHunter
333 Workstation Software (Agilent Technologies, Japan) and OCD raw data were recorded in
334 volts detector signal (V) with the AF⁴ analytical software (Postnova Analytics, Landsberg,
335 Germany). Raw data were exported to Excel® (Microsoft Corporation, Redmond, USA) for
336 baseline correction, peak integration and conversion of peak areas to concentrations through
337 multipoint linear calibration. Different pools of elements were considered in this study: a)
338 elemental concentrations assigned to the 1st, 2nd or 3rd size fraction of NNP and fine colloids
339 (see section 3.1 for explanation), b) all particulate elemental concentrations, reflecting the

340 sum of (e.g.) Fe concentrations in the 1st, 2nd and 3rd fractions combined, and c) the total
341 concentration of an element in the sample prior to fractionation. The collective term ‘colloids’
342 is occasionally used in our study as an encompassing term for the whole size range of
343 nanoparticles and colloids. Concentrations are primarily given in $\mu\text{mol/L}$ for Al, Si, P, Ca, Mn
344 and Fe, and in mmol/L for org C.

345 Stream water pH at sampling time was classified according to the Soil Survey Division of the
346 Natural Resources Conservation Service, U. S. Department of Agriculture [USDA, 1993], in
347 order to clarify the influence of stream water pH and associated covariates on the
348 relationships between NNP and fine colloid concentrations and total concentrations.
349 According to this classification, acidic is defined as $\text{pH} < 6.6$, neutral pH between 6.6 and 7.3
350 and alkaline pH values > 7.3 . Thus, pH was transformed into a semi-quantitative variable,
351 where each range of values is assigned to a given category.

352 Predictability of elemental concentrations through total concentrations was assessed through
353 \log_{10} transformation of the elemental concentrations in the fractions and the total sample
354 concentrations. Here, we only considered regressions that achieved an $r \geq 0.71$. Further, sites
355 were classified according to location (North, Middle, South) in Europe. To test if this zoning
356 was able to differentiate element distributions of the NNP and other fine colloidal fractions,
357 we focused on particulate Fe as redox-sensitive element, and particulate Si as an indicator of
358 siliceous bedrock and clay minerals. Also, we classified the study sites by major soil types
359 (dystrophic, eutrophic and semi-terrestrial), and bedrock lithologies (siliceous, calcareous, and
360 flysch), as well as two main forest types (coniferous/needle vs. broadleaf vs. mixed, see Table
361 1). Dystrophic soils included Podzols, as well as coniferous Cambisols, Leptosols and
362 Regosols; eutrophic soils were deciduous Cambisols, Leptosols, and Mollisols; semi-
363 terrestrial soils were Fluvisols and Gleysols (the sole Histosol was not included in this group
364 comparison). Siliceous bedrock included all bedrock types except calcareous stone, limestone
365 and flysch. Flysch was assigned to a specific bedrock group, because it usually contains both
366 carbonates and silicate minerals; the respective soils sampled were Gleysols (Table 1).

367 Further, the dependency of elements in the NNP and fine colloid fractions on the total
368 elemental concentration as well as the potential predictability of NNP and fine colloidal
369 composition were analyzed through correlation analysis with Pearson r coefficients, pairwise
370 deletion of missing data (JMP 12.2.0, SAS Institute Inc., USA) and significance testing using
371 non-parametric group comparisons with the Mann-Whitney U-test for comparisons between
372 two sample sets and with the Kruskal-Wallis ANOVA for comparisons among more than two

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373 sample sets (Statistica, Version 13, Dell Inc., Tulsa, USA). To facilitate the examination of
374 controlling factors of NNP and fine colloid composition, correlation matrices followed by
375 principal component analysis (Statistica, Version 13, Dell Inc., Tulsa, USA) served as an
376 additional tool to reduce the number of variables and reveal a first structure in the
377 relationships between the variables. Through this, we aimed at an identification of the site
378 parameters, which are influential on particulate elemental concentrations. Varimax raw was
379 applied as the rotational strategy for the analysis, to maximize the variances of the squared
380 raw factor loadings across variables for each factor. Here, casewise deletion of missing data
381 was undertaken to ensure that the same number of cases entered into every analysis. Initially,
382 calculations of the Kaiser-Meyer-Olkin Measure of Sampling Adequacy (KMO value; IBM
383 SPSS Statistics 22) were performed to extract site parameters suitable for PCA analysis.
384 When using all data, KMO was 0.5 and the PCA result was not stable against random
385 elimination of input data; only with selected input variables a $KMO > 0.6$ was achieved and
386 the PCA was stable against variations in input data. As a follow-up tool, stepwise multiple
387 regression was used, but it did not yield meaningful results due to the remaining complex
388 interplay of the data.

389

390 3. Results and discussion

391 3.1 Fractionation of nanoparticles and fine colloids

392 Similarly to findings for a forested watershed in Germany [Gottselig *et al.*, 2014], the
393 application of the AF⁴ technique to other forested sites across Europe revealed distinct
394 fractions of nanoparticles and fine colloids depending on the element investigated (Figure 2a,
395 b; cf. supplementary material, Table S2). In total, three fractions of NNP and/or fine colloids
396 were distinguishable for most (out of 96 samples, in 58.3% org C and Si were found in all
397 three fractions, in > 85% for Ca and P, and in > 95% for Al, Mn and Fe; cf. supplementary
398 material, Table S2) samples. The fractograms included a peak of small-sized nanoparticles (1st
399 fraction), a second peak consisting of intermediate-sized nanoparticles (2nd fraction) and a 3rd
400 peak containing the largest-sized nanoparticles and fine colloidal matter (see also peak
401 separation by dashed lines on the x-axis in Figure 2). The peak pattern for each sample is
402 represented by the fractograms of each element (see Figure 2). The second peak as shown for
403 Krycklan, Sweden, was mainly defined through the Ca signal (violet; Figure 2a, b) due to the
404 absence of other elemental peaks in the 2nd fraction. P was variably detected in one, two or

405 three size fractions (Figure 2c, d; cf. supplementary material, Table S2). Hence, three
406 different size fractions were isolated in this work, in close agreement with *Stolpe et al.* [2010],
407 who also found three to four fractions of NPP and fine colloids in the lower Mississippi River,
408 the largest river in North America.

409 Nanoparticles were the exclusive constituent of the first two fractions and, based on
410 hydrodynamic diameters, accounted for approximately 20% in the third fraction. The first and
411 second fractions consisted of nanoparticles with standard equivalent hydrodynamic diameters
412 ranging from 1 kDa [equivalent to 0.66 nm, equation 2.2, *Erickson*, 2009] to 20 nm, and from
413 above 20 nm to 60 nm, respectively. The third fraction included nanoparticles larger than
414 60 nm up to fine colloids of approximately 300 nm in diameter. The DLS measurements
415 revealed this maximum particle size for all measured samples [c.f. *Gottselig et al.*, 2014;
416 *Gottselig et al.*, 2017]. Hence, all detected NNP and fine colloids fell into the operationally
417 defined ‘dissolved phase’ ($< 0.45 \mu\text{m}$). Substantial signals of the elements Fe, P, Mn, Al, C
418 and Si were recorded in all three size fractions with varying intensities, confirming
419 widespread occurrence of NNP and fine colloids in the size range $< 450 \text{ nm}$.

420 *Figure 2*

421 The fractograms for P are markedly different among three sites spanning across one transect
422 in Europe (Pallas in North Europe, Bode in Middle Europe, and Ribera Salada in South
423 Europe; PA, BO and RS in Figure 2c), consistent with the hypothesis that NNP and fine
424 colloid composition and size distribution vary across the continental scale. More generally,
425 we observed differences in the P distribution within NNP and fine colloids among the various
426 forested headwater catchments in Europe: i.e., sometimes the particulate P was associated
427 with clearly distinct fractions (e.g. PA; Figure 2c), whereas for other samples a less distinct
428 fractionation of P (e.g. BO; Figure 2c) was observed. This exemplary described variation of
429 elemental concentrations in the three fractions was observed for all recorded elements,
430 supporting the general hypothesis that there are differences in the elemental composition
431 between fractions and among the selected European streams. These patterns were found to be
432 related to site-specific properties such as climate, water chemistry, soil type and total stream
433 water elemental concentrations, i.e., we tested in the following to systematize the differences
434 according to element composition and site properties.

435 3.2 Significance of NNP and fine colloids for element partitioning in water samples

436 The percentages of elements bound to NNP and fine colloids (i.e., percentage of all particulate
437 elemental to total elemental concentration) demonstrated the substantial contribution of NNP
438 and fine colloids to element fluxes in natural waters. The average percentages of elements
439 found in the NNP and colloid phases were 53% for Fe (within the bounds for an interquartile
440 range of 42-65%), 50% for P (36-70%), 26% for Mn (4-47%), 41%, for Al (28-56%), and
441 20% for organic C (5-28%), but only 2% for Si (0.1-0.4%) and 4% for Ca (0-5%; n=96). The
442 respective median values were 55% (Fe), 51% (P), 10% (Mn), 37% (Al), 11% (org C), 0.2%
443 (Si) and 1% (Ca). Further, up to 99% of Fe, 96% of P and Mn, 95% of Al, 92% of org C, 46%
444 of Si and 27% of Ca were found associated with NNP and fine colloids, relative to the bulk
445 elemental concentrations measured offline in the untreated samples. Overall, the percentages
446 reflected a substantial contribution of the NNP and fine colloidal fractions within the
447 operationally defined 'dissolved' elements Fe, P, Al, org C and Mn (in descending order).
448 Previous research on the significance of colloid-bound elements within the operationally
449 defined 'dissolved' fraction also indicated maximum Fe binding in fine colloidal form
450 between 80 to 100% with averages between 50 and 90% [Hill and Aplin, 2001; Jarvie et al.,
451 2012; Martin et al., 1995], for organic C between 40 and 80% with averages between 20 and
452 60% [Jarvie et al., 2012; Martin et al., 1995; Wen et al., 1999], and for Al around 40 to 50%
453 with averages around 45 to 55% [Hill and Aplin, 2001; Jarvie et al., 2012]. Hill and Aplin
454 [2001] determined that the fine colloidal fraction accounted for up to 50% of Mn (average
455 23%) and up to 30% of Ca (average 20%), but only up to 10% of Si (average 0%). Dahlqvist
456 et al. [2004] found an average of 16% fine colloidal Ca in an Arctic river and in Amazonian
457 rivers (also assessed with FFF). Data on total P are scarce, but Jarvie et al. [2012] reported
458 that a fraction of up to 90% (averaging 66%) of organophosphorus compounds was associated
459 with fine colloids in mixed land-use sites, and Missong et al. [2016] and Jiang et al. [2015]
460 also detected organophosphorus in the NNP and fine colloid fractions in soil samples. In
461 summary, the present data indicate that the particulate form of elements is substantial in
462 streams, and that there are varying contributions of NNP and fine colloids to overall element
463 fluxes across Europe.

464 3.3 Predictability of NNP and fine colloid elemental composition

465 The discrepancy between NNP and fine colloid and total elemental concentrations is
466 potentially due to dissolved species in size ranges below the membrane MWCO when
467 excluding the presence of larger particles. Two types of relationships between NNP and fine

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468 colloid concentrations and total concentrations could be observed, independent of the fraction
469 in question. For Si, P, Ca and Mn, we found scattered relationships between total
470 concentrations and NNP/fine colloid concentrations (Figure 3, left panels). The concentrations
471 of these elements that were bound to NNP and fine colloids did not change systematically
472 with total elemental concentrations. All three size fractions of these elements showed such
473 scattered relationships, although their median concentration varied (Table 2). By contrast, for
474 Fe, Al and org C, we found positive log-log relationships between total concentrations and
475 colloidal concentrations (Figure 3, right).

476 The regression slopes of the log-log relationships between the particulate and total element
477 concentrations differed among the three size fractions of Fe, Al and org C (Table 2), which
478 could reflect differences in Fe, Al and org C speciation as stream water variables change, but
479 could also be related to site differences in the surface properties of mineral binding partners
480 (which were not investigated here). Most interestingly, the log-log slope of the 1st size
481 fraction Fe was 1.0 (Table 2; Figure 3, right panels). This implied that across all European
482 sites, on average, a constant proportion of total Fe was present in this very fine
483 nanoparticulate fraction (<20 nm), and thus was independent of their stream water pH. This
484 proportion was estimated to be 15%. Slopes for Fe in the 2nd and 3rd fraction, as well as for Al
485 and org C for of all three fractions, were not parallel to the 1:1 line (not shown), instead
486 indicating power-law relationships (rather than a fixed NNP or fine colloid fraction). In
487 contrast, for the elements that did not change systematically with total elemental
488 concentrations (Ca, Si, Mn, P) the median varied among the different size fractions as well as
489 the percentage of particulate elemental concentration present in the fractions (cf. Table 2).
490 The reasons for the different regression slopes and medians are still unclear and warrant
491 investigation in future studies, potentially in combination with measurements of discharge-
492 dependent concentration variations as shown in e.g. *Trostle et al.* [2016].

493 *Figure 3*

494 *Table 2*

495 The majority of acidic sites were located in Northern Europe, neutral sites in Middle Europe
496 and alkaline sites in Southern Europe (Table 3). These three geographical regions are shown
497 in Figure 1, with borders at around 56 and 48°N. Most of the sampling sites in the Middle
498 Europe region, i.e., between these latitudes, had neutral pH. A fairly equal amount of Middle
499 Europe sampling sites could be involved among the three pH classes (Table 3), however, they

500 may not constitute a grouping by themselves, but rather a transition zone between the
501 Northern and Southern European regions.

502 With some overlaps, the pH differences and the North-Middle-South groupings were reflected
503 in the distribution patterns of elements among NNP and fine colloids (Figure 3). The elements
504 with positive log-log relationships (e.g., right panels in Figure 3) exhibited some data point
505 stratification, with lower elemental NNP and fine colloid concentrations at the Southern
506 European and alkaline sites (red dots in Figure 3), and higher concentrations at the Northern
507 European and acidic sites (green dots in Figure 3). Whether the main driver of this variation
508 was really pH, or a co-variate related to pH, warrants further attention (see also discussion
509 below). The total concentrations of Ca, Si, Mn and P increased from the Northern, acidic sites
510 to the more alkaline streams in the South (Figure 3, left panels). Such behavior could well be
511 expected for Ca but not necessarily for the other three elements [e.g. *Song et al.*, 2002]. The
512 concentrations of Ca, Si, Mn and P within NNP and fine colloid fractions did not vary
513 systematically with total concentration, but were roughly constant in their median value as the
514 total concentrations increased from the Northern, acidic, sites to the more alkaline, Southern,
515 sites. This implies that the elemental proportions that were bound to NNP and fine colloids
516 decreased from North to South.

517 Eleven data points at three sites did not follow the clear regional stratification in the
518 relationships between total and NNP/fine colloid concentrations (Figure 3); six Southern
519 water samples for Ca (scattered relationship; two at SC and four at LZ) and five Northern
520 water samples for Fe (all at AM; see Table 1 for site abbreviations). A concise explanation of
521 their anomalous behavior could not be found, especially because the other elements did not
522 exhibit this anomalous behavior, either in these samples or in any other samples. Site
523 characteristics (Table 1) and stream water parameters at sampling (supplementary material,
524 Table S1) showed no evident outliers in comparison to other sites within the same
525 geographical region, with the exception of the three sites closest to the coast.

526 *Table 3*

527 The presented data clearly showed the possibility to predict the concentrations of particle-
528 bound elements, as some were independent of total concentrations (Ca, Si, Mn, P) while
529 others were linked (Fe, Al, org C). Future research should address potential temporal patterns
530 of NNP and fine colloid composition across an even larger, global scale.

531 *3.4 Controlling factors of NNP and colloid composition*

532 The variable composition of NNP and fine colloids between sites and between sampling
533 locations of one site can potentially be linked to differences in site parameters on larger (e.g.
534 MAT or forest cover) or smaller (e.g. pH value or electrical conductivity) scale. As would be
535 expected for large data sets, many statistically significant ($p < 0.05$) correlations for, e.g., all
536 particulate org C, Al, Ca and Fe concentrations were found, but few strong correlations ($r >$
537 0.71) were found with site parameters (supplementary material, Table S3). Total Ca
538 concentrations were tightly correlated with electrical conductivity ($r = 0.96$), which is
539 unsurprising because Ca is often a significant fraction of total ionic strength, while all
540 particulate Ca showed strong correlations to all particulate org C ($r = 0.84$) followed by
541 catchment size ($r = 0.81$). In contrast, correlations between all particulate Si, P, Ca and Mn
542 and their total concentrations were weak ($r < 0.02$; partially negative values), as were the
543 correlations between total element concentrations of, e.g., Si and Mn and concentrations of
544 other elements or site parameters ($r < 0.49$). However, concentrations of all particulate Si
545 were positively related to concentrations of all particulate Al ($r = 0.72$), and especially
546 strongly ($r = 0.98$) for Si and Al in the 3rd size fraction, reflecting the presence of both
547 elements in layer silicates such as clay minerals.

548 When particulate concentrations were correlated with site parameters, these correlations were
549 rarely consistent among all size fractions. Marked differences were observed, for instance,
550 between correlations of site parameters with the 1st and 2nd fractions vs. 3rd fractions for Al
551 and Si (supplementary material, Table S4). The correlations thus showed that relationships
552 between site parameters and NNP and fine colloid concentrations differed, depending on the
553 fraction in question, and that NNP and fine colloid concentrations cannot be explained
554 through linear relationships alone.

555 At a KMO criterion > 0.6 , we did not observe significant alterations in factor loadings with
556 random elimination of data, and PCA was run stably with all particulate elemental
557 concentrations, pH, MAT, conductivity, water temperature and elevation, for instance. The
558 PCA extracted four factors with eigenvalues > 1 that jointly explained 75% of the total
559 variance. The resulting factor loadings revealed four distinct groupings of variables: 1) site
560 parameters such as pH, water temperature and MAT, 2) particulate Al and Si, 3) particulate
561 org C, Ca, and Fe, and 4) particulate P (see supplementary material, Table S5).

562 *Mattsson et al.* [2009] showed a link between DOC and climatic and topographic factors
563 through the strong positive correlation between DOC and latitude; here, however, the
564 colloidal org C was rather related to that of Ca and Fe, this grouping even remained stable
565 when including other site parameters into PCA at worse KMO test results. Fe (and Ca) are
566 known to be key elements in reacting with soil C during microaggregation processes [see e.g.
567 *Kögel-Knabner and Amelung, 2014*], i.e., our data would be in line with particles being
568 released from riparian soils during riverbank erosion. Besides, our data showed that the NNP
569 and fine colloid concentrations of Al and Si loaded highest at onto factor 2, thus supporting
570 the results from above-mentioned correlation analyses (supplementary material, Table S3) and
571 indicating that clay minerals are always present within the third fine colloid fraction. Finally,
572 the PCA analyses revealed that one factor can solely be assigned to particulate P. This is
573 congruent with the simple correlation analyses and confirms that P cannot be predicted by
574 simple linear statistical approaches across different geographic regions (see section 3.2).
575 Overall, the factor loadings thus confirmed that different processes controlled the fate of
576 different elements, while there was apparently no simple linear relation to site factors. Hence,
577 we elucidated the contribution of soil, geology, vegetation and pH class as additional controls
578 of NNP and FC properties.

579 The pH value is often a master variable controlling chemical forms in solution [*Perry et al.*,
580 2008] and may also determine the size and elemental composition of NNP and fine colloids
581 [*Neubauer et al.*, 2013]. pH-dependent element abundances in a ‘dissolved’ state are well
582 understood in the context of nutrient availability [*Perry et al.*, 2008], but not yet with respect
583 to NNP and fine colloids. The geographic zoning of the streams more or less coincided with
584 three dominant stream water pH classes (Figure 1, Table 3). As shown for the 3rd size fraction
585 in Figure 4a, though also valid for all particulate Si (supplementary material, Figure S1),
586 plotting Fe against Si clearly separated the acidic (Northern) streams from the alkaline
587 (Southern) ones. Similar results were also obtained when, e.g., plotting particulate Fe against
588 particulate Ca as an indicator of calcareous bedrock (Figure 4b; illustrated for the 2nd fraction;
589 valid also for the 1st fraction but not for the 3rd one; supplementary material, Figure S1). The
590 findings can be reconciled with a study on Fe in boreal catchments across different pH values
591 [*Neubauer et al.*, 2013]. Fe entering stream waters is instantly oxidized and forms
592 Fe(oxy)hydroxides or complexes with organic matter [*Ekstrom et al.*, 2016], while formation
593 of Ca- or Si-rich particles is likely independent from such processes. Overall, and despite the
594 many complex factors regulating specific element concentrations in NNP and larger colloids,
595 there are thus strong indicators of a geographic (or pH-dependent) zoning of the composition

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596 of these particles. Forest biomass and soils, for instance, co-vary along our geographic
597 transects, potentially affecting the pools and formation of humus and secondary minerals.
598 Relevant factors could also be any co-variates that induce non-linear variations in element
599 speciation across the pH range of 4.2 to 9.5 (Figure 4; supplementary material, Table S1).

600 *Figure 4*

601 *3.5 Impact of specific soil types and land-use on element concentrations*

602 Whengrouping the sites, e.g., according to soils, bedrock, and dominant forest type, at least
603 one particulate elemental concentration was affected (Table 4), and the effects found for total
604 particulate elemental concentrations were largely reflected in the individual size fractions as
605 well (supplementary material, Tables S6-8).

606 Sites characterized by semi-terrestrial soils with better hydraulic connectivity to the streams
607 showed significantly higher concentrations of colloidal Si than their counterparts with
608 terrestrial soils (Kruskal-Wallis ANOVA; $p < 0.05$; Table 4). However, the more frequent
609 redox cycles at the semi-terrestrial sites [Blume *et al.*, 2009] did not correlate with higher
610 concentrations of redox-sensitive elements, at least as this particular sampling time. Since
611 semi-terrestrial soils are usually poor in soil structure [Blume *et al.*, 2009], higher particulate
612 Si concentrations in the streams could be related to riverbank erosion, but more data at higher
613 temporal resolution would be needed to investigate this hypothesis.

614 Stream composition frequently correlates to the dominant bedrock [Krám *et al.*, 2012]. For
615 the elements with positive log-log relationships (org C, Al, Fe; right panels of Figure 3), a
616 significant differentiation between siliceous and calcareous rocks was found. The
617 concentrations of org C, Al, Si, and Fe were higher for the siliceous sites (Table 4). Overall it
618 appeared that element release from siliceous sites was facilitated relative to the calcareous
619 counterparts, which was accompanied by the release of these elements in all fractions of NNP
620 and fine colloids (supplementary material, Table S6-S8). Particularly high concentrations of
621 Al and Si were found in the streams with flysch (Table 4), likely reflecting riverbank erosion
622 of clay minerals (3rd colloidal fraction; supplementary material, Table S8) from the Gleysols
623 in vicinity of the rivers. Note, however, that among our sites, bedrock classification yielded
624 substantially more data points for siliceous than for calcareous rocks and flysch.

625 When the data were grouped according to the dominant forest type, the coniferous class
626 differed significantly from the broadleaf class for all particulate org C, Al, P, Ca and Fe

627 concentrations, even for those of Si and Mn (Table 4; the one mixed stand was not included in
628 this analysis). Notably, the element concentrations were generally larger in the coniferous tree
629 stands than the broadleaved ones, consistent with the tendency for coniferous stands to have
630 more acidic stream waters [Allaby, 2006] and usually siliceous bedrocks (Table 1). In fact,
631 almost 90% of the acidic sites were associated with dominant coniferous forest types (cf.
632 Table 1 and supplementary material, Table S1). These conditions might generally favor NNP
633 and fine colloid formation because low pH increases the density of positive charges of metal
634 oxides and organic matter, which can then bind to negatively charged surfaces such as fine
635 clay minerals as also outlined before [see also Tombácz *et al.*, 2004]. Indeed, when grouping
636 our sites according to main pH classes as outlined above, the concentrations of particulate org.
637 C, Al, and Fe were generally larger for the acidic sites (in Northern Europe) than for the
638 alkaline ones (in Southern Europe). Interestingly, however, P did not exhibit this pH effect
639 despite pH is the main variable affecting P availability and mobility in soils; hence, further
640 analyses are necessary to help explain this effect.

641 *Table 4*

642

643 *4. Conclusions*

644 Stream water sampling at 26 forested headwater catchments across Europe revealed
645 substantial binding of Fe, P, Al, Mn and org C to NNP and fine colloids. Overall, up to an
646 average of $53 \pm 21\%$ of the total content of these elements in the stream waters occurring in
647 three distinct particulate size fractions (1st: < 20nm, 2nd: 20–60nm, and 3rd size fraction: >60–
648 300nm). Particulate concentrations of org C, Fe and Al increased with total concentrations of
649 these elements from the South to the North, coincident with decreasing pH values and
650 increasing portions of coniferous forests and siliceous bedrock. The sampled sites could be
651 divided into sites that were characterized by the presence of Ca-containing NNP and fine
652 colloids in alkaline stream waters, and sites with an increasing predominance of Fe-NNP and
653 fine colloids (acidic stream waters) because the Fe concentration superimposed Ca. This
654 distinction was found for the 1st and 2nd NNP fractions, whereas 3rd size fraction (larger NNP
655 and fine colloids) mainly consisted of Al and Si-bearing clay minerals at all sites.

656 Interestingly, substantial amounts of P, which previously had been assigned to the
657 operationally defined dissolved phase, were found to be associated with NNP and fine
658 colloids. While P was mainly bound to Fe-containing particles of the 1st size fraction in more

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659 acidic Northern European headwaters, it was associated with Ca-bearing particles of the 2nd
660 size fraction in Southern European headwaters. Also, variations of total P were not correlated
661 straightforwardly with variations of site characteristics across our sampling sites. Further
662 efforts will be needed to better understand the complex interplay between total and colloidal P
663 fluxes across the globe.

664

665

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688

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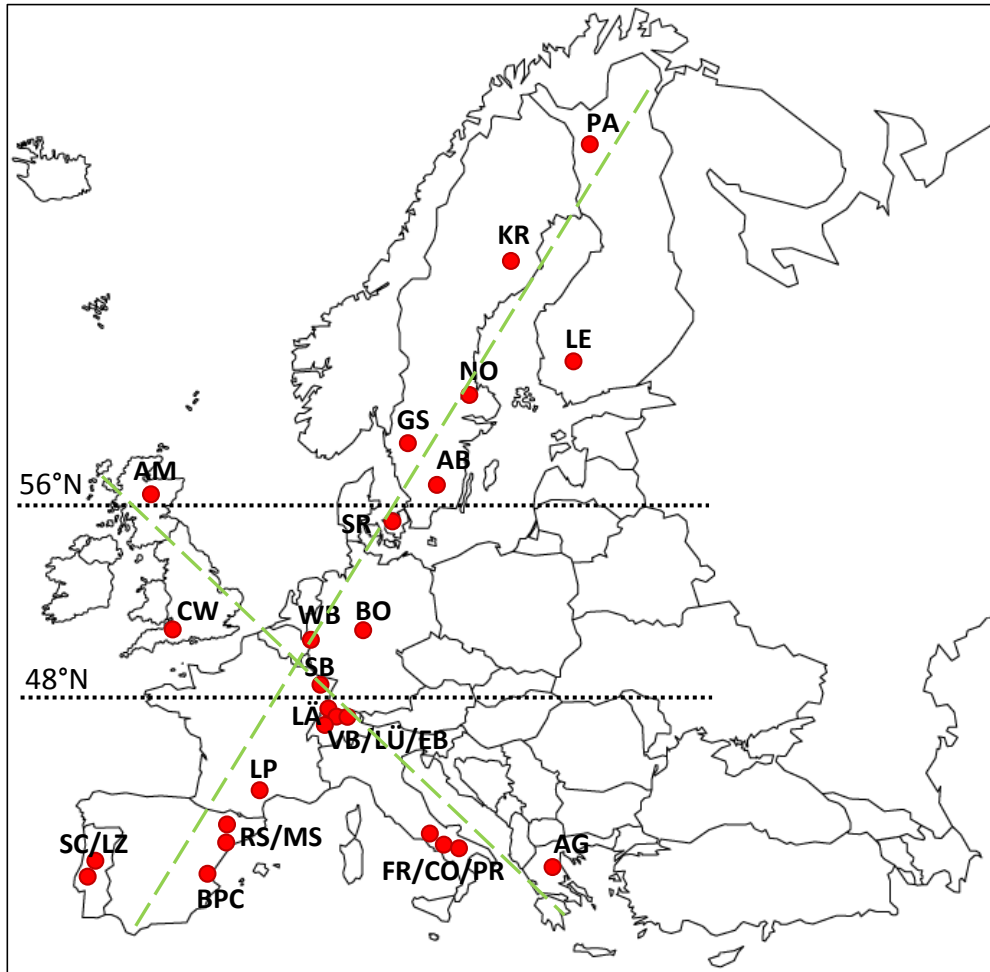
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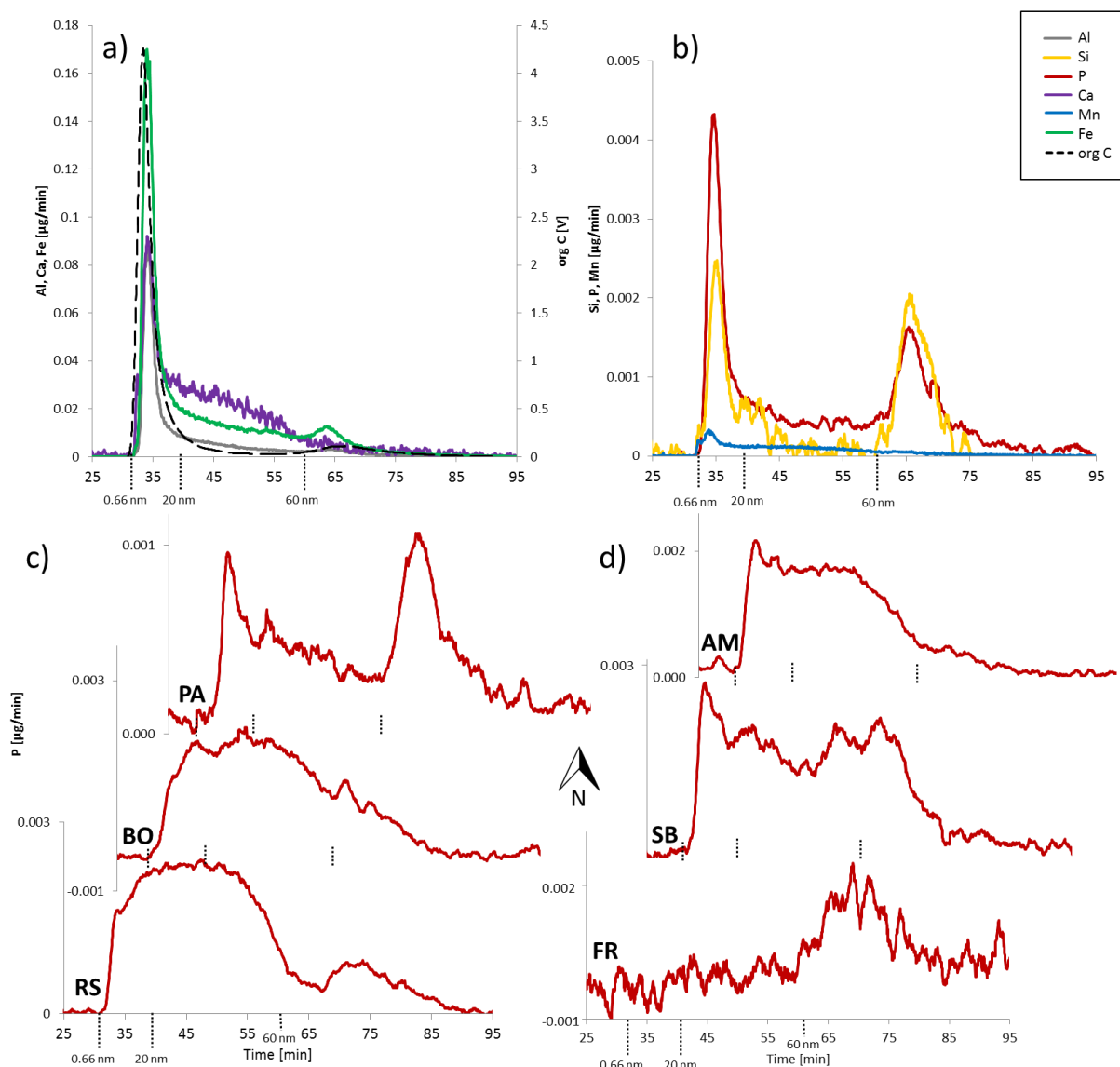
867 *Figure 1: Location of the 26 sampling sites in Europe along two transects (green dashed lines). Site*
 868 *abbreviations are as follows: Pallas (PA) and Lettosuo (LE), Finland; Krycklan (KR), Norunda (NO), Gårdsjön*
 869 *(GS) and Aneboda (AB), Sweden; Soroe (SR), Denmark; Allt a'Mharcaidh (AM) and Cotley Wood (CW), United*
 870 *Kingdom; Wüstebach (WB) and Bode (BO), Germany; Lägeren (LÄ), Vogelbach (VB), Lümpenenbach (LÜ) and*
 871 *Erlenbach (EB), Switzerland; Franchesiello (FR), Costiglione (CO) and Piano Rabelli (PR), Italy; Agia (AG),*
 872 *Greece; Strengbach (SB) and La Peyne (LP), France; Ribera Salada (RS), Montseny (MS) and Baranco de*
 873 *Porta Coeli (BPC), Spain; Sierra de Cima (SC) and Lourizela (LZ), Portugal. Black dotted lines indicate*
 874 *geographical separation between northern (north of 56°N), middle (between 48°N and 56°N) and southern*
 875 *(south of 48°N) sites.*

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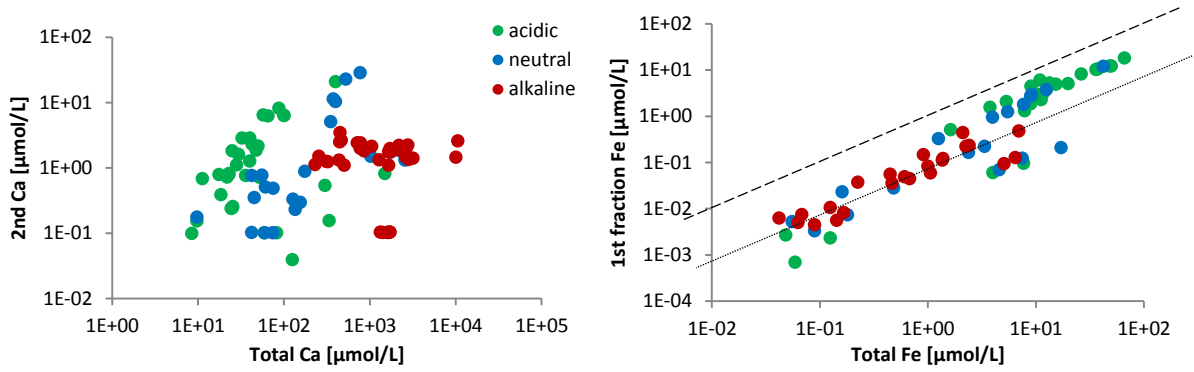
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 879 *Figure 2: AF⁴-ICP-MS and AF⁴-OCD raw data fractograms. a) Fractogram of Al, Ca, Fe and org C of one*
 880 *sampling point at Krycklan, Sweden; b) Fractogram of P, Si and Mn of same sampling point as a) at Krycklan,*
 881 *Sweden; c) Fractogram of P of three sampling points at sites in South, Middle and North Europe (increasing °N,*
 882 *y-axis), North: PA = Pallas, Finland, Middle: BO = Bode, Germany, South: RS = Ribera Salada, Spain d)*
 883 *Fractogram of P of three sampling points at sites in South, Middle and North Europe (increasing °N,*
 884 *North: AM = Allt a' Mharcaidh, Scotland, Middle: SB = Strengbach, France, South: FR = Franchesiello, Italy.,*
 885 *X-axes represent the method time in minutes. Focus time was partially cut off. Y-axes for Al, Si, P, Ca, Mn and*
 886 *Fe reflect mass flow in µg/min and for org C detector signal in V. Fraction borders apply to the ICP-MS signal;*
 887 *for the OCD evaluation these borders were modified because OCD peaks exhibit peak broadening due to the*
 888 *high volume of the OCD reactor.*

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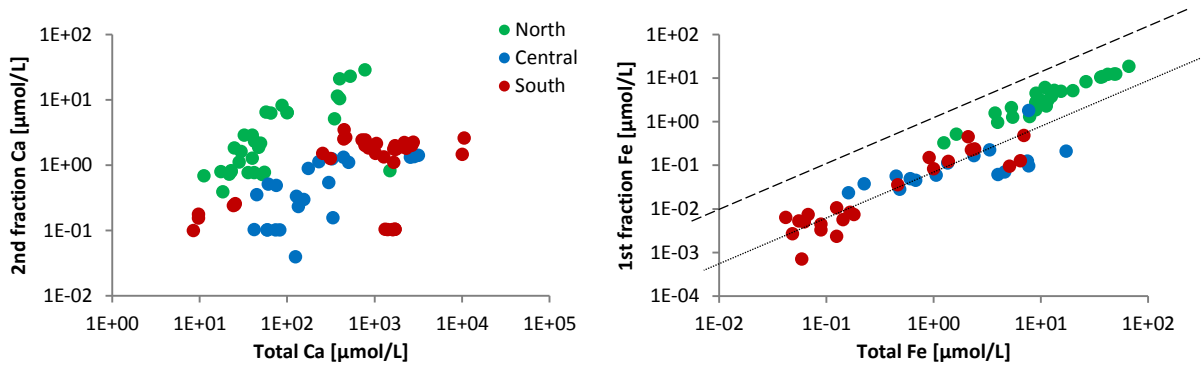
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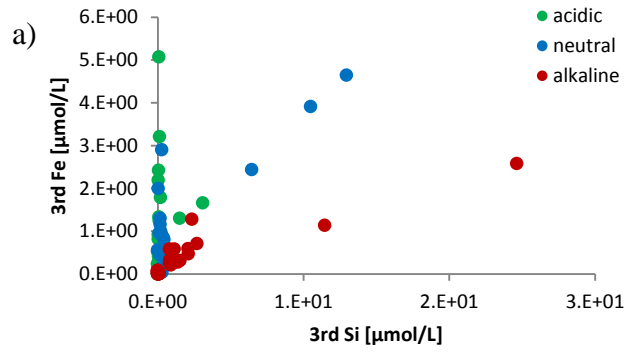
892 *Figure 3: Examples for the two relations of particle concentration as function of the total element*
 893 *concentrations. Top left: Scatter diagram of \log_{10} -transformed data of 2nd fraction Ca, as an example of the*
 894 *behavior of Si, P, Ca and Mn across all fractions; top right: Linear distribution of \log_{10} -transformed data for 1st*
 895 *fraction Fe, as an example of the behavior of Fe, Al and org C across all fractions; color coding represents pH*
 896 *class of the site (cf. Table S1); acidic pH <6.6, neutral pH 6.6-7.3, alkaline pH >7.3. Bottom left and right:*
 897 *Same data as top left and right, but with color coding according to geographic regions (cf. Figure 1). 2nd*
 898 *fraction Ca was chosen opposed to 1st fraction Ca for the left diagram because the 2nd fraction often exhibited a*
 899 *Ca peak (cf. Figure 2a). Dashed line represents 1:1 line and dotted line average proportion of total Fe present*
 900 *in the 1st fraction. n = 96.*

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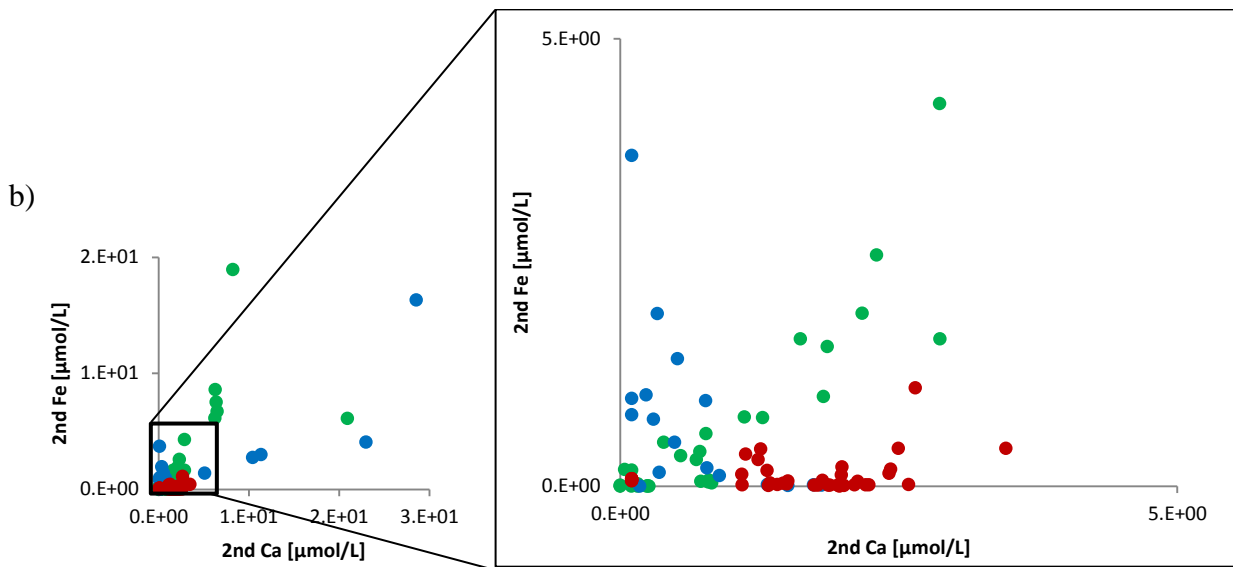


Figure 4: Example data plots of a) 3rd fraction Fe over 3rd fraction Si, and b) 2nd fraction Fe over 2nd fraction Ca with zoom window. Color coding according to site pH class, acidic pH = green dots (pH < 6.6), neutral pH = blue dots (pH 6.6–7.3), alkaline pH = red dots (pH > 7.3). $n = 96$.

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904 Table 1: Characteristics of each European site. Climate data, bedrock and soil type and dominant forest type
 905 provided by site operators. Abbr. = abbreviation, MAT = mean annual temperature [°C], MAP = mean annual
 906 precipitation [mm], catch = catchment size [km²], elev = average elevation [m], slope = average slope, forest =
 907 proportion forest cover, MAR = mean annual runoff [mm].

site	abbr.	MAT	MAP	soil type	dominant forest	bedrock type	catch	elev	slope	forest	MAR
Aneboda	AB	5.8	750	Podzol	coniferous	Granite ^s	0.19	225	0.13	0.73	280
Agia	AG	15.8	691	Cambisol	broadleaf	Gneiss ^c	0.75	916	0.28		
Allt a' Mharcaidh	AM	5.8	1110	Podzol	coniferous	granite ^s	9.79	716		0.02	
Bode	BO	7.1	1600	Cambisol	coniferous	shale&greywacke ^s	1.27	515	0.07	1.00	
Barranco de Porta Coeli	BPC	14.5	450	Fluvisol	mixed	sandstone ^s	3.20	523	0.21	0.50	
Costiglione	CO	15.9	1183	Cambisol	broadleaf	Carbonatic ^c	11	563	0.32	1.00	225
Cotley Wood	CW	10.1	1044	Cambisol	broadleaf	siltstone	0.50	146	0.08	1.00	
Erlenbach	EB	6.0	2294	Gleysol	coniferous	flysch	0.73	1330	0.24	0.39	1778
Franceschiello	FR	15.9	1183	Cambisol	broadleaf	Carbonatic ^c	11	563	0.32	1.00	225
Gårdsjön	GS	6.7	1000	Podzol	coniferous	granite ^s	0.07	127	0.22	0.65	520
Krycklan	KR	1.8	614	Podzol	coniferous	greywacke ^s	679	260		0.87	311
Lettosuo	LE	4.6	627	Histosol	coniferous	gneiss	1.25	111	0.01	1.00	413
Lägeren	LÄ	8.4	930	Cambisol	broadleaf	Limestone ^c		680	0.35	1.00	
Montseny	MS	9.0	870	Inceptisol	coniferous	schist					
La Payne	LP	12.0	818	Leptosols	broadleaf	schist ^s	110	305	0.25	1.00	
Lümpenenbach	LÜ	6.0	2426	Gleysol	coniferous	flysch	0.88	1260	0.15	0.19	2001
Lourizela	LZ	13.8	1300	Cambisol	coniferous	schist ^s	0.65	365	0.37	1.00	775
Norunda	NO	5.5	730	Regosol	coniferous	granite ^s	6084	45		1.00	250
Pallas	PA	-1.4	484	Podzol	coniferous	granite ^s	5.15	308	0.08	0.60	220
Piano Rabelli	PR	15.9	1183	Cambisol	broadleaf	Carbonatic ^c	11	563	0.32	1.00	225
Ribera Salada	RS	15.6	800	Cambisol	broadleaf	Carbonatic ^c		1483		1.00	
Soroe	SR	8.5	564	Mollisol	broadleaf	(glacial moraine) ^c		37	0.07	1.00	
Strengbach	SB	6.0	1400	Podzol	coniferous	granite ^s	0.80	1015	0.15	1.00	814
Serra de Cima	SC	13.8	1300	Cambisol	broadleaf	schist ^s	0.52	432	0.16	1.00	775
Vogelbach	VB	6.0	2159	Gleysol	coniferous	flysch	1.58	1285	0.23	0.63	1601
Wüstebach	WB	7.0	1220	Cambisol	coniferous	shales ^s	3.85	612	0.04	1.00	280

908 ^s: siliceous bedrock group; ^c: carlcareous bedrock group (see later Table 4)

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909 Table 2: Fraction-specific median, slope and intercept values for predictability of elements (cf. Figure 3);
 910 Si/P/Ca/Mn: fraction specific median concentrations represent midpoint of the data point distribution and
 911 numbers in parentheses represent the percentage of e.g. 1st fraction Si as sum over all samples relative to all
 912 particulate Si, Fe/Al/org C: linear regression slope (m) and intercepts (b) of log₁₀ transformed data. n = 96;
 913 unit: μmol/L, org C: mmol/L.

	Si	P	Ca	Mn	Fe		Al		org C	
	<i>median</i>				<i>m</i>	<i>b</i>	<i>m</i>	<i>b</i>	<i>m</i>	<i>b</i>
<i>1st</i>	0.03 (6.1)	0.04 (18.3)	0.67 (42.1)	0.001 (32.9)	1.00	-0.83	0.76	-0.55	1.71	-1.72
<i>2nd</i>	0.02 (3.1)	0.12 (53.2)	1.32 (49.5)	0.003 (37.3)	0.85	-0.47	0.65	-0.57	0.88	-1.55
<i>3rd</i>	0.08 (90.8)	0.08 (28.6)	0.24 (8.4)	0.002 (29.7)	0.72	-0.26	0.50	-0.07	0.56	-1.23
<i>all part.</i>	0.17	0.28	2.38	0.007						

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914 *Table 3: Number of sampling points in each pH class (acidic pH <6.6, neutral pH 6.6-7.3, alkaline pH >7.3) per*
915 *geographic region (Figure 1). n = 96.*

	acidic	neutral	alkaline	total sampling points
North	24	7	0	31
Middle	5	10	8	23
South	8	2	32	42

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918 Table 4: Mean values of all particulate molar elemental concentrations (mmol/L for org C, $\mu\text{mol/L}$ for Al, Si, P,
 919 Ca, Mn) across classes representing groupings of site characteristics. Significantly different classes per category
 920 and per element are marked by a, b and c; $p < 0.05$.

		org C	Al	Si	P	Ca	Mn	Fe	number of sampling points
soil class	<i>dystrophic</i>	0.44 a	0.59 a	0.36 a	0.32 a	6.14 a	0.03 a	3.72 a	45
	<i>eutrophic</i>	0.03 b	0.04 b	1.12 b	0.21 a	1.80 a	0.03 b	0.54 b	34
	<i>semi terrestrial</i>	0.08 ab	0.05 ab	4.14 c	0.39 b	3.80 b	0.01 ab	1.04 ab	12
bedrock class	<i>siliceous</i>	0.37 a	1.77 a	0.35 a	0.32 a	5.50 a	0.03 a	3.12 a	54
	<i>calcareous</i>	0.03 b	0.15 b	0.08 b	0.24 a	2.06 ab	0.04 a	0.09 b	22
	<i>flysch</i>	0.08 b	3.36 c	4.96 c	0.30 a	3.89 b	0.01 a	1.24 a	10
dominant forest type	<i>coniferous</i>	0.47 a	2.50 a	1.13 a	0.30 a	6.64 a	0.031 a	5.11 a	54
	<i>broadleaf</i>	0.03 b	1.02 b	1.16 b	0.20 b	1.77 b	0.028 b	0.56 b	26
pH class	<i>acidic</i>	0.59 a	2.46 a	0.25 a	0.24 a	5.65 a	0.03 a	6.79 a	31
	<i>neutral</i>	0.39 a	1.71 ab	0.47 a	0.39 a	7.89 a	0.03 a	3.47 ab	24
	<i>alkaline</i>	0.04 b	1.62 b	2.11 a	0.29 a	2.47 a	0.03 a	0.76 b	41

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