

Characteristics of sulfide bearing soil materials in peat extraction areas in N-Finland

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14 Abstract

15

16 Concern has been raised about the potential formation of acid sulfate soils and associated
17 environmental problems related to peat extraction and, thus, peat, sediment and till
18 characteristics of 15 well drained peat extraction fields were investigated in northern and
19 northwestern Finland. The aim was to identify and characterize the occurrence/abundance of
20 potential acid (hypersulfidic) and actual acid sulfate soil materials as well as metals with regards
21 to their depositional environment (marine/non-marine), black schists and soil material
22 properties. Sulfide-bearing marine sediments were commonly found; the highest contents and
23 thickness of sulfide sediments were found in areas <50 m above the current sea level (a.c.s.l.),
24 while the sulfide contents were relatively low in the mineral soil materials (mainly till) in the
25 non-marine areas (> 100 m a.c.s.l.). The highest content of sulfides in sediments were typically
26 found just below the peat layer. The sulfides existed mostly as pyrite (up to 3.5 wt % S) but
27 were occasionally also mixed with more reactive metastable sulfide (Fe:S ratio in the order of
28 1:1), which coincide with high Fe concentrations, indicating that an abundance of Fe²⁺ can
29 diminish the rate of pyrite formation. Sediments contained very high amounts of potential

30 acidity, but in-field oxidation of the sediments was very limited. Although the sulfur contents
31 were much lower (max 0.3 % S), several of the till samples still became acidic (pH<4) upon
32 oxidation, and contained, thus, some amounts of potential acidity due to a pore buffering
33 capacity. Consequently, during peat extraction most of the acidity is still retained in sediments
34 limiting environmental consequences and, thus, focus should be on appropriate management to
35 prevent oxidation and leaching after peat extraction has been finished. Locally high Mn and Zn
36 concentrations were found in the sediments in black schist areas, indicating that Zn and Mn
37 have migrated with the ground water from the schists to the sediment layers. In several black
38 schist areas, the peat layer contained high amounts of sulfides with a corresponding high
39 potential acidity as well as elevated As, Pb and Zn. This indicates an upward transport of sulfur
40 and some metals (As, Pb and Zn) through capillary rise and/or plant uptake and/or through
41 lateral water transport from surrounding black schist affected soil material. Air pollution, i.e.
42 atmospheric distribution, was most likely a source for high concentrations of Cd, Hg and Sr
43 concentrations in the peat.

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46 **Keywords: Acid sulfate soils, peat extraction, black schist, sulfide species, potential acidity**

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49 **1. Introduction**

50

51 Large areas of sulfide bearing sediments are worldwide located along deltas, coastal plains and
52 inland settings (170,000 km²; Andriess and van Mensvoort, 2005) and if exposed to oxidation,
53 these sediments will commonly become very acidic (hypersulfidic; Sullivan et al., 2010) and
54 develop acid sulfate soils (pH <4). These sediments pose a great threat to their surrounding
55 aquatic environment if disturbed (Hamming and van den Elelaar, 1993; Palko, 1994; Lin and
56 Melville, 1994; Sammut et al., 1996; Portnoy, 1999; Roos and Åström, 2005; Powell and
57 Martens, 2005; White et al., 2007; Macdonald et al., 2007). There are extensive studies on acid
58 sulfate (a.s.) soil formation related to intensive agricultural drainage, lowering the groundwater
59 level and exposing the upper 1-2 meters of sediment for the microbiologically mediated
60 oxidation of sulfides. As a result, extreme amounts of acidity and metals mobilized from

61 minerals due to the low pH are flushed to the recipient streams (Willett et al., 1993; Åström and
62 Spiro, 2000; Sundström et al., 2002, Smith et al., 2003; Burton et al., 2006; Macdonald et al.,
63 2007; Wu et al., 2013; Nystrand and Österholm, 2013), e.g. the highest metal concentrations in
64 Finland are found in areas with a.s. soils (Sundström et al., 2002; Roos and Åström, 2005).
65 Studies on acid sulfate soils in peatlands, where the peat or underlying sediment commonly
66 contains significant loads of sulfides, are, on the contrary, scarce, because they have been of
67 less economic importance. Worldwide, peatlands cover an estimated area of 400 million ha,
68 which represents 3% of the total land surface area. Most (c. 350 million ha) peatlands are
69 situated in the northern hemisphere, covering large areas in North America, Russia and Europe.
70 In Finland about 30% (i.e. about 10 million ha) of the land surface is covered by peatland
71 (Strack, 2008). By 2000, about 50% of the total peatland area in Finland had been drained for
72 forestry, agriculture or peat extraction (Turunen, 2008; Saarinen et al., 2013), the latter having
73 become an important industry in Finland the last decades (Pepper and Gentry, 2014) accounting
74 for almost 90% of the world's production and consumption of energy peat together with Ireland,
75 Russian Federation, Belarus and Sweden (Strack, 2008). Consequently, peat areas are
76 continuously being used for different kind of land uses regardless of the political interest in air
77 pollution issues including peat extraction.

78

79 In Finland sulfide bearing sediments that were deposited in the former Baltic Sea (mainly during
80 the Litorina Sea stage 3000-8000 BP) are today found in coastal areas up to 100 m above the
81 current sea level (a.c.s.l.) due to strong post glacial land uplift. When merging from the sea,
82 they were subjected to wetland conditions, where peat started to form and has since then if
83 undisturbed contributed to the protection of the underlying sediments from oxidation. In
84 addition, peatlands in Finland also cover and prevent the oxidation of large areas of sulfide
85 bearing till derived from Proterozoic black schists in the bedrock. Peat extraction has mainly
86 been associated with large fluxes of suspended humic matter and humic acids deteriorating
87 recipient water courses and, thus, been subjected to restrictions aiming to reduce these loads.
88 However, during recent years major concern has been raised about the potential formation of
89 acid sulfate soils and associated environmental problems related to peat extraction that requires
90 more research in this area. The focus on this study will be on the peat and mineral soil horizons
91 in peat extraction areas. Moreover, the focus will be on identifying sulfides (i.e. metastable

92 sulfides and pyrite) as only limited studies (e.g. Boman et al., 2008) have addressed the issue.
93 The aim is to identify the occurrence/abundance of sulfides, the corresponding distribution of
94 hypersulfidic soil materials and actual acid sulfate soils as well as metals with regards to their
95 depositional environment (marine/non-marine), black schists and soil material properties.
96 Hypotheses are proposed: (1) Easily identified black iron metastable sulfides and pyrite (i.e.
97 hypersulfidic materials), are common in areas where sediments have been deposited in marine
98 environments but may also occur in soil materials of non-marine environments with black
99 schists, (2) The depositional layers of sulfidic sediments are more common in low attitude
100 regions as has been found in W Finland and thicker due to a longer time for sedimentation, (3)
101 Actual acid sulfate soils in marine sediments are common in peat extraction areas but due to
102 moderate drainage depth, the oxidation depth is relatively shallow as compared to acid sulfate
103 soils on farmlands, (4) Peat has a high sulfur content but is generally not hypersulfidic and is,
104 thus, of minor environmental concern, and (5) Metal concentrations are enhanced in soil
105 materials of peat extraction areas in the vicinity of black schists.

106

107

108 **2. Study area**

109

110 The characteristics of soil materials for 15 peat extraction fields in northern and northwestern
111 Finland were investigated (Fig. 1 and Supplementary Fig. S1-S15) where peat extraction had
112 been conducted for several years. In two of the areas, Hangassuo and Karjoneva (Fig. 1 and
113 Supplementary Fig. S7 and S10), peat extraction had already been stopped and subsequently
114 trees had been planted and vegetation had started to grow. Due to annual peat harvesting, there
115 was no significant vegetation on the other peatlands. The studied peat extraction areas were
116 drained in accordance with conventional practice with small (c. 60 - 80 cm deep) ditches with
117 20 m spacing to deeper (100-150 cm) collector drains that lead the waters to sedimentation
118 basins and pumping basin from which the water was pumped out of the field. Inflow to the
119 fields was prevented by surrounding drains.

120

121 The study area was situated 30-180 m above the current sea level (a.c.s.l.). Sediments deposited
122 in brackish sea water (ancient Litorina Sea up to 8000 a BP) can be found up to c. 90-100 m

123 a.c.s.l., i.e. sediments where sulfides may have formed from sea water sulfate. They have
124 emerged from the sea far away from the current shoreline due to the strong postglacial isostatic
125 land uplift in the region. Older sediments with little or no influence of brackish water (no sulfide
126 formation) may be found below the Litorina sediments and at some distance above 100 m a.c.s.l.
127 these sediments are underlain by a more or less continuous sheet of locally derived glacial till.
128 The bedrock in the northern part of the study area consists mainly of mica schists with some
129 quartzite intrusions and near the city of Oulu (Fig. 1), mainly mica schists and granites
130 dominate. In the southern part, the bedrock varies between granodiorites, granites, gneisses,
131 migmatites and mica schists. The bedrock can, thus, locally be a source of sulfide-derived
132 acidity (geogenic sulfuric acid), but the bedrock is generally inert as far as short-term acid-base
133 reactions (Åström et al. 2005) and are so on not a major source of acidity in the studied area.
134 However, several areas are located on or near Proterozoic black schist occurrences (Table 1)
135 and due to glacial abrasion and transport, the underlying till might occasionally contain sulfides
136 originating from these sulfidic bedrock formations. Consequently, significant occurrences of
137 sulfides in mineral soils, with a different origin, may also be found in peat areas >100 m a.c.s.l.

138

139 The annual climatic and hydrological cycles in the area is characterized by four distinct seasons.
140 The winters (December-April) are generally long and characterized by freezing temperatures
141 and a snow cover around 40 to 80 cm (Pirinen et al., 2012). The snow cover melts in April/May,
142 resulting in annual water flow peaks. The summers (June-August) are rather mild with mainly
143 base flow conditions. The autumns are generally characterized by rainfalls, resulting in higher
144 flow peaks. Annual mean rainfall and temperatures are c. 480 mm and c. 3 °C, respectively
145 (Pirinen et al., 2012).

146

147

148 **3. Methodology**

149

150 To distinguish between different depositional environments, the studied peat areas were divided
151 in to three groups (Table 1): “The lower Litorina areas” (30-50 m a.c.s.l.), “The higher Litorina
152 area” (50-100 m a.c.s.l.), and “The non-Litorina areas” (>100 m a.c.s.l.).

153

154 60 separate soil profiles and 22 separate till samples were taken from 15 active or former peat
155 extraction areas in Western and Northwestern Finland (Table 1, Fig. 1 and Supplementary Fig.
156 S1-S15). Sampling locations were randomly chosen but, in a manner, to equally cover the areas
157 studied and by considering roads for accessibility (Supplementary Fig. S1-S15). Till sampling
158 sites were not specifically chosen, but in 22 of the 72 chosen sampling sites till occurred right
159 under or near the peat layer.

160

161 Depending on the size of each extraction area, 2-7 profiles were sampled from each area
162 (Supplementary Fig. S1-S15). During sampling, the soil materials in each profile were
163 categorized according to grain size according to the Wentworth scale (estimated crudely in the
164 field), color and other visual features (e.g. oxidation depth and ground water depth). It is notable
165 that peat extraction areas with previous acidic and metal-rich run-off water indicators by
166 collaborating companies were prioritized, which increased the possibilities of finding sulfidic
167 or sulfuric materials. Consequently, the results do not represent the relative abundance of peat
168 extraction areas with sulfidic and/or sulfuric materials as a whole.

169

170 Soil profiles (depth of around 2 m) were sampled with an handheld auger (\varnothing 25 mm) from 7
171 horizons/depth intervals (when possible) and by taken in account the mineral grain sizes, i.e.
172 the depth intervals/samples were divided so that one interval only contained one mineral grain
173 size. The sampled horizons/depth intervals were: one sample from the lowermost peat layer (50
174 cm), the upper meter of mineral soil matter with c. 20 cm depth intervals and one additional 50
175 cm sample below this. It is notable that around 75% of the profiles sampled had a peat thickness
176 <1 m and, thus, most of the peat sampled could be classified as an “upper” peat sample (e.g.
177 might be influenced by atmospheric depositions). Before preservation, the soil samples were
178 first homogenized in separate plastic bags, and then separately preserved in double plastic bags
179 in order to exclude air. The fresh soil samples were then immediately frozen in dry ice to
180 minimize oxidation of possible existing sulfides and later stored in a freezer prior to analysis.
181 Till samples were due to depth and unsuitability of the auger not possible to sample from every
182 investigated area, i.e. most till samples were sampled from areas on or near black schist
183 occurrences as the till layers in these areas generally were situated right under the peat.

184

185 After sampling, the pH was immediately measured on every layer of the profile by inserting an
186 electrode (ExStik pH Meter PH100) directly into the fresh sample. All samples were analyzed
187 for total S and several metals (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Cs, Fe, Hg, K, La, Mg, Mn,
188 Na, Ni, Pb, Rb, Sr, Ti, U, V, Y and Zn) in a commercial accredited laboratory with an ICP-MS
189 and/or ICP-AES after a digestion in aqua regia. The analytical precision of the analysis was
190 controlled by duplicate samples, blank samples and by randomizing the whole series. The
191 analytical precision (relative standard deviation; Gill, 1997) for S and the studied metals was
192 <10%. Moreover, pH incubation was performed in the laboratory on all soil samples for a period
193 of 16 weeks to simulate the natural oxidation behavior of possible existing sulfidic materials
194 (Creeper et al., 2012; Sullivan et al., 2018; Österholm et al., unpublished results), i.e. to identify
195 the presence of potential a.s. soils. Acid sulfate soils are in Finland defined as soils, sediments,
196 tills and organic materials (e.g. peat) containing hypersulfidic materials, which upon natural
197 oxidation in the field or during incubation in the laboratory form sulfuric acid that lowers the
198 pH to ≤ 4 for sediments and tills and to ≤ 3 or ≤ 3.5 if the pH drop is >1 unit for organic materials
199 (Hadzic et al. 2014; Österholm et al., unpublished results). The lower limit for peat is based on
200 the fact that peat naturally is more acidic (pH c. 4-6) due to humic acids (e.g. Pettersson 1992;
201 Kortelainen 1993; Weil and Brady, 2017). The pH incubation was performed by letting the
202 samples (a 1 cm thick layer of soil sample) incubate at room temperature in 15 ml plastic cups
203 with the screwcaps loosely fastened. During the incubation, the soil water content was assessed
204 to ensure that it was optimal for incubation; i.e. the incubation soil materials were kept in a
205 moist state (near field capacity) by rewatering as required during the incubation period.
206 Incubation pH was measured with an ExStik pH Meter PH100 at the start (week 0) and at the
207 end (week 16) of the incubation.

208

209 For soil samples 40-60 cm below the peat-sediment boundary the content of organic matter as
210 well as metastable iron sulfides and pyrite were determined. The organic matter content was
211 estimated as loss of weight on ignition (LOI) by combusting a dried sample in a muffle furnace
212 at 500 °C during 4 h (Radojevic and Bashkin, 1999). Operationally defined metastable iron
213 sulfide (acid volatile sulfur, AVS) and pyrite (Cr(II)-reducible (CRS)), i.e. the main sulfide
214 species responsible for acidification, were determined by a diffusion-based method developed
215 by Toivonen (2013) and based on Burton et al. (2008), Hsieh and Shieh (1997), Hsieh and Yang

216 (1989) and Ulrich et al. (1997). The steps for the determination of AVS and CRS with the
217 diffusion method in accordance with Toivonen (2013): The surface of the frozen sample was
218 scraped off to ensure that the sample was undisturbed. A subsample was weighed and dried in
219 105 °C for determination of dry weight. 300-600 mg (dry equivalent) of wet soil was weighed
220 into a 50 ml reaction flask, and a small tube containing a 7 ml alkaline zinc solution (4% Zn
221 acetate) was inserted. For the extraction of AVS, 10 ml of 6 M HCl and 2 ml of 1 M ascorbic
222 acid was added into the reaction chamber in an anoxic environment. After a 24-hour reaction
223 time on a shaking board, the small tube with precipitated Zn sulfide was removed, and
224 quantified via iodometric titration. For the determination of CRS, a 1.9 M Cr solution was made
225 by dissolving chromium(III)chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ purity 98%) in 10.4 M HCl.
226 Metallic Zn was added under anoxic conditions (constant purging with N_2) to allow Cr(III) to
227 reduce to Cr(II), which was indicated by a color change from dark green to dark blue. A new
228 tube with a fresh alkaline Zn solution was added to the reaction chamber, and about 12 ml of
229 acidic Cr(II) solution was added under an anoxic environment. The reaction was allowed to
230 take place during 36 hours on a shaking board, after which the trapped Zn sulfide was quantified
231 via iodometric titration.

232

233 From selected peat and mineral samples, sulfides were also studied with a scanning electron
234 microscope (SEM; Leo Gemini 1530). To indicate effects of possible sulfide oxidation, water
235 samples (1-2 samples/area) from all studied peat areas were taken from ditch network outlets
236 (Supplementary Fig. S1-S15). Water pH (ExStik pH Meter PH100) and specific electric
237 conductivity (EC; ExStik EC meter) were measured directly in field. Concentrations of SO_4 and
238 Cl were analyzed with ion chromatography in an accredited laboratory. Moreover, water
239 measurements (pH and EC) were conducted in ditches in several of the studied peat extraction
240 areas to locate occurring “hot spot” areas, i.e. areas with ongoing sulfide oxidation
241 (Supplementary Fig. S1, S4, S6-S12 and S15).

242

243

244 4. Results

245

246 4.1 General soil properties

247

248 A typical soil profile consisted of an organic rich peat layer with underlying postglacial
249 sediments. The thickness of the peat layer varied from 0 to 2.5 meter (Table 1), depending on
250 the amount of peat already extracted from the areas. The sediment under the peat was generally
251 0.5 to 2 meter thick (Table 1) and lacked structure. At the 22 sites where till was sampled, the
252 grain size varied from muddy fine silt to coarse sand including larger pebbles and boulders.

253

254 In the three lower Litorina areas studied, fine silt was the main grain size (Table 1) with an
255 organic content (LOI) generally above 2% (Fig. 2 and Table 2), called muddy fine silts or mud
256 (generally known as "gyttja") where LOI was over 6% (Korhonen et al., 1974) (Fig. 2 and Table
257 2). For sediments in the nine higher Litorina areas, the median content of organic material was
258 clearly smaller (medians for areas 0.4-4.0%; Fig. 2) compared to those in the lower Litorina
259 areas, but in some profiles still relatively high (>6%; Table 2). Moreover, the grain size
260 variation was bigger in the higher Litorina areas, from clay to coarse sand (Table 1). In
261 sediments of the three non-Litorina areas the grain size varied also from clay to sand (Table 1)
262 and the content of organic material was lowest (median $\leq 1.5\%$; Fig. 2 and Table 2).

263

264

265 4.2 Sulfur

266

267 In the lower- and higher Litorina areas the median total S concentrations in peat samples (0-0.5
268 m above mineral soil) of different peat extraction sites were generally around 0.5% and only a
269 few individual profiles having concentrations above 1% (up to 6.9% and 1.9% in Hakasuo and
270 Hautasuo, respectively; Fig. 3 and 4). Of the three non-Litorina areas, the median total S
271 concentration was remarkably high (2%) in Heinineva and relatively high (0.9%) in
272 Laukkuvuoma (Fig. 3 and 4). It is notable that these two sites as well as Hakasuo and Hautasuo
273 are located in or close to black schist areas, while the lower Litorina areas, a bit further away
274 from black schist areas have relatively low total S concentrations in the peat layers ($<0.6\%$; Fig.
275 3 and 4). The lowest concentrations ($<0.23\%$; Fig. 2 and 4) were found in the areas without any
276 influence of black schists (e.g. Jakosuo and Ahmaneva; Fig. 2). According to SEM images S
277 occurred in the peat partly as framboidal pyrite, in loose clusters and as individual pyrite crystals

278 (Fig. 5). The framboidal pyrite were generally between 5 to 25 μm in diameter, but occasionally
279 also up to 40 μm in Heinineva situated on black schists. The individual pyrite crystals were
280 generally in size from 0.5 to 3 μm and had an octahedral and/or equant anhedral (i.e. rounded
281 globular) shape. Occasionally also an organic coating partly surrounded the framboidal pyrite.
282

283 Total sulfur concentrations in the sediments below the peat varied considerably within and
284 between the peat extraction areas (Fig. 3), but some general trends outlined below were found.
285 Total sulfur concentrations correlated with LOI (Fig. 6) and median concentrations were highest
286 in extraction areas in the lower sulfidic Litorina sediments (0.8-1.2%; Fig. 2), also being higher
287 than those in fine sediments throughout western Finland (Table 2). The highest total S
288 concentrations (up to 1.9%) were in these areas mostly found in the typically muddy finer silt,
289 20-80 cm, below the peat layer (see in Fig. 3c "Arpela28"), with a significant decrease below
290 this depth. Consequently, the sulfide layers were relatively thin (mostly less than a meter; Fig.
291 3). In the higher sulfidic Litorina sediments situated below the highest shoreline of the ancient
292 Litorina Sea, the sulfide layers were somewhat thinner and, in contrast to the lower Litorina
293 sediments, concentrations tended to peak in the typically muddy clay or silt marine sediments
294 immediately, 0-20 cm, below the peat layer (Fig. 3). Also, the median total S concentration
295 were lower (0-0.7%; Fig. 2) and similar to those found in fine sediments throughout western
296 Finland (Table 2), although some very high total sulfur concentrations (up to 4.6%; Fig. 3b)
297 also were found in these areas. In the non-Litorina areas the total sulfur concentrations were
298 generally considerably lower (median 0.0-0.2%; Fig. 2). Only in Laukkuvuoma, situated on
299 black schists, there were some enhanced total S concentrations (up to 2.5%; Fig. 3a). In the
300 sediments, the vast portion of total sulfur occurred in the sulfide form, almost exclusively as
301 pyrite (CRS-S) with concentrations up to 3.5%, with the exception of Arpela and Suksiaapa
302 where metastable iron sulfides (AVS-S) dominated with concentrations up to 2.4% and 0.9%
303 respectively (Fig. 2), giving the sediments a generally easily detectable black color (Fig. 7).
304 The pyrite framboids seen on SEM images were around 5-20 μm in diameter, but occasionally
305 also up to 35 μm in diameter in Arpela, and the individual pyrite crystals were similar to those
306 found in the peat; i.e. around 1-2.5 μm in size with an octahedral and/or equant anhedral shape.
307

308 In till the total sulfur concentrations varied from less than 0.02% up to 0.3% (Table 3), being

309 equal or above 0.1% in 30% of the samples. SEM images showed that sulfur occurred in the till
310 generally as larger framboidal pyrite (up to 33 μm in diameter) and as individual octahedral
311 and/or equant anhedral pyrite crystals (1-3 μm in size; Fig. 5).

312

313

314 **4.3 Acidity**

315

316 The field pH of the peat was generally between 4 and 6 (Fig. 8), which is normal due to the
317 high amount of humic acids in the peat (Weil and Brady, 2017). Only three peat samples
318 situated near or on black schist had a pH below or near 3.0 (Fig. 8), indicating limited sulfide
319 oxidation in the peat on extraction sites. However, during the incubation period of 16 weeks in
320 the laboratory, several peat samples underwent a significant acidification (Fig. 8) with end
321 incubation pH for several (28%) samples below 3.5 ($\Delta\text{pH} > 1$) and even below 3.0 (11%). This
322 was particularly true for peat samples on or near black schist areas and where muddy sediment
323 layers were commonly found immediately under the peat layers.

324

325 The field pH of the sediment layers was also generally circumneutral (over 6; Fig. 8), indicating,
326 together with the lack of soil structure development, that oxidation of sulfidic sediments has
327 been very limited and that active a.s. soils are very scarce. Only one sample had a pH < 4 and
328 this sample was taken close to a ditch enabling the soil material to be exposed to oxygen.
329 However, during the incubation period of 16 weeks in the laboratory, the pH decreased from
330 circumneutral conditions to below 4.0 in most samples and below 3.0 in nearly half of the
331 samples (Fig. 8), showing that potential acid sulfate soils (hypersulfidic material) were common
332 and present in all peat areas studied.

333

334 For till, the field pH was 4.2-4.7 in three samples and above 5.0 to circumneutral in the
335 remaining samples (Fig. 8). During the incubation period of 16 weeks in the laboratory, the pH
336 decreased in nearly half of the till samples from circumneutral to below 4 (Fig. 8), indicating
337 that these are potential acid sulfate soils (hypersulfidic material) although their sulfur content
338 is relatively low.

339

340

341 **4.4 Metals**

342

343 In the peat layers considerably high Cd, Hg and Sr concentrations, were found in most of the
344 investigated areas, exceeding those of sediments and till (Fig. 9). Moreover, near or on black
345 schist areas the concentrations for especially Zn, but also somewhat for As and Pb, were
346 enhanced in the peat (Fig. 9).

347

348 In sediments, the metal concentrations were generally similar or lower compared to those in
349 fine sediments throughout western Finland (Table 2) explainable by the coarser grain sizes (less
350 metal bearing fine grained phyllosilicates) in the current study area. However, compared to
351 glacial till (<0.06 mm) in western Finland the concentrations of some elements (e.g. Al, Ba,
352 Mn, Ni and Zn) were slightly enhanced in the lower and higher Litorina areas (Table 2), which
353 can be explained by the somewhat coarser grain sizes in the glacial till. Locally some
354 exceptionally high concentrations (90th percentile and/or maximum concentrations) for Mn and
355 Zn (Table 2) were, though, detected in some of the higher Litorina areas most likely due to the
356 influence of black schists. Also, in two of the non-Litorina areas on black schists, i.e.
357 Laukkuvuoma and Heinineva, the median Zn concentrations were significantly enhanced.
358 Element concentrations were generally highest in the sediment layers immediately below the
359 peat layer coinciding with finer grain sizes. There were, though, some exceptions, in some of
360 the higher and non-Litorina areas metal concentrations peaked again in the lowermost samples
361 also tending to coincide with a finer grain size. In contrast, unrelated to grain size distribution,
362 Fe concentrations were in the sediments in Arpela and Suksiaapa notably high compared to the
363 other studied areas.

364

365 In till, the metal concentrations were generally similar or somewhat lower to those in fine
366 sediments in this study and throughout western Finland (Table 2 and 3), but compared to glacial
367 till (<0.06 mm) in western Finland (Table 2) the concentrations of some elements (e.g. Al, Ba,
368 Cr, Cu, Mn and Zn) were generally up to twice as high in areas situated on black schists (Table
369 3).

370

371

372 4.5 Water quality

373

374 The median pH of the small ditches (Fig. 10) in more than half of the investigated peat areas
375 was >5.5, and below 4.0 in only two areas, Karjoneva (lower Litorina) and Hangassuo (higher
376 Litorina) (Fig. 10). Nevertheless, some local ditches with pH near or below 4 were found in
377 70% of the areas (Fig. 10 and Supplementary Fig. S1, S4, S6-S12 and S15). It is also notable
378 that due to local small hot spots, pH could vary considerably in the small ditches, for instance
379 in Hautasuo the pH in one ditch decreased downstream from 8.3 to 2.5 (Supplementary Fig.
380 S6).

381

382 The median electric conductivity (EC) in the low order streams (Fig. 10) was generally in the
383 order of 100 $\mu\text{S}/\text{cm}$, being highest in the areas with the lowest pH, i.e. Karjoneva (346 $\mu\text{S}/\text{cm}$)
384 and Hangassuo (360 $\mu\text{S}/\text{cm}$) but varied often with more than one magnitude within the same
385 area, occasionally being in the order of 1000 $\mu\text{S}/\text{cm}$ in 30 % of the areas, including Arpela and
386 Karjoneva in lower Litorina areas, Hautasuo, Hangassuo, Suksiaapa and Hakasuo in higher
387 Litorina areas as well as Laukkuvuoma and Heinineva in the non-Litorina areas (Fig. 10). The
388 water pH and EC values in the ditches within an area could be fairly good (high and low,
389 respectively) on several locations, but near a hot spot area with an ongoing sulfide oxidation
390 the pH was low and the EC high (e.g. Supplementary Fig. S6).

391

392 In the outlet waters, representing the overall conditions in peat production areas, pH was mostly
393 relatively high. However, EC was somewhat enhanced (>100 $\mu\text{S}/\text{cm}$) in all measured outlet
394 waters and higher SO_4 concentrations (up to 50 mg/L; Fig. 11) generally coincided with low
395 pH occurrences of low order streams in some of the studied lower and higher Litorina areas
396 (e.g. Hangassuo, Hautasuo and Arpela). Only in Ahmaneva above the Litorina border and in
397 Puuroneva (higher Litorina) further away from black schists, the SO_4 concentrations were low
398 (<10 mg/L; Fig. 11).

399

400

401 5. Discussion

402

403

404 **5.1 Distribution of sulfidic material and sulfidic species**

405

406 In several of the studied peat extraction areas, high total sulfur concentrations were found; in
407 marine sediments mostly in areas below 50 m a.c.s.l., and in the lowest (0-0.5 m above the
408 mineral soil) peat layers in environments with black schist occurrences. The total S in mineral
409 soil materials consisted mostly of sulfides and, thus, the total S concentrations are relatively
410 equal to the sulfide concentrations in the studied areas. The sulfidic sediment layers were,
411 though, relatively thin, generally <1 m and in all layers the sulfides existed mostly as pyrite
412 (CRS), in contrast to farmlands on a.s. soils in Western Finland, that commonly contain a much
413 thicker sulfidic sediment layer and significant amounts of metastable iron sulfide (AVS) giving
414 them an easily detectable black colour (Backlund et al., 2005; Boman et al., 2008). Such black
415 coloration was, though, only seen in Arpela, which together with Suksiaapa were the only
416 studied areas with high metastable sulfide occurrences (Fe:S ratio in the order of 1:1).
417 Metastable sulfides coincided with high abundancies of Fe in Arpela and Suksiaapa, while Fe
418 concentrations in the other studied areas were similar or lower compared to those in fine
419 sediments throughout western Finland. This indicates that the high Fe concentrations promotes
420 the formation of metastable sulfides and/or reduces pyritisation. This is in line with Rickard
421 and Morse (2005), Burton et al. (2007) and Boman et al. (2008), who concluded that a
422 dominance of FeS over other metal sulfides is typical of most natural systems and occurs
423 because of the high Fe concentrations: i.e. an abundance of reactive iron (Fe²⁺) will hold S in
424 FeS and thereby diminishes the generally occurring transformation to pyrite. According to SEM
425 images, the size of the pyrite was in the soils generally also larger than those found in farmlands
426 on potential a.s. soils in Western Finland (Boman et al., 2008) and appeared generally in
427 different neoformal habits, as relatively large aggregated crystals and/or framboidal
428 pyrite. A successive formation of pyrite over a prolonged time in situ has most likely happened
429 (Wilkin et al., 1996). Gallego-Torres et al. (2015) similarly suggested that a difference in pyrite
430 framboid sizes is mainly controlled by the growth time, which again directly is related to the
431 sedimentation rate. Moreover, porosity and structure of sediments can play an important role in
432 the distribution of framboids and may significantly influence their size (Sawlowicz, 2000).

433 However, the larger framboids were found in fine-grained sediments and, thus, the growth by
434 time is more likely the reason for the larger existing framboids. Also in the peat, pyrite occurred
435 as relatively large aggregated crystals and/or framboidal pyrite (up to 40 μm). Pyrite framboids
436 very often reveal a close relationship with organic matter, filling the void spaces and among
437 others forming massive structures in organic remnants (Sawlowicz, 2000, Bush and Sullivan,
438 2002). This most likely depend on the total porosity (i.e. larger existing pores) of peat, which
439 often exceeds 80% (Boelter, 1968, Hayward and Clymo, 1982, Quinton et al., 2009) in
440 combination with a pyrite formation over a prolonged time. Some of the framboidal pyrite seen
441 on the SEM images were partly coated with organic matter, which possibly could prevent
442 oxidation of the pyrite if getting in contact with oxygen. The presence of organic material could
443 continue to block reactive surface sites (Sawlowicz, 2000), but also prevent/inhibit further
444 growth of pyrite framboids and or crystals (Laufer et al., 1985).

445

446 Although substantially high total S concentrations were found in almost every studied peat
447 extraction area, the concentrations varied considerably within and between the areas. In the
448 sediments the highest sulfide concentrations and the thickest sulfidic layers were found in the
449 lower Litorina (< 50 m a.c.s.l.) marine sediments. The thicker sediment layers, containing
450 sulfides in the lower Litorina areas, can partly be attributed to the longer time of sediment
451 accumulation as well as to the increase in erosion and re-deposition of sediments as more land
452 emerges from the sea. The high sulfide contents coincide with high contents of organic matter
453 (OM) and a finer grain size, i.e. low energy waters with decomposing organic matter favorable
454 for anoxic conditions and subsequent sulfide formation. These findings are in line with previous
455 studies for Western Finland where sulfidic soil materials are mostly located at 0-45 m above
456 the current sea level. The median S concentrations were considerably lower in the higher
457 Litorina sediments compared to those in the lower ones, most likely due to a shorter sediment
458 accumulation time. Some notable high total S concentrations were, though, found in the older
459 Litorina sediments, for similar reasons than those in the lower Litorina areas: i.e. for favorable
460 anoxic conditions for sulfide formation in earlier existing lake and/or sea environments during
461 a contact to seawater and with a steady growth of OM needed for sulfide formation (Mattbäck
462 et al., 2017).

463

464

465 **5.2 The influence of black schists**

466

467 Hundreds of kilometers of black schists occur in banded shaped formations in northern and
468 eastern Finland (Arkimaa et al., 2000) and contain up to >20% S (Lahermo et al., 1996) and
469 enhanced concentrations of several other elements, among others As (up to 30 ppm), Ba (up to
470 585 ppm), Cr (up to 189 ppm), Cu (up to 1400 ppm), Mn (up to 8000 ppm), Ni (up to 2600
471 ppm), Pb (up to 194 ppm) and Zn (up to 5300 ppm) (Ervamaa and Heino, 1980; Västi, 2008).
472 In some parts of the world black schists contain even some higher element concentrations (e.g.
473 Hulbert et al. 1992). Black schists have been more easily eroded by glacial ice than other
474 surrounding rock types and can thus enhance sulfur concentrations in soil material and both
475 surface and ground waters (Herranen, 2010; Mäkilä et., 2015). Consequently, till can be mixed
476 with black schists in environments where glacial ice has eroded the underlying bedrock in the
477 surroundings of black schists.

478

479 It is notable that till was not possible to sample from every investigated area (see in
480 "Methodology"), but in those areas sampled, the till below the peat and/or sediment layers did
481 not generally contain high sulfide concentrations but were place-wise somewhat above 0.1% in
482 areas on or near black schist occurrences (e.g. in Heinineva and Hakasuo) and so on the black
483 schists are likely to be related to these slightly enhanced sulfide concentrations. However, also
484 below the highest shoreline of the ancient Litorina Sea with no black schist occurrences some
485 slightly higher sulfur concentrations (0.1-0.3%) were found in the till. The somewhat elevated
486 sulfur contents in the till in areas without black schists may, thus, have been formed in direct
487 contact with seawater, i.e. intrusion of seawater in the pores of the till prior to sedimentation
488 and/or later due to groundwater seepage of sulfate and organic material from surrounding
489 sediments. These findings are in line with those of Mattbäck et al. (2017) studying coarse-
490 grained post-glacial acid sulfate soil materials in western Finland. Although the S
491 concentrations were relatively low, the pH values decreased in nearly half of the till samples
492 from circumneutral to below 4 during a 16 week oxidation (incubation) period. According to
493 Mattbäck et al. (2017) this is most likely due to a poor buffering capacity of coarser grained
494 material caused by the low specific surface area available for cation exchange capacity (CEC)

495 and buffering reactions in the coarse-grained soil material. The poor buffering capacity causes
496 likely a rapid leaching of acidity, but the life span of these hypersulfidic till material is relatively
497 short upon oxidation and might not have long time environmental effects (Mattbäck et al.,
498 2017).

499

500 In the lowermost peat layers (0 – 0.5 m above mineral soil material), the median S
501 concentrations were relatively similar (around 0.5%) in the lower- and higher Litorina areas,
502 with only a few individual profiles having higher concentrations. Some remarkably high total
503 S concentrations (up to 6.5%) were, however, measured in the peat in some of the non-marine
504 areas (in Laukkuvuoma and Heinineva), located in or close to sulfidic-rich black schists.
505 Consequently, enhanced S concentration in the peat are most likely related to black schists. One
506 likely explanation is that sulfur has migrated through mineral-rich soils through capillary flow
507 and/or capillary upraise before reaching the peat via plant uptake. This has also been suggested
508 by Herranen (2010) and Parvianen et al. (2014) investigating S and metal concentrations in peat
509 in Finland. Moreover, the topography of the environment (i.e. controlling groundwater flow
510 paths) can affect the sulfur concentration in peat and, thus, S can also be laterally transported
511 from surrounding black schist areas (Virtanen and Lerssi, 2006).

512

513

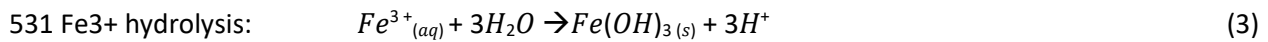
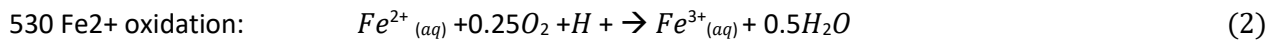
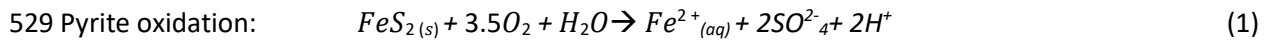
514 **5.3 Actual and potential acid sulfate soils**

515

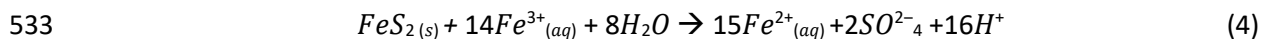
516 In contrast to previously well studied farmlands in Finland (e.g. Österholm and Åström, 2002)
517 or elsewhere (e.g. White et al., 2007, Macdonald et al., 2007, White et al., 1997), oxidation of
518 sulfidic sediments (i.e. actual acid sulfate soils) has been very limited in the studied peatlands.
519 Consequently, during peat extraction most of the acidity is still retained in the sediments with
520 relatively small acid metal loads (i.e. potential acid sulfate soils). However, the low pH and
521 high EC in several ditches and ditch network outlets indicate an existence of small local “hot
522 spot” areas, i.e. areas with ongoing oxidation of hypersulfidic material (e.g. pyrite oxidation:
523 see reaction 1 and 4) and so on a leaching of oxidizing sulfidic materials contributing to the
524 acidity (H⁺) and high ion concentrations (EC) in some of the investigated ditches. Furthermore,
525 the sulfate concentrations were generally correspondingly high in the ditch network outlets. The

526 reactions, i.e. the oxidation of FeS₂ and the production of acidity, can be expressed as follows
527 (Singer and Stumm, 1970; Sobek et al., 1987; Kirby and Cravotta, 2005):

528



532 Further pyrite oxidation by generated ferric iron:



534

535 Reaction 1 shows that 1 mole of FeS₂ will produce 2 moles of H⁺ and although 1 mole of acidity
536 is used in the oxidation of ferrous (Fe²⁺) to ferric (Fe³⁺) iron (equation 2), 3 moles of acidity are
537 produced when the ferric iron is hydrolysed (equation 3). These steps, i.e. the ongoing Fe
538 oxidation/precipitation, were easily seen in several of the investigated ditches as a rusty colored
539 thicker layer on the bottom of the ditches. If the pH of the medium is low enough, ferric iron
540 can also oxidize pyrite to produce ferrous iron, sulfate and more acidity. The entire sequence
541 is, thus, a “self-propagating cycle”, which once underway will accelerate (Caruccio et al., 1988;
542 Gough and Severson, 1995).

543

544 As actual acid sulfate soils were still rare and as the sulfide mostly appeared as pyrite (i.e. no
545 specific detectable colorization), it is relatively hard to identify these heterogeneous soils in the
546 field. Samples from several soil profiles from one area needs to be analyzed for total S to predict
547 whether sulfidic sediments occur in the area. Another easy, but time consuming (often 16
548 weeks), procedure to identify sulfidic (hypersulfidic) soils, till and/or peat is to use pH
549 incubation (Sullivan et al., 2018), which in this study successfully showed the amplitude of
550 hypersulfidic sediments, till and/or peat. It was, thus, shown that after an incubation (i.e.
551 oxidation) time of 16 weeks several samples underwent a severe acidification: to a pH ≤4 in the
552 sediment and till, and to a pH ≤3.5 in the peat with a pH drop of at least 0.5 and 1.0 units,
553 respectively. Consequently, in peatlands like these, there might occur larger environmental
554 problems if oxidation of hypersulfidic materials will take place. This conclusion overturned
555 partly, i.e. in areas with black schists, one of our stated hypotheses, i.e. that peat would contain
556 sulfur, but generally not in a hypersulfidic form and, therefore, would not be of an

557 environmental concern.

558

559

560 **5.4 Distribution of elements in the soil**

561

562 In the investigated peat extraction areas, the vertical metal distribution in the sediment are
563 mainly controlled by inherent grain size; finer soil materials contain higher concentrations of
564 metals (Österholm and Åström, 2002; Toivonen and Österholm, 2011). Moreover, the metal
565 concentrations in the sediment were considered normal, except for Zn and Mn. These relatively
566 mobile elements were occasionally high in areas where black schists occurred, indicating that
567 Zn and Mn have been migrated with the ground water from the schists to the sediment layers.
568 Similarly, most likely due to the influence of metal-rich black schists some enhanced
569 concentrations for Al, Ba, Cr, Cu, Mn and Zn were observed in tills near or on black schists.

570

571 In the investigated peat layer, some high element concentrations were observed exceeding those
572 of sediments and/or till. In most of the investigated areas, the concentrations for Cd, Hg and Sr
573 were considerably high. These concentration peaks in peat show that substantial amounts of
574 elements are introduced not only by weathering and/or capillary and lateral groundwater flow
575 of the underlying geological material, but also by atmospheric deposition. These findings are
576 in line with those of Brun et al. (2010) studying spatial distribution of elements in Norway
577 spruce and Cogging et al. (2006) studying among others Hg in peatlands. Moreover, near or on
578 black schist areas enhanced As, Pb and Zn concentrations were found in the peat. This reflect
579 the relatively easy weathering of the black schist rock type as these elements most likely have
580 been transported to the peat similarly as the sulfur, i.e. with an upward transport of these
581 elements from the till to the peat and/or lateral transport of the elements from surrounding areas.
582 This is in accordance with previous studies done in Finland (Virtanen and Lerssi, 2006 and
583 2008; Parviainen et al., 2014; Mäkilä et al., 2015), where high element concentrations in peat
584 are assumed to be related to black schists. However, air pollution due to industrial production
585 (i.e. atmospheric distribution) are also known to be a major source for among others Pb and Zn
586 (Shotyk, 1995; Rosca et al., 2019) in peat layers, but in these studied black schist-rich areas this
587 is unlikely to be the cause to the enhanced concentrations.

588

589

590 **5.5 Risks after peat extraction**

591

592 Although there were only small hot spot areas with ongoing oxidation of hypersulfides, the
593 oxidation rate is fast, and the environmental consequences will be severe if these kinds of
594 hypersulfidic soils and peat will oxidize. According to Roos and Åström (2005) and Toivonen
595 and Österholm (2011) even notable small hotspot areas can have a severe impact on large water
596 areas. Furthermore, peat extraction sites are generally utilized down almost to the mineral soil,
597 and it is a widespread practice to forest and/or convert used peat areas to farming fields instead
598 of giving them a chance to renew. This can cause substantial environmental problems if these
599 peat areas are situated on hypersulfidic-rich sediments. Under the peat layer, sulfidic materials
600 can, as evidently shown be situated closer to the soil surface (within 20 cm) than in the
601 agricultural soils, where sulfidic materials were generally found at 70 cm or deeper (Yli-Halla
602 et al., 2008; Boman et al., 2010). Consequently, the properties of mineral sub soils (i.e. sulfidic
603 or non-sulfidic material) under the peat are likely to have considerable influence on the
604 suitability for practicing peat extraction and, thus, also for the various post-peat extraction
605 forms. The most effective way to prevent acidification of watercourses due to a.s. soils is to
606 maintain hypersulfides in a reduced state in the soil by controlling excessive lowering of the
607 groundwater level. This can potentially be done if the drain depth does not exceed to the mineral
608 layers. Thus, to convert these peat areas to farming fields and even forested areas with deep
609 ditches would cause enormous environmental damages. The more preferred land uses in the
610 high-risk areas would be to restore the mire or use other forms of rewetting, but also natural
611 vegetation would be a good choice of land use.

612

613

614 **6. Conclusion**

615

616 Sulfide-bearing marine sediments were common in the studied peat extraction sites below the
617 highest shoreline of the former Litorina Sea. The highest contents of sulfide and thickness of
618 sulfidic sediments were found in areas below 50 m a.c.s.l., which partly can be attributed to the

619 longer time of sediment accumulation as well as to the increase in erosion and re-deposition of
620 sediments as more land emerges from the sea. The highest concentration of sulfides in
621 sediments were typically found just below the peat layer and the sulfides occurred mostly as
622 pyrite (up to 3.5 wt % S). In contrast to Midwestern Finland, metastable sulfides were very rare
623 and limited to areas with an abundance of iron, showing that an abundance of reactive Fe^{2+}
624 controls a formation/preservation of FeS instead of a transformation to pyrite. The sulfidic
625 sediment layers were relatively shallow (generally <1 m) but contained a high potential acidity
626 and become acid (pH <4) if oxidized, i.e. they were classified as hypersulfidic (potential acid
627 sulfate soil) material.

628

629 Although the sulfur contents were much lower (max 0.3 % S), some sulfides were also found
630 in the till in the non-marine areas (> 100 m a.c.s.l.). Due to the low buffering capacity of the
631 coarser till material, several of the till samples became acidic (pH<4) upon oxidation
632 (incubation in the laboratory), thus also classified as hypersulfidic material. Some metal
633 concentrations (Al, Ba, Cr, Cu, Mn and Zn) were occasionally elevated in the mineral soils of
634 black schist areas. Moreover, the peat layers in black schist areas contained high amounts of
635 sulfides with a high potential acidity (hypersulfides) as well as elevated As, Pb and Zn. This
636 indicates that sulfur as well as the relatively mobile metal Zn have migrated through capillary
637 rise and/or plant uptake from the mineral soil materials below and/or through lateral water
638 inflow from surrounding black schist affected soil materials. The elevated concentration of As
639 and Pb in the peat of black schist areas were not found to be elevated in the corresponding
640 mineral soil. Cadmium, Hg and Sr, on the contrary, were elevated in peat, unrelated to black
641 schist areas, indicating other sources/processes of accumulation (i.e. atmospheric distribution).

642

643 In contrast to previously well studied farmlands, oxidation of the hypersulfidic sediments has
644 been very scarce in the peat extraction sites despite peat harvesting for decades. As nearly all
645 of the acidity is retained in the sediments, it is most crucial that sites with sulfidic sediments
646 are managed properly to prevent oxidation and leaching after peat extraction has been finished.

647

648

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650

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656

657

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Table 1. General description of the studied peat extraction areas. Sixty soil profiles situated 30 – 180 meter above the current sea level (a.c.s.l.) were taken from 15 active or former peat extraction areas in Western and Northwestern Finland.

Category	Area	Coordinates ETRS-TM35FIN		Above the current sea level (m)	Number of profiles	Sediment thickness median (m)*	Main grain size**	Peat thickness (m)	Distance to black schist areas (km)
"Lower <i>litorina</i> " 30-50 m a.c.s.l.	Arpela	381248	7321872	30	4	0.90	finer silt	0.0-0.5	2.5
	Järvineva	417556	7169045	50	3	0.90	muddy finer silt	1.0-2.0	2.5
	Karjoneva	419910	7166909	50	4	1.40	muddy finer silt	c. 0.5	2.5
"Higher <i>litorina</i> " 50-100 m a.c.s.l.	Hautasuo	451331	7210712	60	7	1.30	finer silt	0.4-1.7	3.0
	Hangassuo	462289	7210739	70	5	1.40	muddy clay	0.2-0.6	3.0
	Suksiaapa	425587	7366748	70	3	1.50	muddy clay	0.2-0.7	1.5
	Hakasuo	474484	7203502	85	7	1.50	coarser sand	0.9-2.4	1.2
	Märsynneva	406933	7146140	85	3	1.50	clayey silt/sand	0.9-1.5	1.2
	Kuuhkamonneva	411359	7138184	90	4	2.15	muddy finer silt	0.3-0.9	0.0
	Leväjätkkä	374171	7343675	90	2	1.45	silt/sand	c. 0.8	0.0
	Puuroneva	396968	7155989	95	5	1.50	coarser silt	0.2-0.7	6.5
	Jakosuo	447533	7275375	100	4	0.80	coarser sand	0.0-0.8	40.0
"Non <i>litorina</i> " >100 m a.c.s.l.	Laukkuvuoma	543620	7110156	100	4	1.00	clayey silt/sand	0.2-1.0	0.0
	Ahmaneva	397378	7149938	100	2	0.70	clay	0.9-1.0	6.5
	Heinineva	543620	7110156	180	3	0.50	clay/silt/sand	0.6-0.9	0.0

*As commonly only a 2 m profile was taken in the field the sediment thickness might have been thicker in some areas.

** The grain size is described according to the Wentworth scale (Wentworth, 1922).

Table 2. Element contents (minimum, maximum, median, 10th and 90th percentiles) of sediment samples taken at a depth of 40-60 cm under the peat/sediment boundary from the studied areas, and of fine-grained sediments and fine fraction (<0.06 mm) of glacial till from western Finland. BD = below detection limit.

	Peat area, NW Finland Lower <i>litorina</i> areas (n=11)					Peat area, NW Finland Upper <i>litorina</i> areas (n=38)					Peat area, NW Finland Non <i>litorina</i> areas (n=7)					Fine sediment, W Finland (n=317)*					Glacial till, W Finland (n=1826)**				
	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max
S (%)	0.02	0.68	0.99	1.51	1.93	0.02	0.03	0.13	1.47	4.58	0.03	0.05	0.16	0.28	0.44	BD	0.04	0.54	1.01	1.78	-	-	-	-	-
LOI (%)	2.07	2.23	5.38	6.94	7.18	0.40	0.64	1.97	5.32	9.24	0.52	0.59	1.12	1.99	2.57	-	-	-	-	-	-	-	-	-	-
C (%)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.34	0.56	1.37	2.40	3.95	-	-	-	-	-
Fe (%)	0.20	1.73	2.92	6.68	7.47	0.46	0.83	2.17	4.12	6.31	0.52	0.70	1.26	2.89	3.28	0.78	2.29	3.80	4.81	5.70	0.13	0.91	1.49	2.69	5.80
Al (%)	0.17	0.73	1.15	1.70	1.80	0.19	0.41	1.03	1.80	2.36	0.29	0.33	0.71	1.49	1.86	0.35	0.96	2.02	2.95	3.58	0.05	0.41	0.78	1.67	2.78
Mg (%)	0.08	0.38	0.62	0.90	0.95	0.10	0.22	0.59	1.02	1.31	0.15	0.17	0.41	0.85	1.04	0.12	0.44	1.04	1.43	1.83	0.03	0.20	0.39	0.86	1.71
K (%)	0.04	0.20	0.30	0.35	0.37	0.04	0.10	0.25	0.42	0.55	0.07	0.07	0.29	0.37	0.44	0.07	0.28	0.60	0.94	1.40	BD	0.10	0.25	0.58	1.45
Ca (%)	0.06	0.29	0.41	0.56	0.62	0.11	0.14	0.35	0.42	0.62	0.15	0.15	0.26	0.46	0.47	0.25	0.37	0.50	0.58	0.75	0.02	0.20	0.29	0.39	0.61
Ti (%)	0.02	0.09	0.11	0.14	0.14	0.02	0.04	0.12	0.15	0.17	0.04	0.05	0.11	0.16	0.17	0.07	0.13	0.22	0.27	0.30	0.01	0.08	0.13	0.22	0.42
Na (%)	0.01	0.03	0.05	0.06	0.10	0.01	0.02	0.04	0.05	0.06	0.02	0.02	0.03	0.04	0.04	BD	0.05	0.10	0.19	0.31	-	-	-	-	-
Ba (PPM)	12	47	68	107	164	16	26	69	111	137	21	24	42	95	113	14	45	87	168	229	2	18	39	91	267
Co (PPM)	6	7	13	17	22	2	4	11	17	27	3	3	7	14	15	2	7	13	18	31	BD	2	5	13	32
Cr (PPM)	5	25	37	59	61	8	14	40	57	72	10	12	32	51	59	11	28	48	62	76	3	12	23	50	116
Cu (PPM)	12	14	30	56	57	6	9	24	37	98	5	6	17	34	37	2	14	27	46	65	0	8	15	37	137
La (PPM)	6	17	26	31	32	8	10	23	33	37	9	11	22	32	35	13	25	38	50	62	4	15	22	36	80
Mn (PPM)	29	169	378	827	923	47	87	215	531	3060	59	68	134	345	372	90	223	448	713	1147	14	92	160	288	1160
Ni (PPM)	3	14	21	35	36	5	8	24	37	41	6	7	17	31	35	6	16	31	42	58	2	6	12	30	143
Pb (PPM)	1	4	7	9	9	2	2	6	9	12	2	2	4	9	10	BD	6	12	17	25	BD	0	8	16	141
Th (PPM)	1	5	7	9	9	1	3	7	10	14	3	3	7	9	11	BD	5	10	16	22	BD	2	6	11	37
V (PPM)	5	26	38	75	78	8	17	40	65	75	12	15	33	54	64	12	28	50	64	76	5	17	29	61	155
Zn (PPM)	31	33	64	85	280	6	17	51	81	1165	10	11	27	119	184	18	43	90	114	142	2	18	34	75	194

*Data from Åström and Björklund (1997)

*Data of the Geological Survey of Finland (1992)

Table 3. Element contents (minimum, maximum, median, 10th and 90th percentiles) of till samples taken from the studied areas. NA=not analysed.

	Till, NW Finland					Till, NW Finland					Till, NW Finland				
	Lower <i>litorina</i> area (n=1)					Higher <i>litorina</i> area (n=13)					Non <i>litorina</i> area (n=10)				
	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max	Min	10 %	Median	90 %	Max
S (%)	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.05	0.15	0.31	0.02	0.02	0.04	0.15	0.18
LOI (%)	NA	NA	NA	NA	NA	0.34	0.40	0.64	0.72	0.74	0.43	0.49	0.65	3.63	5.55
Fe (%)	1.43	1.43	1.43	1.43	1.43	0.27	0.60	1.77	2.78	3.10	0.64	0.73	1.17	2.17	2.20
Al (%)	0.60	0.60	0.60	0.60	0.60	0.18	0.23	0.89	1.63	1.97	0.37	0.41	0.52	1.10	1.23
Mg (%)	0.37	0.37	0.37	0.37	0.37	0.05	0.10	0.56	0.95	1.16	0.22	0.23	0.32	0.68	0.72
K (%)	0.12	0.12	0.12	0.12	0.12	0.03	0.04	0.39	0.84	1.31	0.09	0.13	0.16	0.33	0.37
Ca (%)	0.26	0.26	0.26	0.26	0.26	0.05	0.10	0.16	0.18	0.19	0.13	0.14	0.22	0.39	0.43
TI (%)	0.08	0.08	0.08	0.08	0.08	0.03	0.03	0.17	0.36	0.37	0.05	0.09	0.10	0.21	0.23
Na (%)	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.03	0.02	0.02	0.03	0.04	0.04
Ba (PPM)	55	55	55	55	55	15	18	70	109	230	27	28	40	77	79
Co (PPM)	5	5	5	5	5	1	3	7	11	14	3	4	4	11	11
Cr (PPM)	23	23	23	23	23	7	11	33	48	64	10	12	19	42	44
Cu (PPM)	18	18	18	18	18	4	6	18	33	47	6	10	13	32	33
La (PPM)	15	15	15	15	15	5	9	14	17	24	13	13	17	27	28
Mn (PPM)	115	115	115	115	115	23	64	161	237	459	83	86	130	241	371
Ni (PPM)	11	11	11	11	11	2	6	18	31	44	7	7	9	26	27
Pb (PPM)	3	3	3	3	3	2	2	3	6	19	2	2	3	6	6
Th (PPM)	5	5	5	5	5	0	3	4	5	10	3	3	5	8	10
V (PPM)	34	34	34	34	34	5	11	37	52	72	13	14	21	41	45
Zn (PPM)	19	19	19	19	19	4	8	35	60	72	15	18	21	55	73

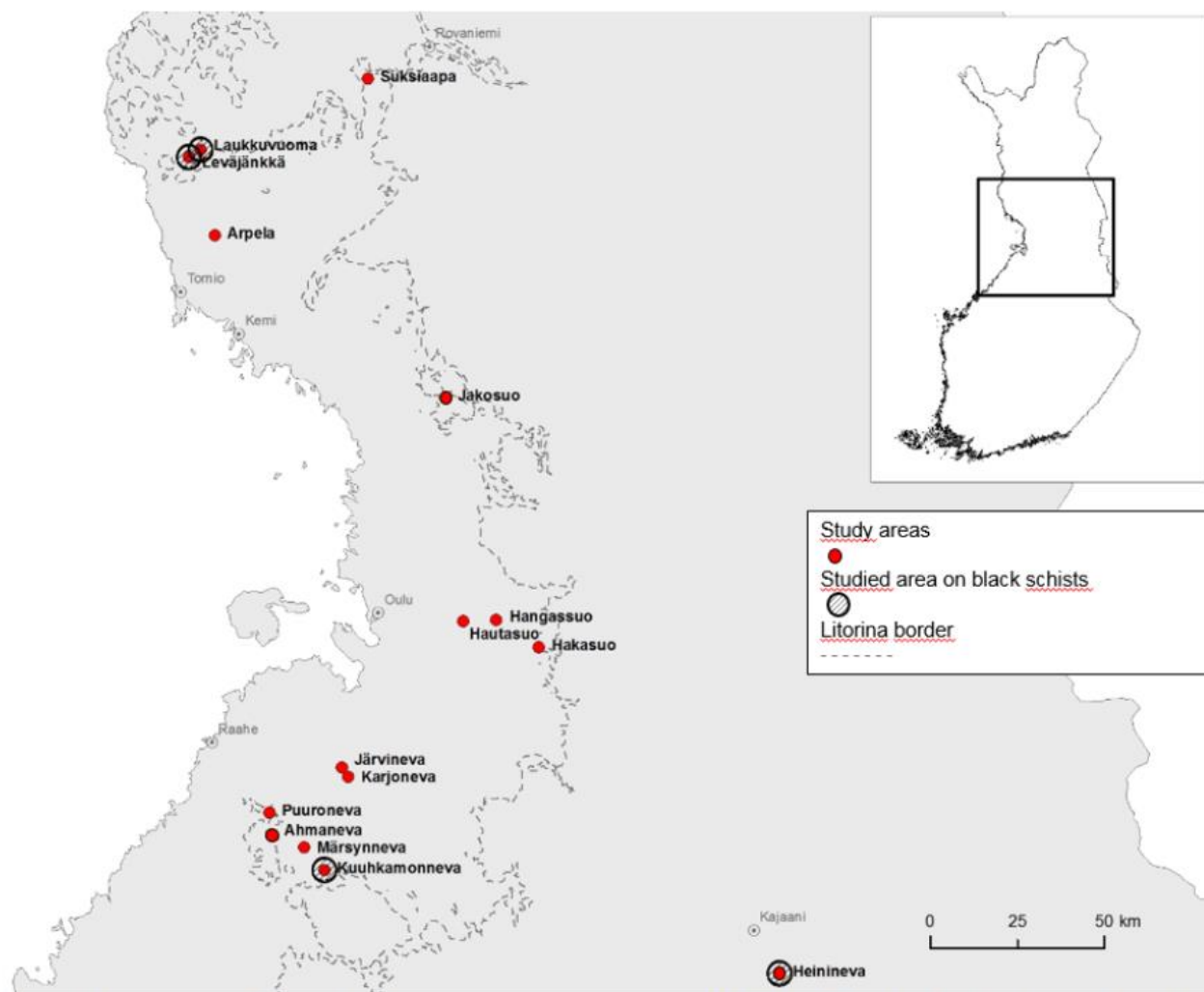


Fig. 1. Location of the studied peat extraction areas in W Finland, including information if the areas are located on black schist or not. The highest cost line for the ancient Litorina Sea is also shown.

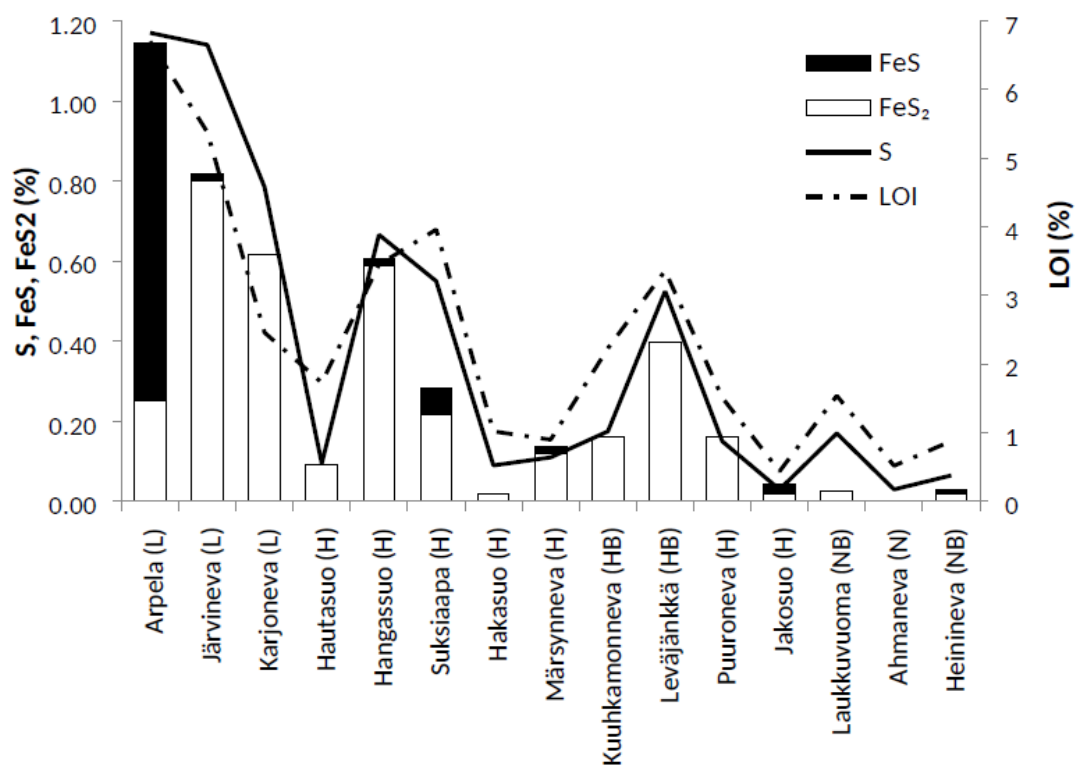
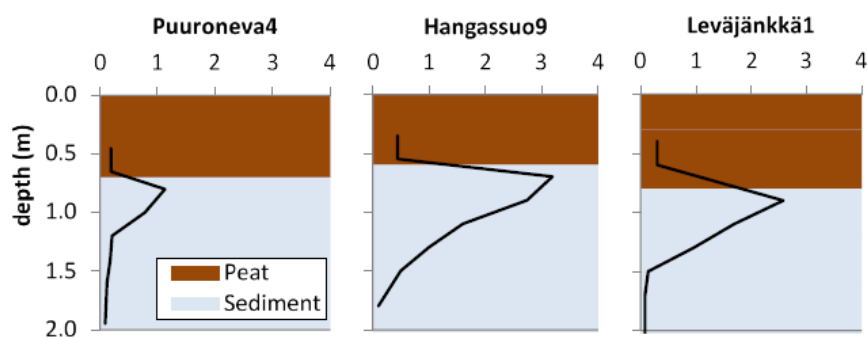
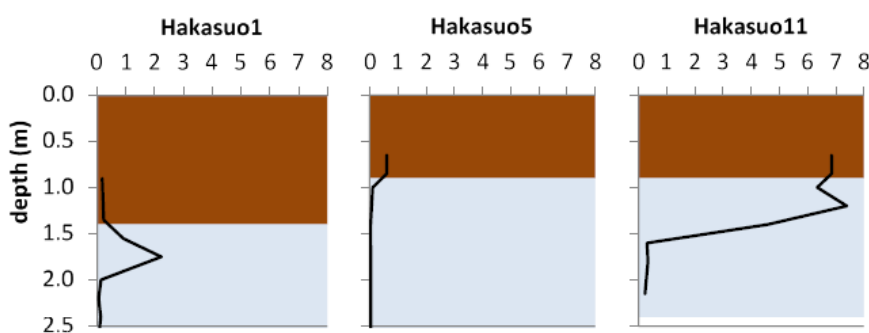


Fig. 2. Median concentrations in the sediment at a depth of 40-60 cm under the peat/sediment boundary for total sulfur (S), monosulfide (FeS), pyrite (FeS₂) and organic matters (LOI) in the 15 studied active and former (Karjoneva and Hangassuo) peat extraction areas. The areas are sorted according to their current height above the sea level from left (30 m above the sea level) to right (180 m above the sea level). L=Lower litorina area; H=Higher litorina area; N=Non-litorina area; B=on black schists.

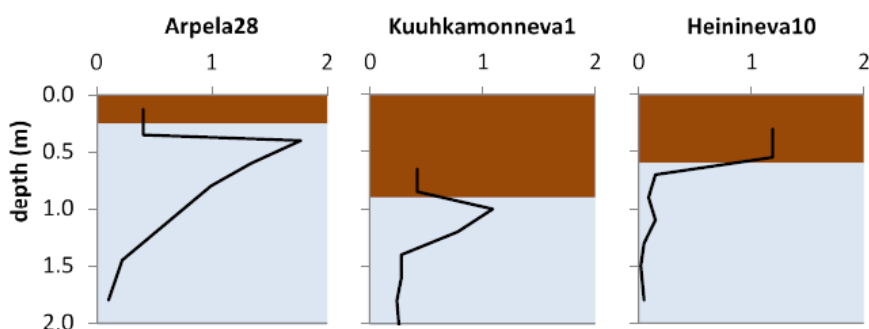
(A)



(B)



(C)



(D)

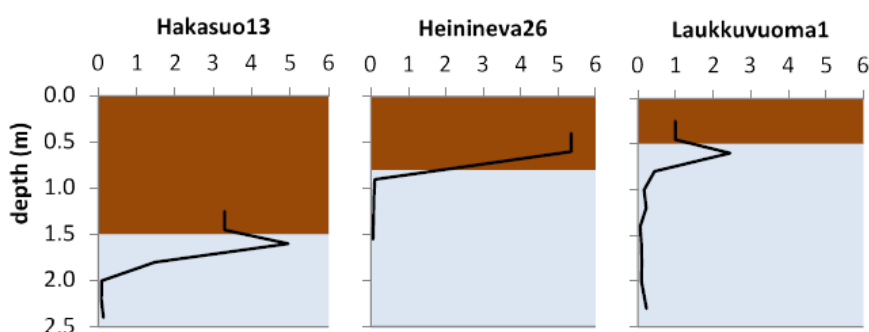


Fig. 3. The total sulfur concentration (%) in the selected profiles. (A) Sulfide-bearing generally muddy/silty marine sediments were commonly found just below the peat layer, especially in the older sulfidic sediments situated below the highest shoreline of the ancient Litorina Sea (i.e. the upper litorina areas). Within a studied area (B) and between peat extraction areas (C) the sulfur concentration varied generally considerably. (D) The highest sulfate concentrations in the peat layers were generally found in or near areas with black schists.

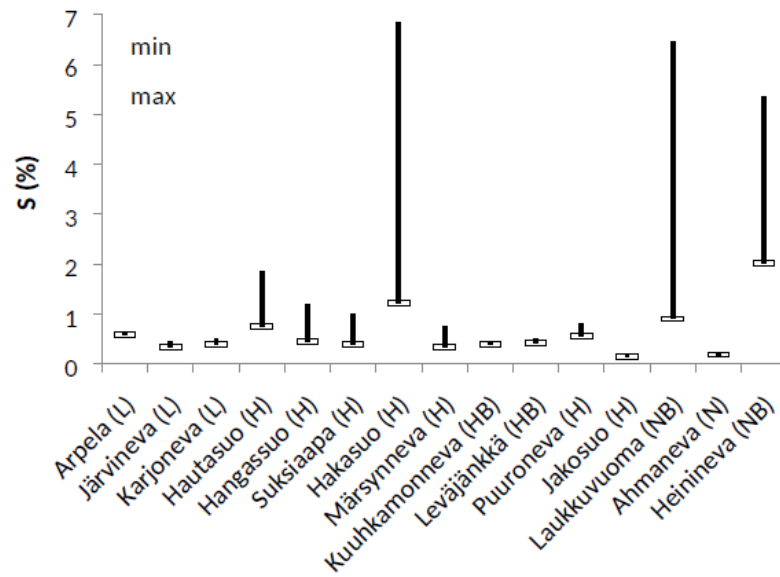


Figure 4. For each area minimum, median and maximum total S concentrations in the peat. The areas are sorted according to their current height above the sea level (a.c.s.l.) from left (30 m above the sea level) to right (180 m above the sea level). Kuuhkamonneva, Leväjänkkä and Heinineva were situated on black schists and Hakasuo and Märsynneva were situated 1.2 km from black schists. L=Lower litorina area; H=Higher litorina area; N=Non-litorina area; B=on black schists.

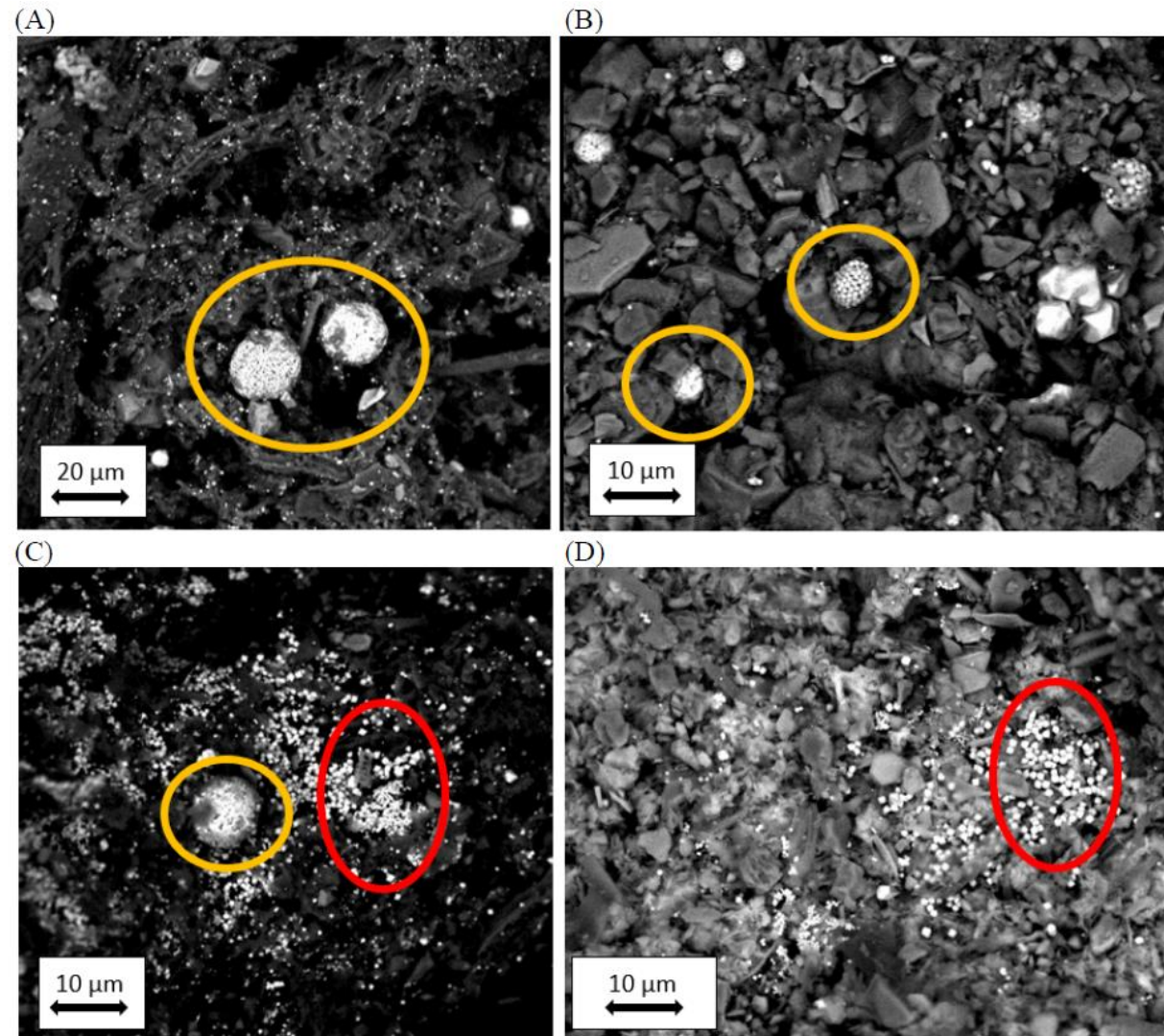


Fig. 5. Scanning electron micrographs (SEM) of framboidal pyrite (A, B and C; some examples marked with a yellow circle) and loose pyrite crystals (mostly seen in C and D; ; some examples marked with a red circle) in freeze-dried samples from the sulfidic sediment layer in Järvineva (B) and Arpela (D), and the peat layer in Heinineva (A and C).

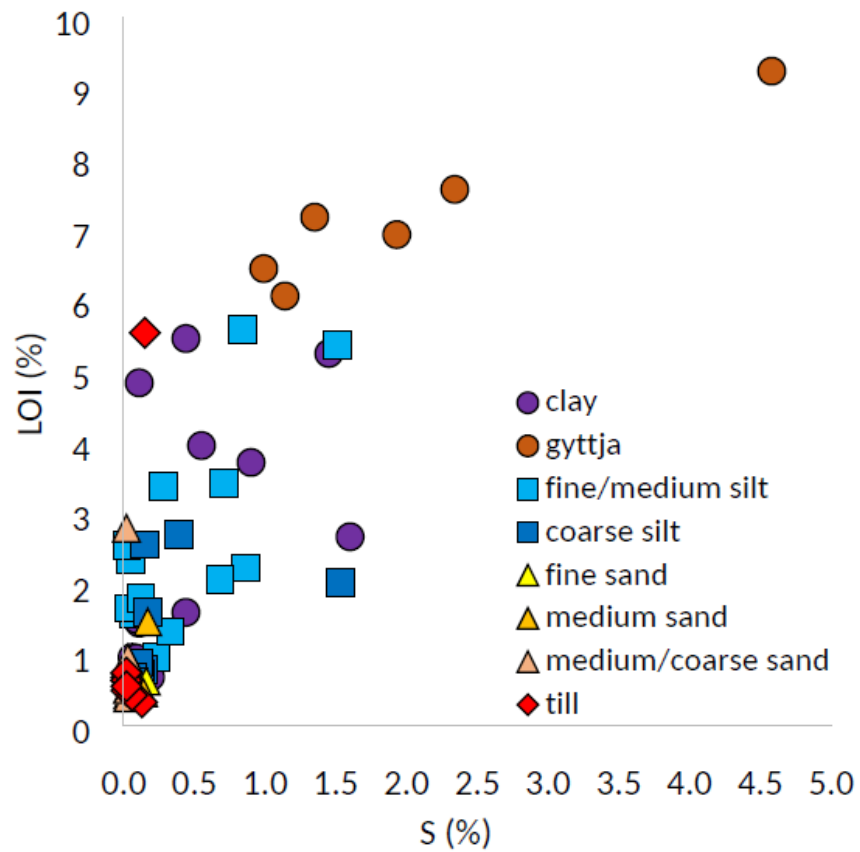


Figure 6. Relationship between organic matters (LOI), sulfur (S) and grain size.



Fig. 7. Monosulfides are visible in reduced soils as a black color and could therefore been spotted. However, the trickier recognizable pyrite was more common in the areas and, thus, sulfides were hard to find without analyzing the soil samples.

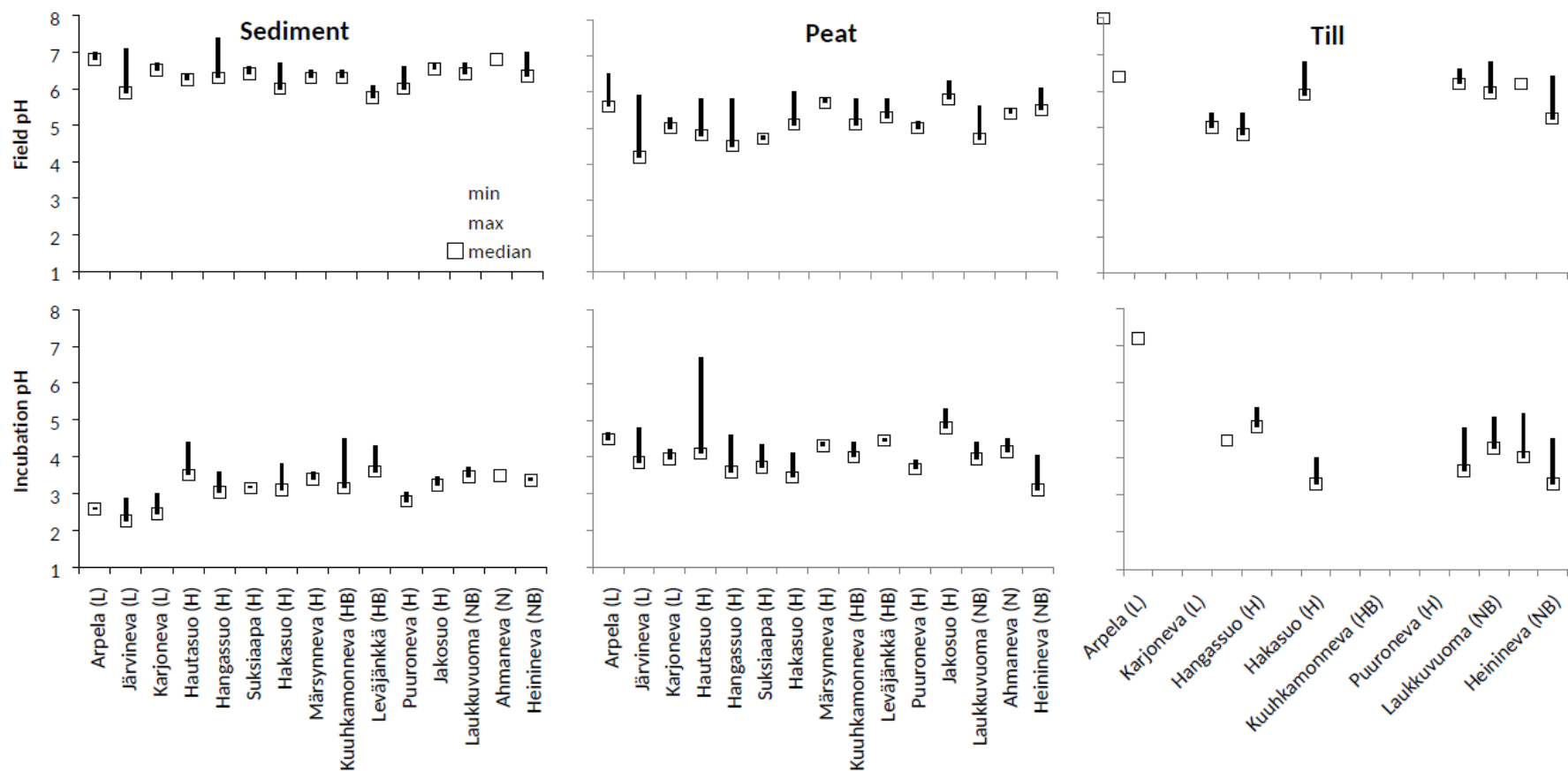


Fig. 8. For almost each area minimum (min), median and maximum (max) field pH and 16 weeks incubation pH in the sediment (at a depth of 40-60 cm under the peat/sediment boundary), in the peat and in the till. The areas are sorted according to their current height above the sea level from left (30 m above the sea level) to right (180 m above the sea level). L=Lower litorina area; H=Higher litorina area; N=Non-litorina area; B=on black schists.

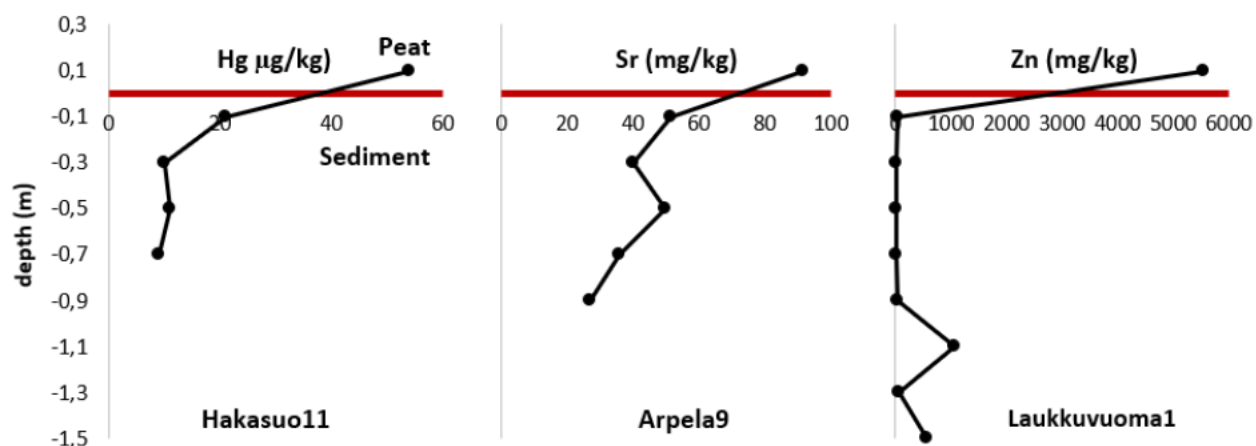


Fig. 9. The concentration for Hg, Sr and Zn shown in selected profiles. In the peat layer (above the brown line) considerable high Cd, Hg and Sr concentrations were found in most of the investigated areas. Near or on black schist areas (as in the studied area “Laukkuvuoma”) also the concentration for Zn were enhanced in the peat layer.

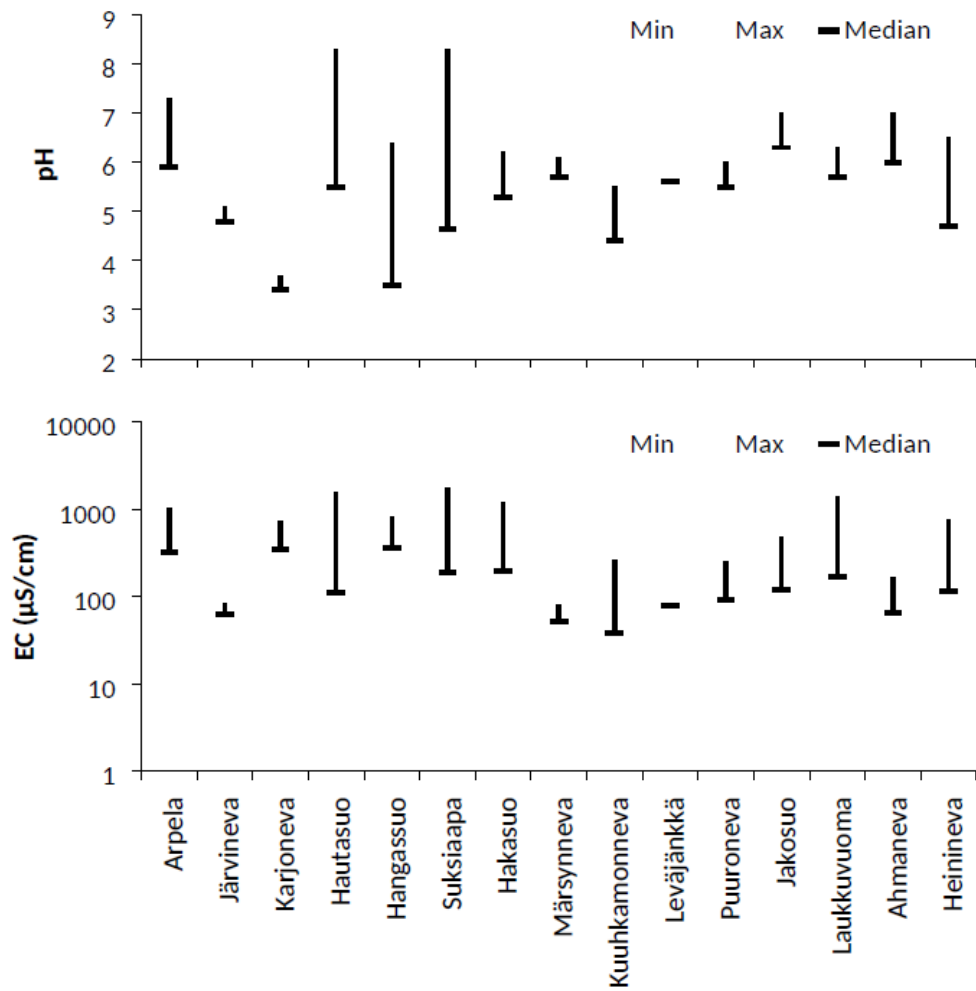


Fig. 10. For each area minimum, median and maximum pH and EC in the low-order streams.

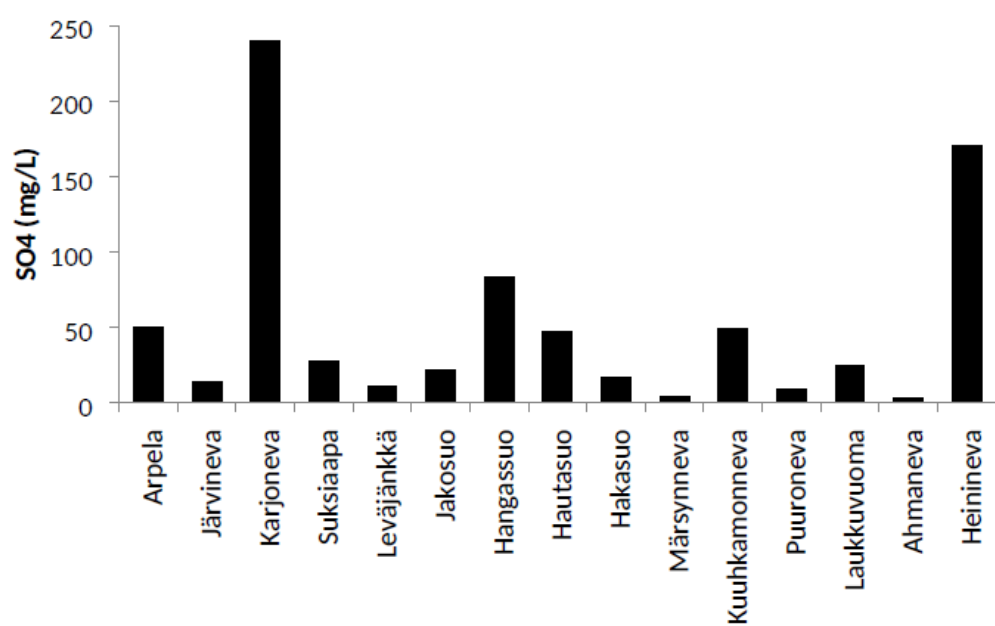
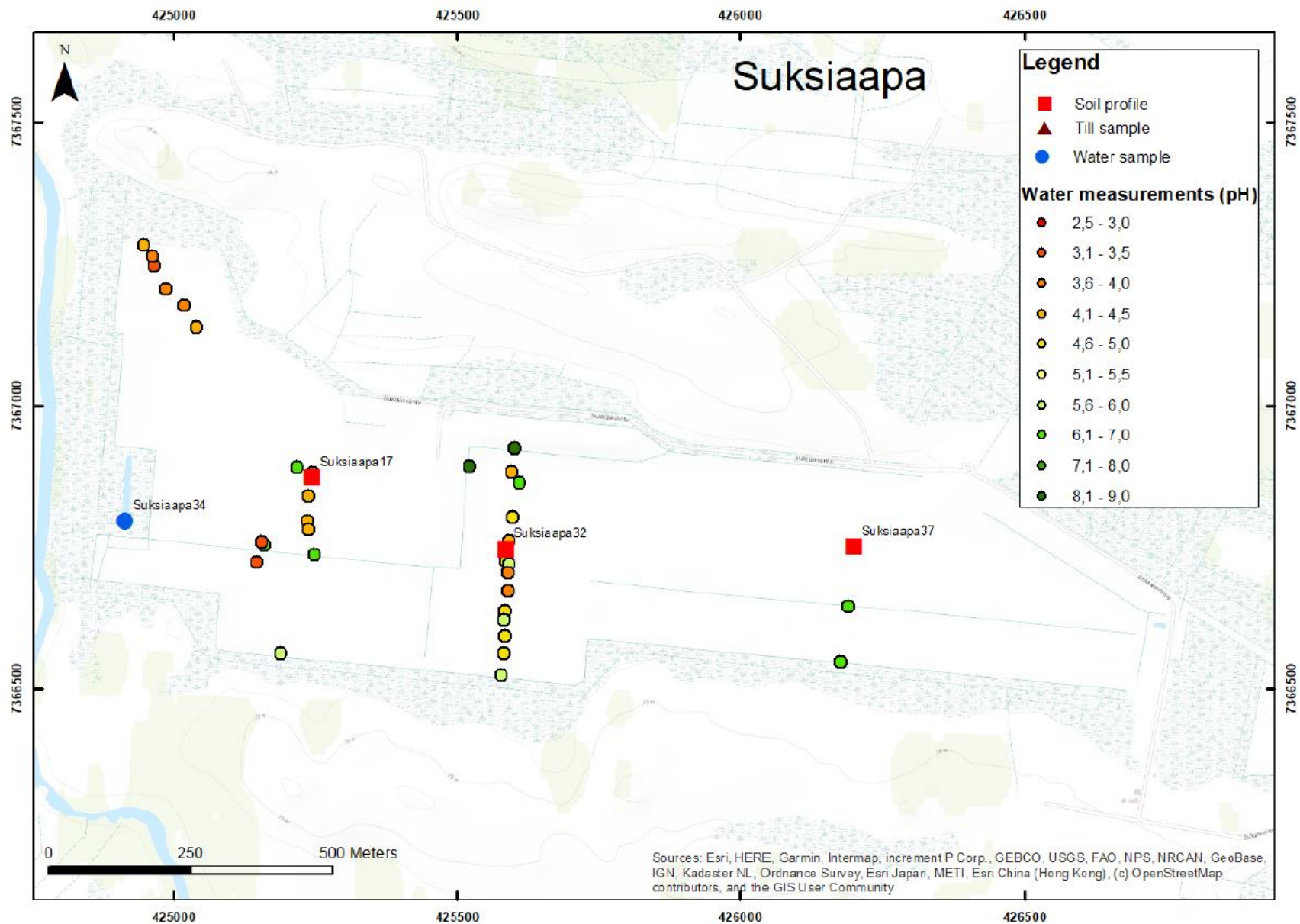
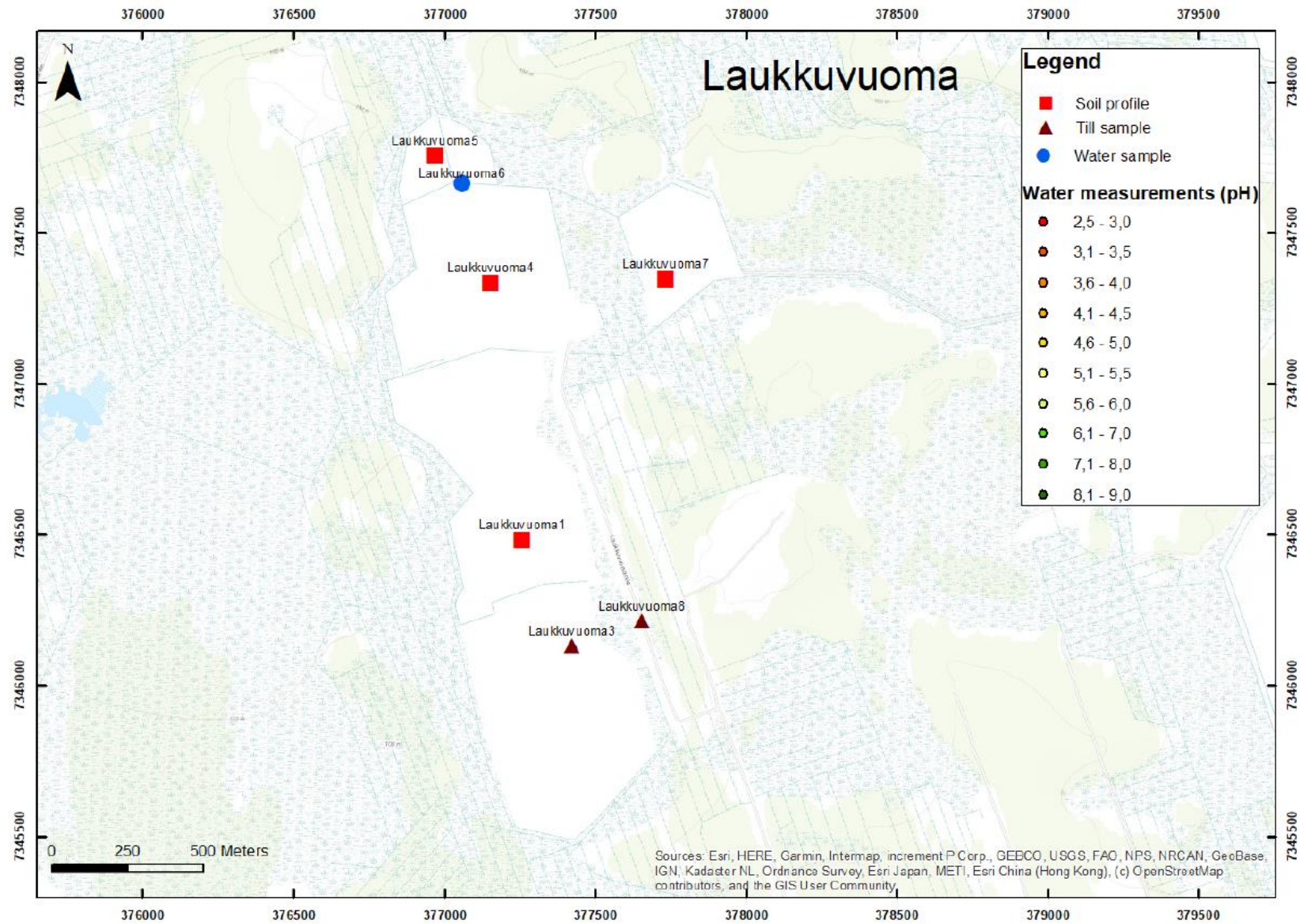


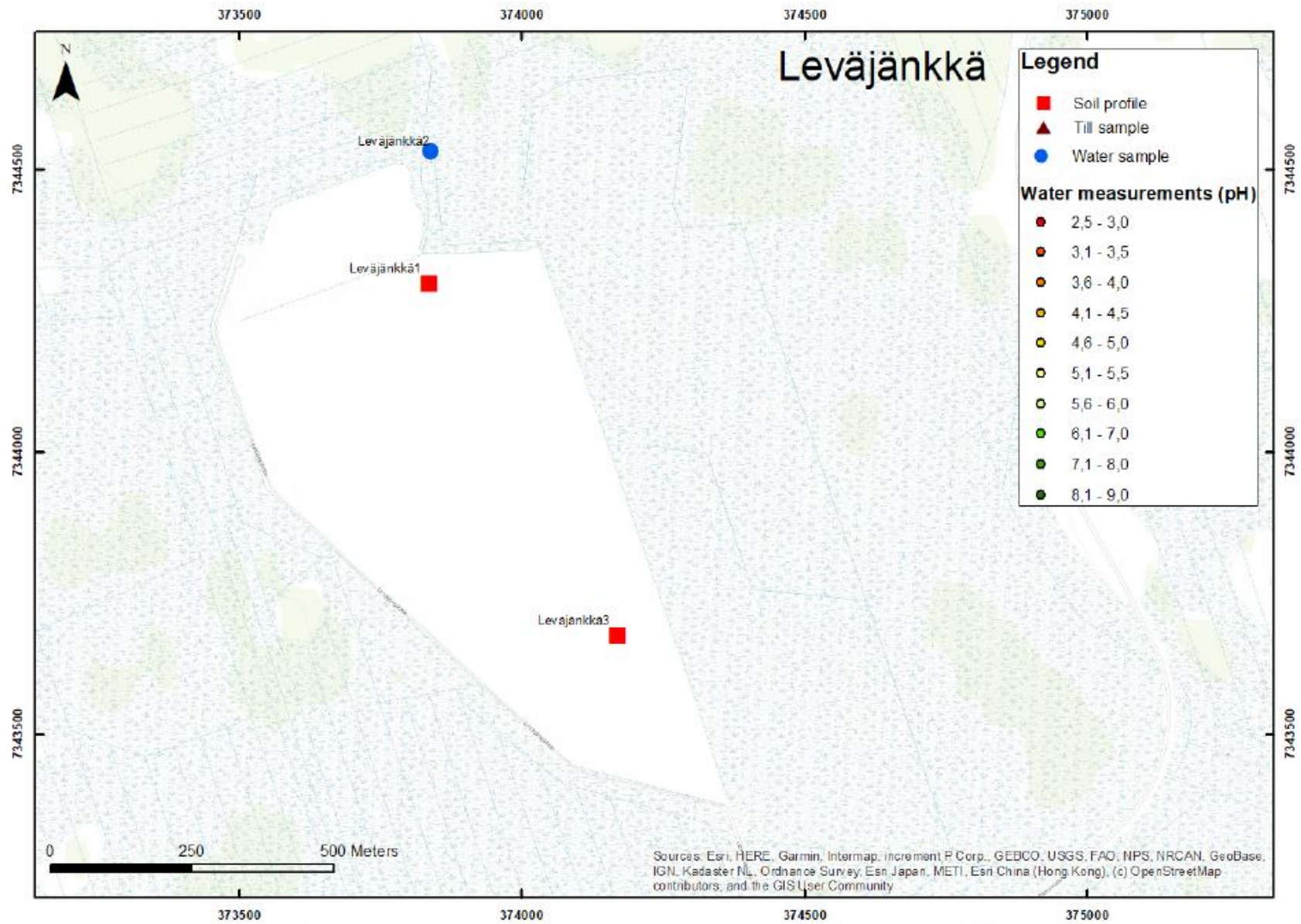
Fig. 11. The sulfate concentration in the main water course for each area.



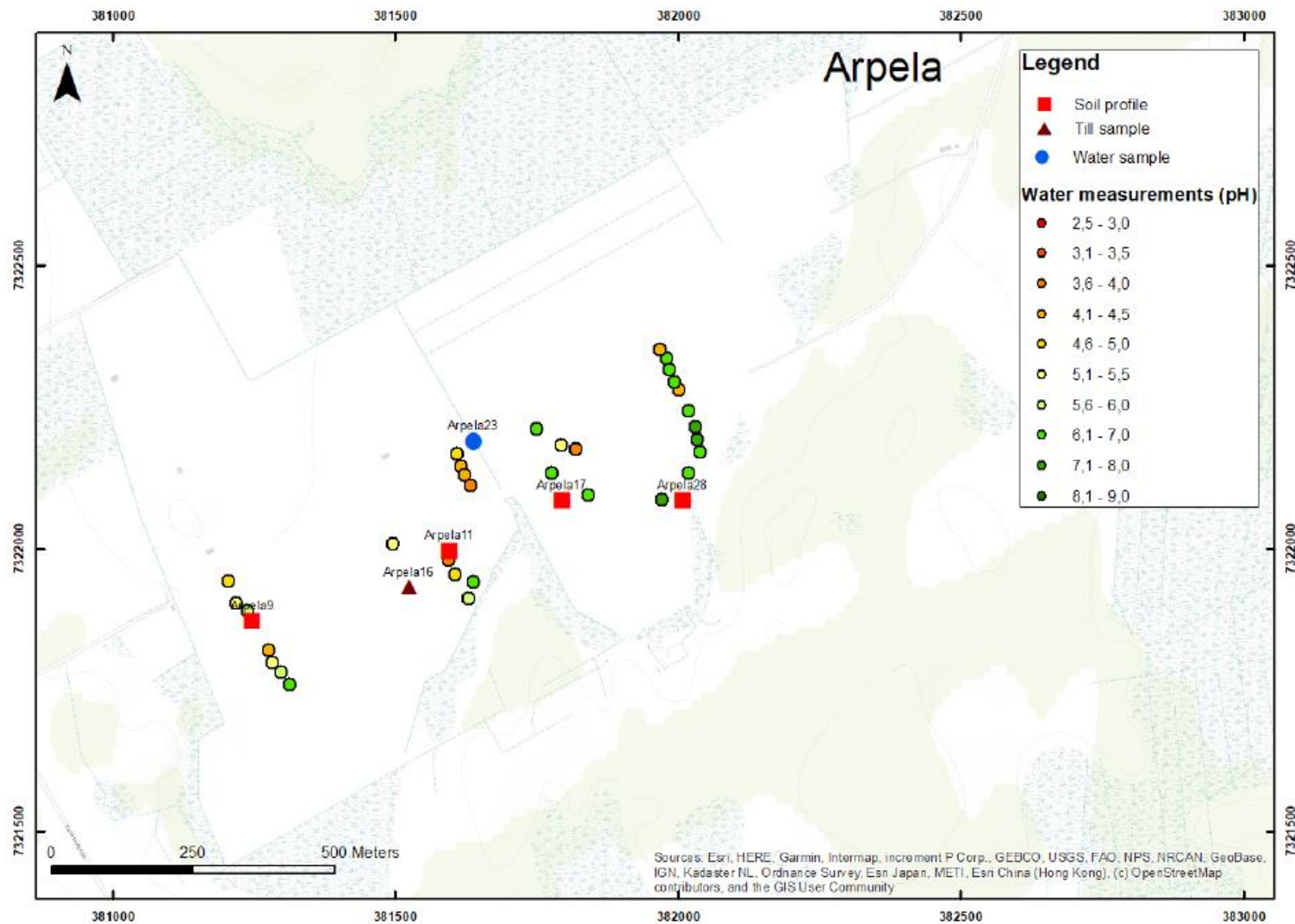
Supplementary Figure S1. Sampling and water measurement locations in the peat extraction area Suksiaapa. The scale of the map is 1:8000.



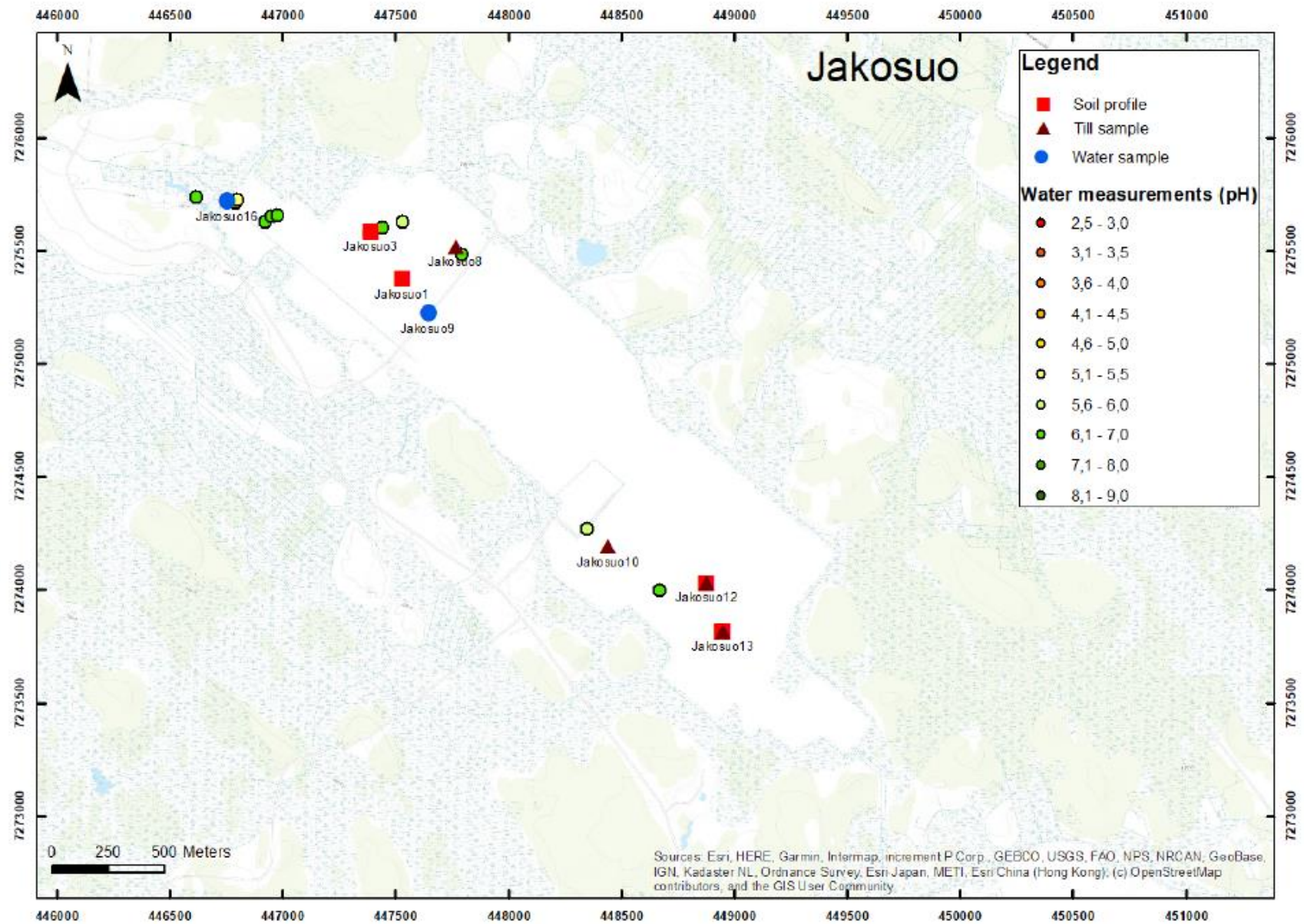
Supplementary Figure S2. Sampling and water measurement locations in the peat extraction area Laukkuvuoma. The scale of the map is 1:15000.



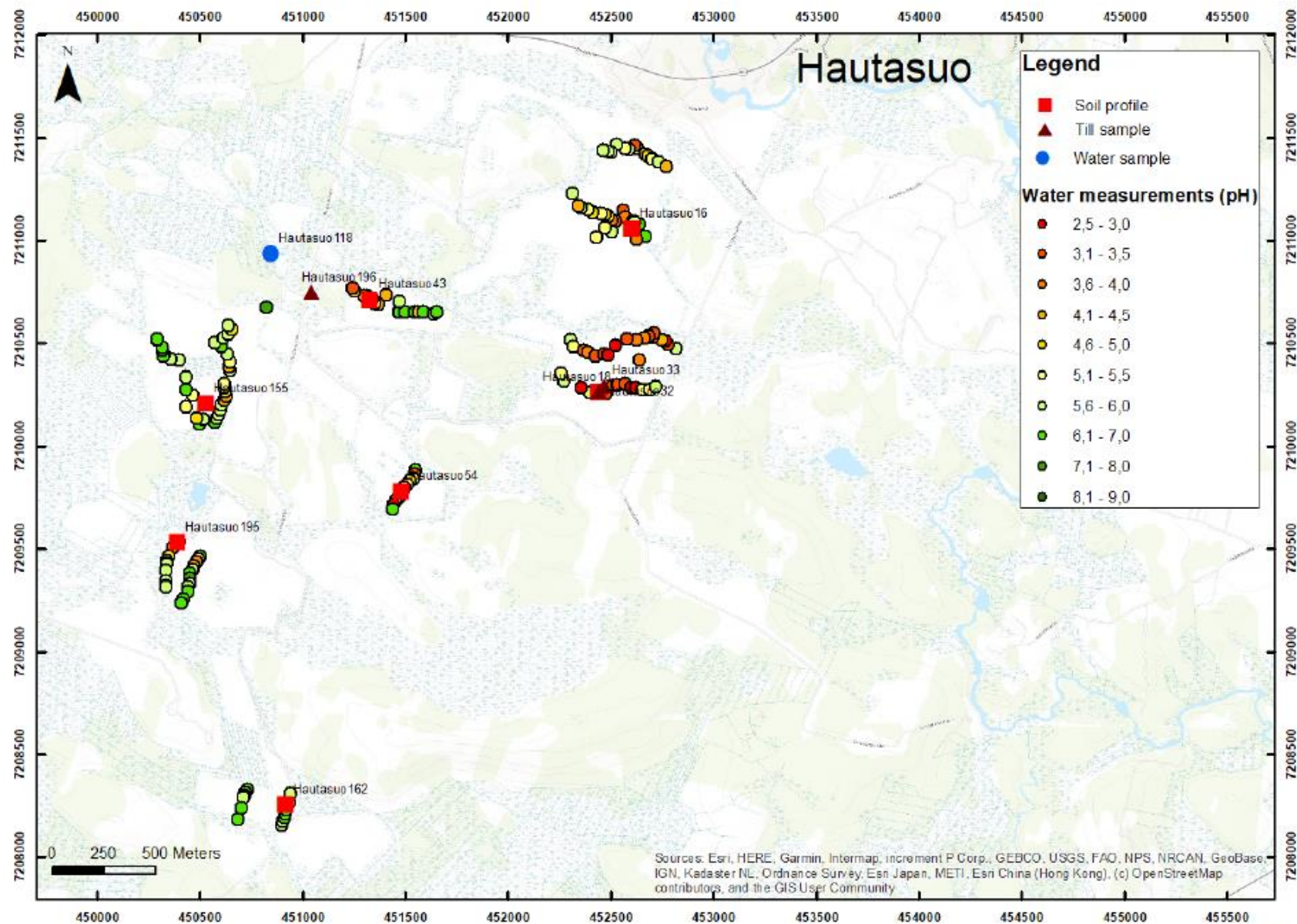
Supplementary Figure S3. Sampling and water measurement locations in the peat extraction area Leväjänkkä. The scale of the map is 1:8000.



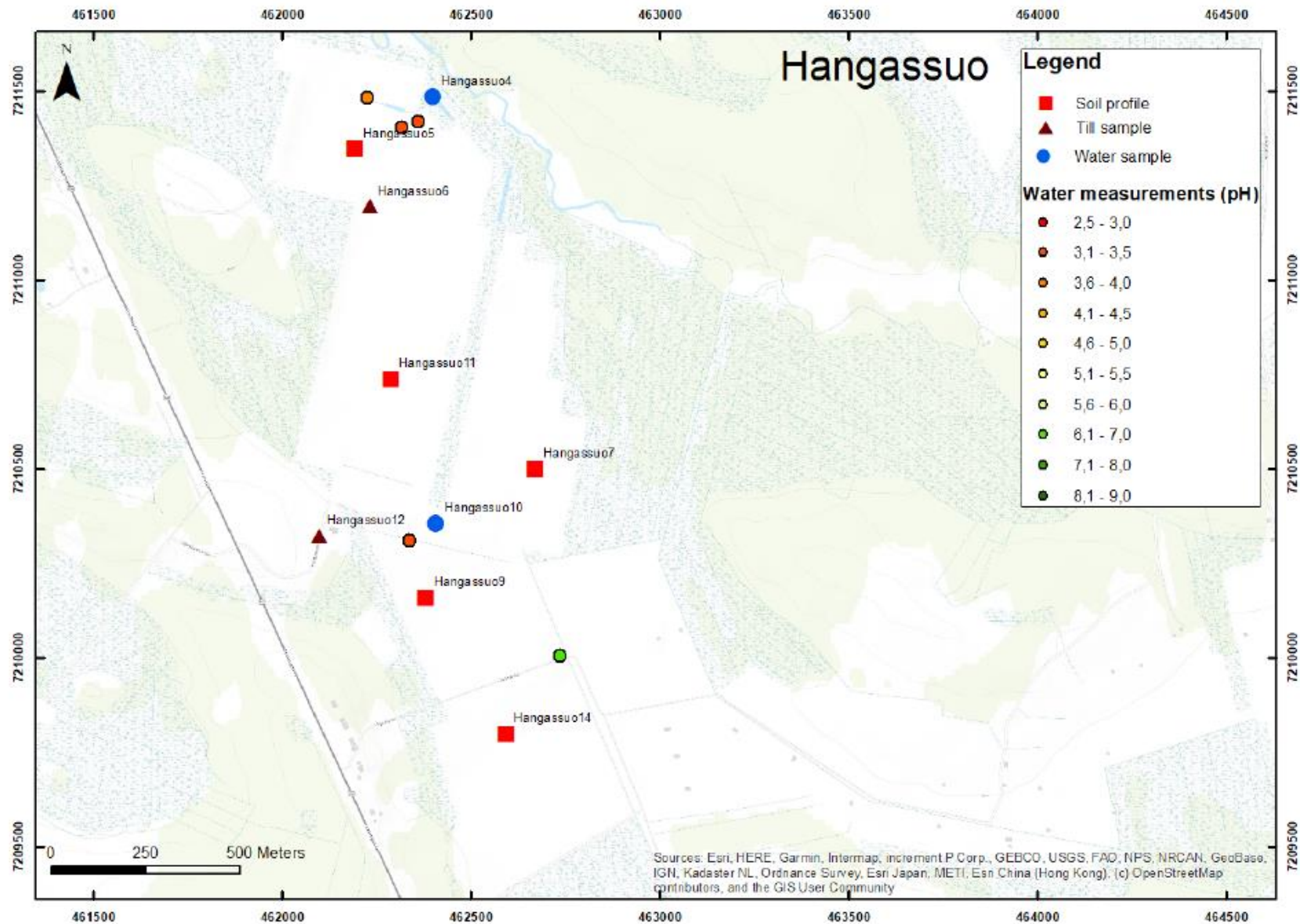
Supplementary Figure S4. Sampling and water measurement locations in the peat extraction area Arpela. The scale of the map is 1:8000.



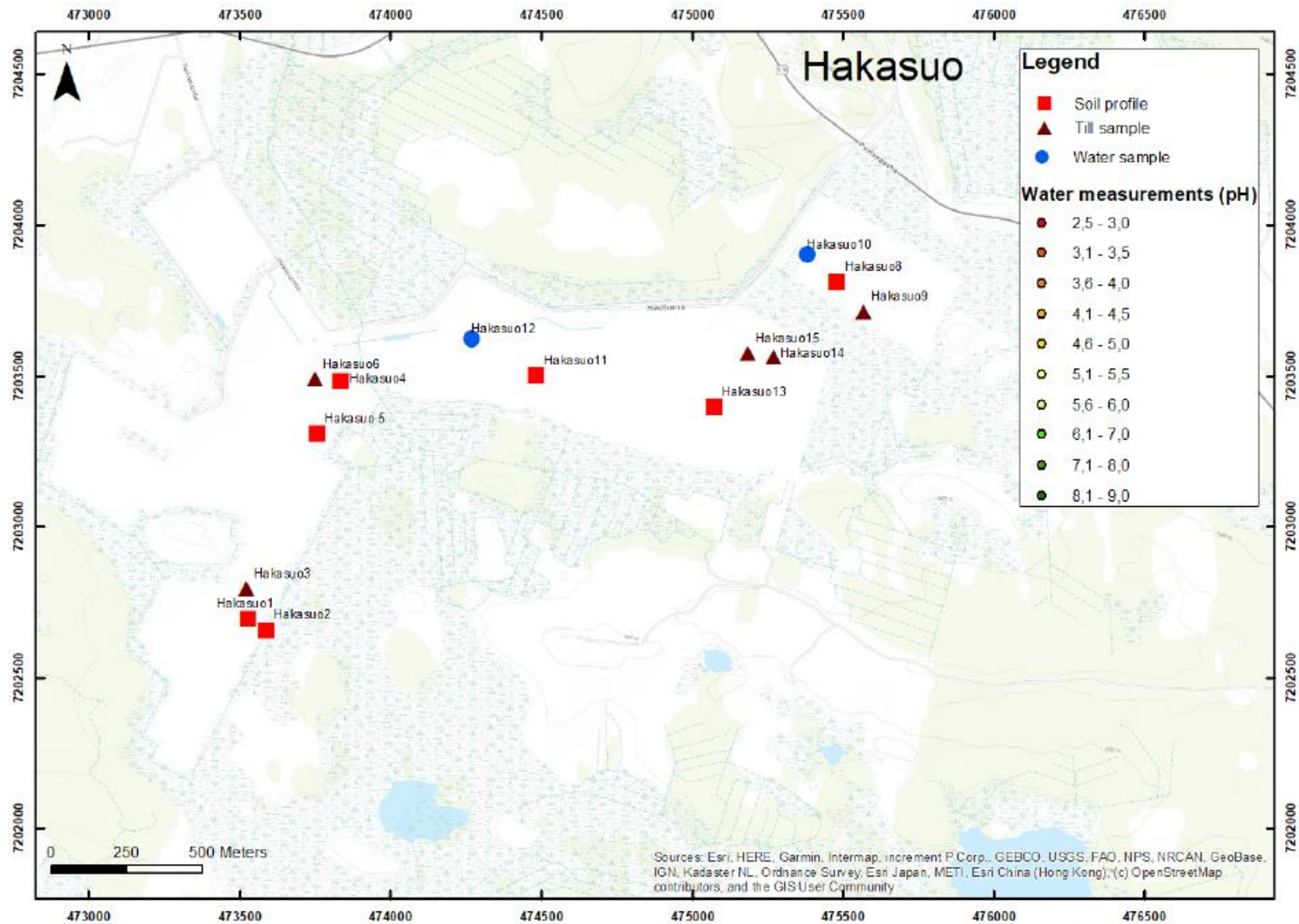
Supplementary Figure S5. Sampling and water measurement locations in the peat extraction area Jakosuo. The scale of the map is 1:20000.



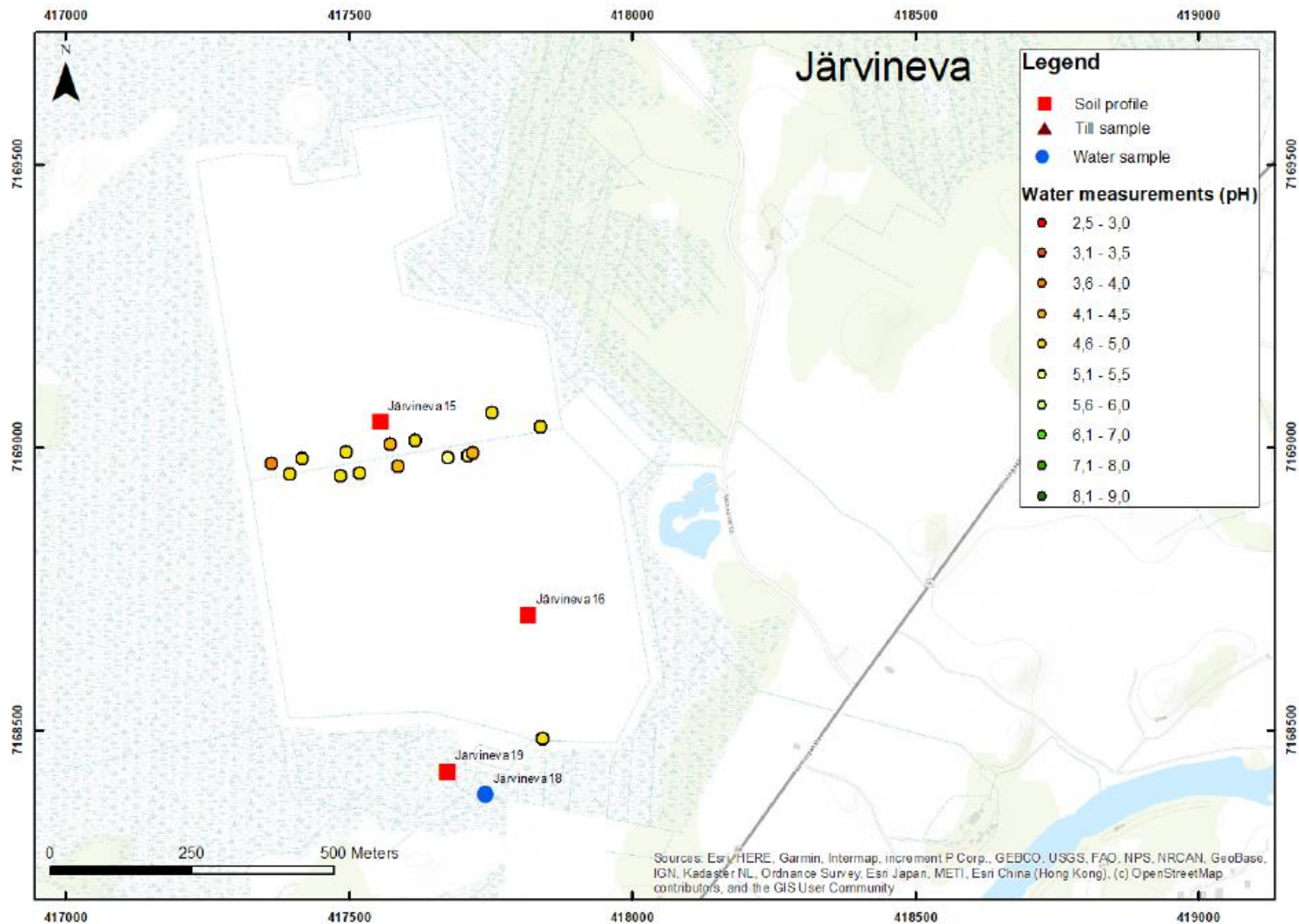
Supplementary Figure S6. Sampling and water measurement locations in the peat extraction area Hautasuo. The scale of the map is 1:22000.



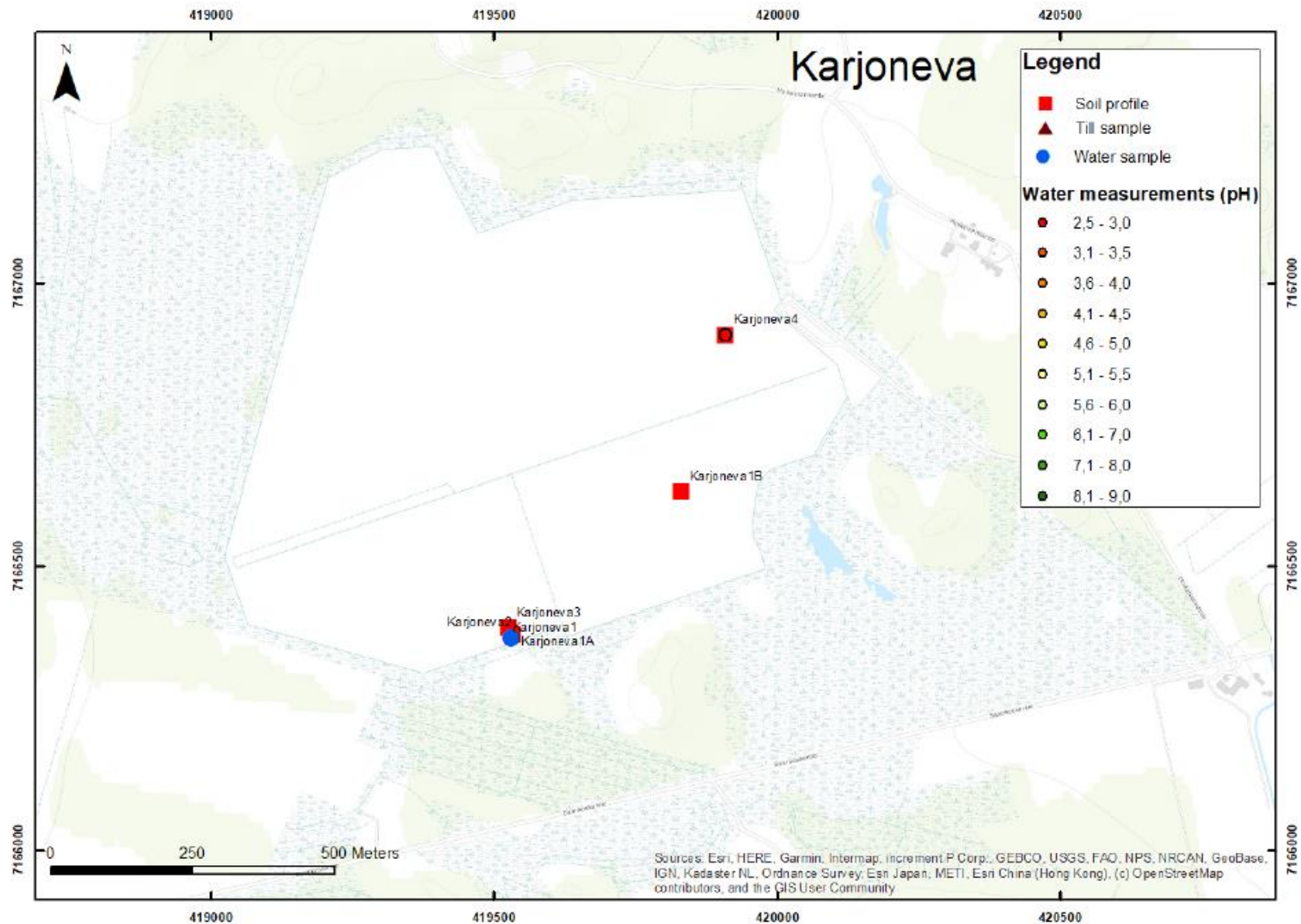
Supplementary Figure S7. Sampling and water measurement locations in the peat extraction area Hangassuo. The scale of the map is 1:12000.



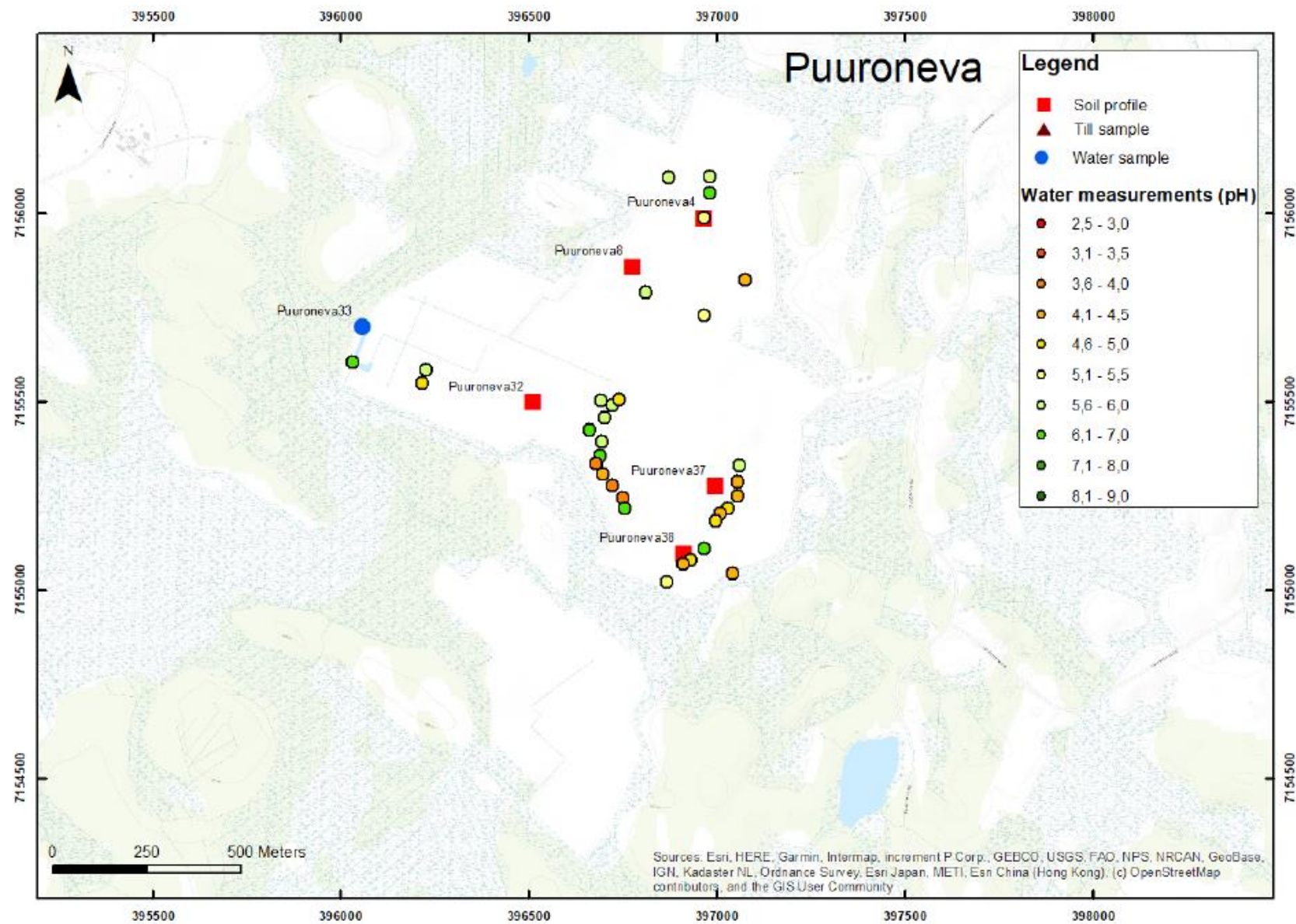
Supplementary Figure S8. Sampling and water measurement locations in the peat extraction area Hakasuo. The scale of the map is 1:15000.



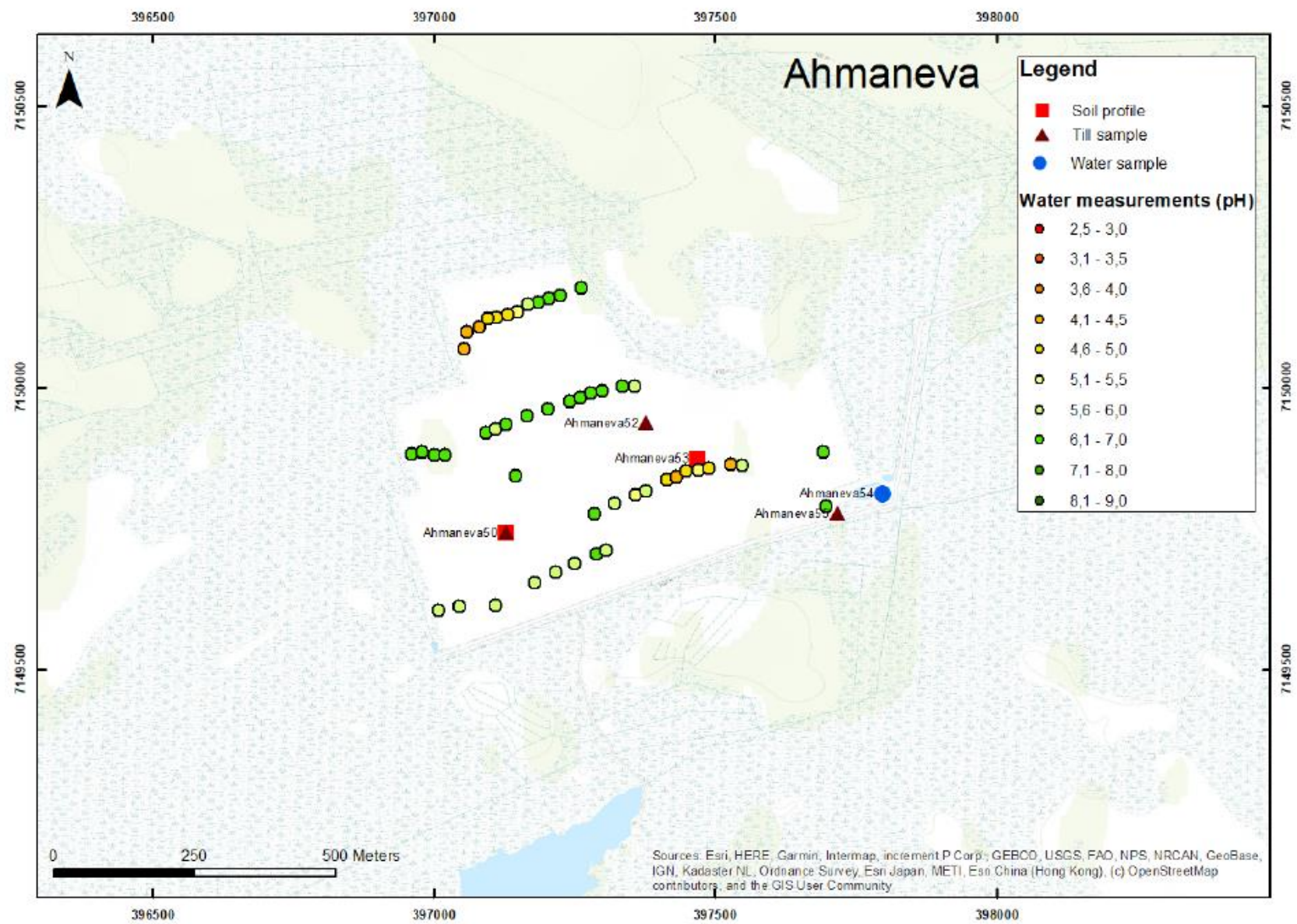
Supplementary Figure S9. Sampling and water measurement locations in the peat extraction area Järvineva. The scale of the map is 1:8000.



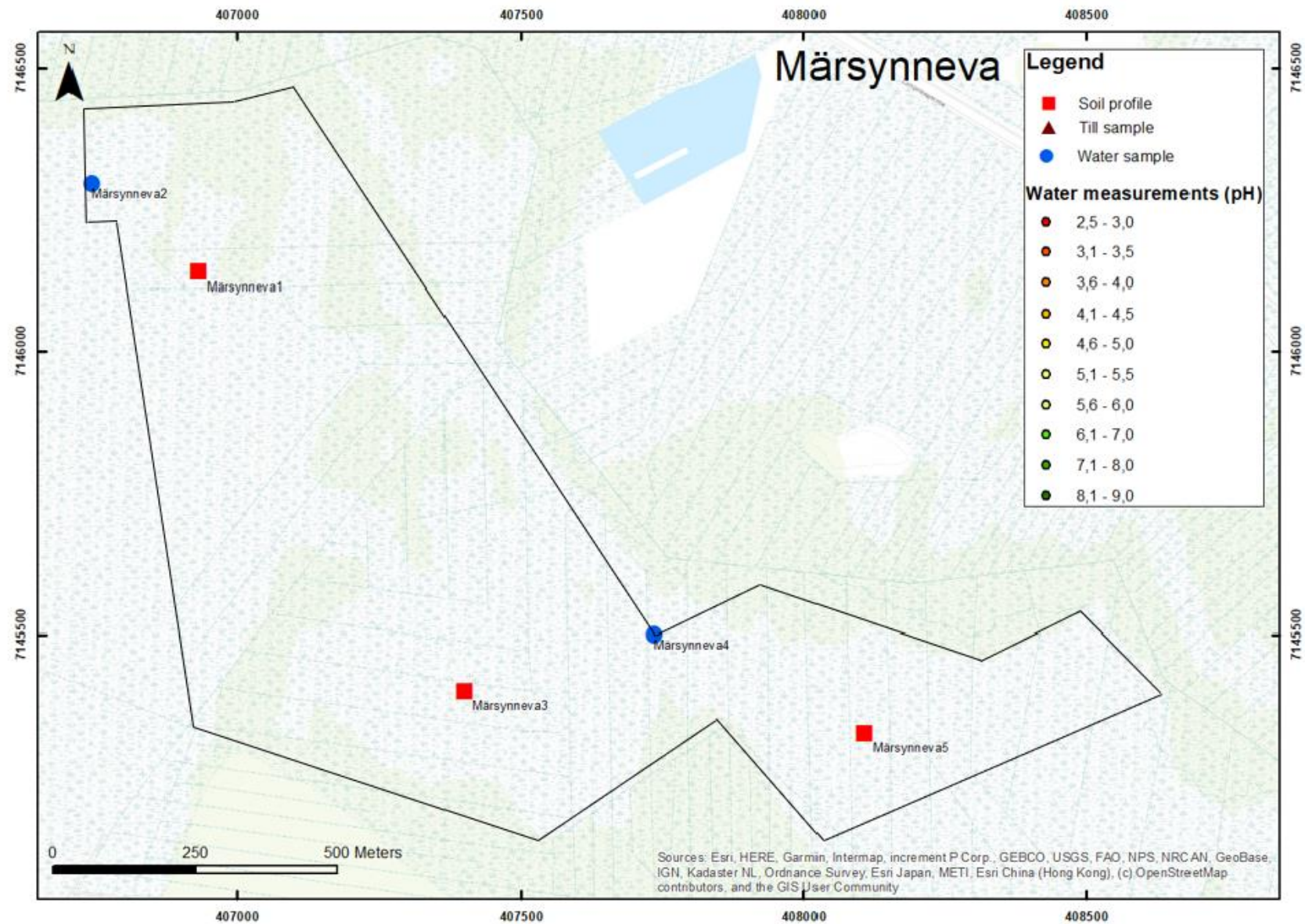
Supplementary Figure S10. Sampling and water measurement locations in the peat extraction area Karjoneva. The scale of the map is 1:8000.



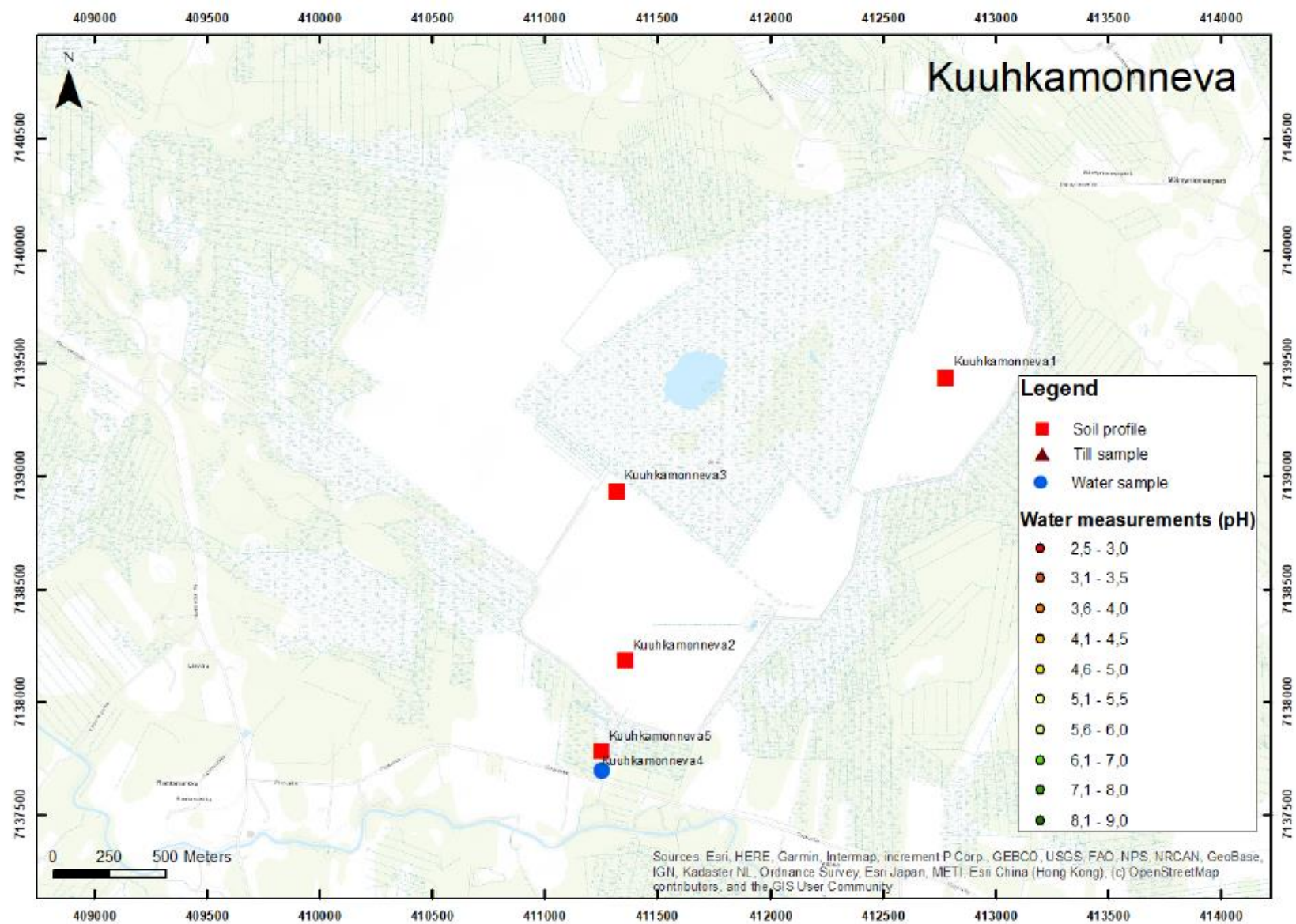
Supplementary Figure S11. Sampling and water measurement locations in the peat extraction area Puuroneva. The scale of the map is 1:12000.



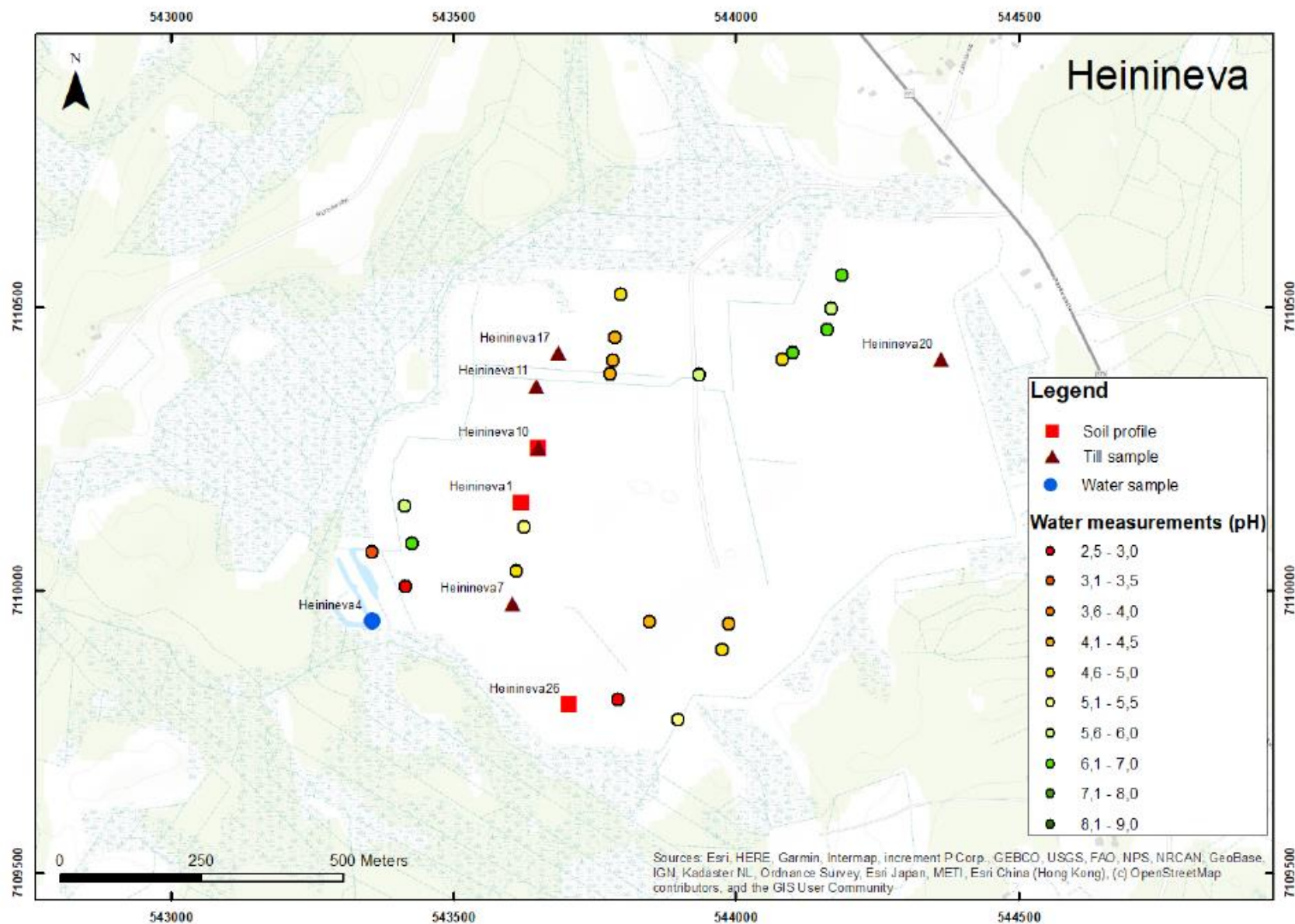
Supplementary Figure S12. Sampling and water measurement locations in the peat extraction area Ahmaneva. The scale of the map is 1:8000.



Supplementary Figure S13. Sampling and water measurement locations in the peat extraction area Märsynneva. The scale of the map is 1:8000.



Supplementary Figure S14. Sampling and water measurement locations in the peat extraction area Kuuhkamonneva. The scale of the map is 1:20000.



Supplementary Figure S15. Sampling and water measurement locations in the peat extraction area Heinineva. The scale of the map is 1:8000.

