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1 **Opportunities of electrokinetics for the remediation of mining sites in**
2 **Biga peninsula, Turkey**

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20

21 **Abstract**

22 This study investigated the geological conditions of Biga Peninsula. There are
23 metamorphic rocks, ophiolitic melange, plutonic rocks, subvolcanics, volcanic rocks
24 and volcanoclastics along with marine and terrestrial sediments in the region. This
25 variety of rocks and the associated minerals resulted in many interesting metallic ores
26 and coal for commercial exploitation. The mining exploitations in Biga Peninsula
27 (Turkey) pose an environmental risk due to the release of contaminants, metals and
28 arsenic, to the soil and waterbodies. This study analyzed the potential release of As and
29 metals (Al, Fe, Mn) from a sediment sampled in a mine pond. The extraction column
30 tests proved that those contaminants can be dissolved from the sediment using
31 deionized water as eluent. The electrokinetic treatment of the sediment was able to
32 remove Al and Mn, but the removal of Fe and As was negligible. The fractionation of
33 As and metals in the sediment confirmed that the electrokinetic treatment was able to
34 mobilize the contaminants. Based on the results of this study, it has been hypothesized
35 that the toxic elements could be removed by electrokinetics using facilitating agents,
36 neutralizing the alkaline environment of the cathode and increasing the treatment time.

37

38 **KEYWORDS:** mine sediment; heavy metals; arsenic; electrokinetic remediation

39

40 **1. Introduction**

41 Soil can be polluted by heavy metals and metalloids via natural routes, although the
42 main contamination sources are related to human activities. These activities include
43 mining, ore processing and smelting, agricultural additives, storage of chemicals, and
44 inappropriate management of wastes. Mining activities are one of the major sources of
45 metal contamination, and show many different environmental effects as it was proved in
46 a variety of studies (Beane et al., 2016). Mines are active in relatively small areas but
47 they show large environmental impacts in the surrounding environment
48 (Hudson-Edwards, 2016) even after the cease of the activity. Thus, abandoned mine
49 areas are a major environmental concern because of the degraded land devoid of
50 vegetation and the continuous release of acid water and toxic elements from the mine
51 and mine tailings (Karaca et al., 2018). As an example, the accumulation of mine
52 tailings containing sulfide minerals such as pyrite (FeS_2), arsenopyrite (FeAsS), galena
53 (PbS), orpiment (As_2S_3), realgar (AsS), chalcopyrite (CuFeS_2) and sphalerite ($(\text{Fe}, \text{Zn})\text{S}$)
54 results, at medium and long term, in the release of acid mine drainage loaded with toxic
55 elements (Anawar, 2015). When tailings are in contact with air, the oxidation of sulfide
56 results in the production of sulfuric acid and the release of the metals from the minerals.
57 Moreover, the acid effluent favors the desorption of more metals and toxic elements
58 from the mineral matrix (Karaca et al., 2018). This process is accelerated with the
59 presence of some autotrophic microorganisms that use the oxidation of inorganic
60 substrates (sulfide, ferrous iron,...) in their metabolism (Baker and Banfield, 2003). As
61 a result, the mine and the surroundings (soil and waterbodies) are contaminated with
62 toxic heavy metals and other elements, e.g. arsenic. Those toxic elements affect the soil
63 and water ecosystems and may enter the food chain due to easy accumulation in internal
64 organs causing deadly diseases (Lee et al., 2007).

65 Arsenic is a toxic element of special concern in the acid mine drainage due to its high
66 toxicity for living organisms (Kim and Yung, 2004). The main geogenic sources of high
67 arsenic levels in soil and groundwater in the environment are sulfide minerals, volcanic
68 rocks, hydrothermal activities and fossil fuels (Bissen and Frimmel, 2003; Gunduz et al.,
69 2010). Studies in Turkey in recent years have proved the pollution of the natural
70 medium with arsenic (Aksoy et al., 2009; Gunduz et al., 2010; Sener and Karakus,
71 2017), often associated to mining and related activities.

72 Another environmental problem in abandoned mine sites are the ponds and waterbodies
73 formed by accumulation of water in the uneven surface. The sediments in these ponds
74 contain high concentrations of heavy metals and other toxic elements, previously
75 released from the ore and minerals in the mine. These pollutants pass from the solid to
76 the liquid phase through dissolution/precipitation and adsorption/desorption reactions.
77 Redox reactions changing the speciation of metals are also common. The mobilization
78 of these pollutants increases the risk of contamination in soil and waterbodies in the
79 surrounding ecosystems. Thus, a detailed study of the composition and reactivity of
80 these sediments is necessary to evaluate their risks for the natural wildlife and public
81 health, as well as in the design of any rehabilitation program of abandoned mine areas
82 (Rodríguez, 2009).

83 The objective of this study is the assessment of the environmental issues in present and
84 former mining areas in Biga peninsula (Turkey). This region is well-known for an
85 intense mining activity. The main materials extracted in Biga peninsula are coal and
86 metal ores (Pb-Zn, Au-Cu and Au-Ag). Contamination of soil and pond sediments with
87 toxic elements (Al, As, Ba, Fe and Pb) has been reported in the Biga mining sites
88 (Karaca and Reddy, 2014; Karaca et al., 2017). The actual concentration of the toxic
89 elements is not as important as the solubility of those elements when the solid matrix is

90 in contact with water. Thus, the first step in the assessment of the environmental impact
91 is the determination of the physicochemical characteristics of the solid matrix.
92 Leachability of arsenic and heavy metal species from rocks and sediments is linked to
93 various parameters namely: pH, temperature, grain size, mineralogy, chemical
94 composition, metal speciation, and adsorption/desorption reactions (Bundschuh et al.,
95 2013). A variety of methods based on sorption/desorption experiments are available to
96 assess the potential mobility and interactions of pollutants over time (Rauret, 1998).
97 Thus, extraction and leaching tests come to the forefront to assess the potential risks
98 associated to the release of pollutants from the solid matrix (Grathwohl and van der
99 Sloot, 2007; Grathwohl and Susset, 2009). Other selective extraction methods are useful
100 to determine the speciation of pollutants, their bioavailability for plants and soil
101 organisms, and for land use assessment (Rao et al., 2008).

102 Extraction methods can be classified in two groups: single and sequential extraction
103 methods. The single extraction methods are useful to estimate the bioavailability of the
104 toxic elements when the solid matrix is in contact with water. The sequential extraction
105 methods can also determine the bioavailability of toxic elements but they can also be
106 used to investigate the possible long-term release of polluting material entering water
107 from the solid matrix (Grathwohl and Susset, 2009). Column leaching tests are used to
108 assess the extent of the leaching of a pollutant in specific solid-liquid conditions
109 (pH,...). Studies from literature showed that a combination of extraction and column
110 tests are useful to assess the speciation and fate of metals in soils (Tam and Song, 1996).
111 This information can be used in the risk assessment and in the design of rehabilitation
112 strategies (Salomons, 1995).

113 Electrokinetic remediation seems to be a promising and time-effective technique for the
114 rehabilitation of mine sites affected by toxic elements (Reddy and Cameselle, 2009).

115 This technology has shown several successes when dealing with solid matrices
116 contaminated with organic and inorganic elements, although organics are not of special
117 concern in mining areas (Demir et al., 2015).

118 The main objective of this study is the characterization of pond sediments from specific
119 mine sites in Biga Peninsula. The geology of the region was analyzed to determine the
120 origin (minerals and rock formations) of the toxic elements released from the solid
121 matrices. The characterization of the pond sediments will allow to assess their
122 environmental impact as well as the capability of electrokinetic remediation for the
123 restoration of contaminated sites.

124

125 **2. Geological description of Biga Peninsula**

126 The mining areas studied in this work are located in Biga Peninsula, in the northwestern
127 part of Turkey (Fig. 1). The Biga Peninsula is a typical geological laboratory in terms of
128 rock and mineral variety. There are many different rock groups with different
129 formations and ages as described in Table 1

130 The basement of these rock groups is composed of Paleozoic-aged metamorphic rocks
131 (Kazdağ metamorphic complex). The Mesozoic Karakaya complex and meta-ophiolitic
132 rocks are located above this basement over a tectonic contact. In Cenozoic times,
133 widespread magmatic rocks (plutonic, subvolcanic and volcanic) and shallow marine
134 and lacustrine clastic sediments developed.

135

136 **2.1. Mineral resources and exploitations in Biga peninsula**

137 Biga peninsula is rich in metallic minerals (Au, Ag, Pb, Zn, Cu, Fe, etc.), industrial

138 minerals (kaolin, quartz, feldspar, etc.) and energy raw materials (coal, bituminous shale,
139 geothermal resources, etc.) mainly due to the variety of rocks in the Biga Peninsula. A
140 significant portion of these resources are extracted in open pit mines or underground
141 exploitations.

142 Most of the metallic mines in the region are found in calc-alkaline magmatic rocks or
143 their differentiation products related to collision and post-collision in the
144 Eocene-Oligocene and Miocene periods (Yigit, 2012). Lignite beds are located within
145 Miocene fluvial and lacustrine sediments. Lignites are extracted and used in the thermal
146 power plants found in the region.

147

148 **2.2. Impacts of mining exploitations in Biga peninsula**

149 There is a large variety of mining sites in Biga Peninsula, and therefore large impacts in
150 the soil, waterbodies and ecosystems have been found in a number of investigations. As
151 an example, in the Çan-Etili (Çanakkale) basin, the mine wastes and pond sediments
152 were found to contain large amounts of toxic heavy metals that contaminate the
153 surrounding ecosystems (Karaca and Reddy, 2014; Karaca et al., 2017). Areas with
154 similar problems can be found in the Gönen district, located in the East of Biga
155 peninsula. In addition to the metallic mines, this area contains some coal mines,
156 abandoned or in exploitation. The contaminants from the mines represent a serious risk
157 for the population in Gönen district because this is a very populated area (73,300 as per
158 the 2017 census) and some population nuclei are located close to the mines. As an
159 example, Sebepli village (in Gönen district) is only 500 m far from an abandoned mine
160 where acid ponds and mine wastes release toxic elements to the soil and water

161 (Supplementary material, Fig. SM-1a). This situation makes urgent a detailed
162 investigation of the toxic elements released from the mines and their influence in the
163 soil and water quality, with the final objective to assess the risk for the population.

164 The former mining activities have left behind piles of excavated soil, accumulation of
165 mine wastes and pits where the ore was extracted. Over time, the rain and surface runoff
166 fill in the pits forming numerous ponds in the uneven surface of the mine area. The
167 physicochemical characteristics of the water in the pond and the sediments in the
168 bottom are related to the minerals and elements in the mine tailings and mine soil. Often,
169 the pH of the mine ponds is very acid (even below pH 2) due to the presence of sulfide
170 minerals and the formation of acid mine drainage. Heavy metals and other toxic
171 elements are also common in the water pond and in the bottom sediments (Fig. SM-1b).
172 Thus, mine sites containing these acidic ponds shows a great danger to the environment
173 and public health.

174 Acidic mine lakes are a problem worldwide because of the negative effects on soil and
175 water quality and the spread of the harmful contaminants to the surrounding
176 environment. This may create a serious environmental risk, not only within the pond
177 and the mine area but also in downstream environments: soil and water resources
178 (Salmon et al., 2008; Geller et al., 2009). The water in ponds occurring in abandoned
179 mine sites may flow into rivers and waterbodies in the area (Fig. SM-1c), and
180 sometimes pond water is used for irrigation purposes (Fig. SM-1d) extending the
181 contamination to agricultural land, crops and food chain.

182 Previous studies in this region have proven that pond sediments contain significant
183 amounts of metals that show environmentally-harmful effects (Karaca and Reddy, 2014;
184 Karaca et al., 2017). The dominant metals in mine tailings in the region are Pb (79-103

185 mg kg⁻¹), As (43 mg kg⁻¹), Ba (190-300 mg kg⁻¹), Ni (470 mg kg⁻¹), Al (9700 mg kg⁻¹)
186 and Fe (18113 mg kg⁻¹); in pond sediments the most abundant elements are Pb (64-90
187 mg kg⁻¹), Ba (310-380 mg kg⁻¹), Ni (570 mg kg⁻¹), Al (1100 mg kg⁻¹) and Fe (42280 mg
188 kg⁻¹); and the concentration in rocks are Pb (96 mg kg⁻¹), Ba (279 mg kg⁻¹) and Ni (760
189 mg kg⁻¹) (Karaca and Reddy, 2014; Karaca et al., 2017). Column extraction tests, TCLP
190 (toxicity characteristic leaching procedure) and SPLP (Synthetic Precipitation Leaching
191 Procedure) were conducted to assess the possible the environmental effects of mine
192 tailings, sediments and solid matrixes in the mines. Acidic conditions have been
193 observed in the mine solid materials as well as the effluents in contact with tailings and
194 sediments. These acidic conditions cause the release of metals from the solid materials
195 and their dissemination in the area. Extraction tests, TCPL and SPLP can be used to
196 determine the elements that are more likely to be released and cause an environmental
197 impact. These elements will be the target elements in any restoration program. Thus, the
198 electrokinetic treatment of the mine solid matrixes will be designed to remove the toxic
199 elements identified in the leaching and extraction tests.

200

201 **3. Materials and methods**

202 **3.1. Sediment sampling and characterization**

203 This study used the sediments from the bottom of a mine pond located in Sebepli village
204 in Gönen district (Fig. SM-1a). The physical and chemical features of the sediments and
205 the metal content were determined. The physicochemical characteristics include: pH,
206 oxidation reduction potential (ORP), electric conductivity (EC), salinity (NaCl
207 equivalent), specific gravity (dry basis), water content (% wt.), organic content (dry

208 basis), permeability, and grain size distribution. Metal content in the solid samples was
209 determined by the USEPA method 3050. The solid samples were digested with nitric
210 acid and hydrochloric acid. The solubilized metals were determined by ICP-OES
211 (Inductively Coupled Plasma Optical Emission Spectrometry).

212

213 **3.2. Column extraction tests**

214 A glass column 30 cm length and 2.5 cm inner diameter was used. A known mass of
215 sample was placed in the column. Porosity and pore volume were determined.
216 Deionized (DI) water was flushed through the column from the top at a constant flow
217 rate. The effluent was collected in the bottom of the column and referred to the number
218 of pore volume flushed. pH, ORP (oxidation-reduction potential) and EC (electric
219 conductivity) was measured in the effluent. The heavy metal concentration in the
220 effluent was determined by ICP-OES.

221

222 **3.3. Sequential extraction**

223 The method described by Tessier et al. (1979) was applied for the sequential extraction
224 of metals and other elements from the sediment sample. In the Tessier method, the total
225 content of a chemical species is divided into five fractions: I-exchangeable, II-bound to
226 carbonates, III-bound to Fe–Mn oxides, IV-bound to organic matter, and V-residual (the
227 fraction linked to the crystalline structure of the solid matrix). The sequential extraction
228 analysis was applied to the sediment specimen before and after the EK test. The analysis
229 was performed using 2 g of solid sample and the corresponding extracting solution as

230 described by Tessier et al. (1979). All the analyses were run in duplicate to assure the
231 validity of the results.

232

233 **3.4. Electrokinetic test**

234 The electrokinetic setup used in this study consists of a soil compartment (22.3 cm
235 length, 4 cm diameter), two electrode compartments, electrolyte solution reservoirs and
236 a power supply. The electrokinetic cell was made of Plexiglas. Graphite electrodes were
237 used in each electrode compartment.

238 The preparation of the sample for the electrokinetic test includes the mix of dry pond
239 sediment with DI water up to a moisture content of 42%. Then, the sample was
240 compacted in the central compartment of the electrokinetic cell. Electric potential
241 gradient of $1 \text{ DCV}\cdot\text{cm}^{-1}$ (22.3 V) was applied to the sediment specimen for 18 d. At
242 regular intervals, electric current intensity and electrolyte solution inflow/outflow in the
243 anode and cathode reservoirs were measured. After completing the test, the sample was
244 extruded from the cell and divided into five equal portions. After the test, water content,
245 and other physicochemical characteristics were measured in the sediment specimen.
246 Arsenic and heavy metal content were determined for each portion by ICP-OES after an
247 extraction by acid digestion. Additionally, the sequential extraction analysis as per
248 Tessier et al. (1979) was applied to each soil portion and the results were compared with
249 the sequential extraction before the electrokinetic treatment.

250

251 **4. Results and discussion**

252 **4.1. Characteristics of pond sediment**

253 The sediments from the bottom of a mine pond close to Sebepli village (Gönen) were
254 sampled. Considering the importance of the physicochemical characteristics of the
255 sediments to assess the environmental risk, a detailed analysis of the sediment was done.
256 The first sampling of the sediment was in September 2017. Considering the local
257 climate and the seasonal rains, no water was found in the pond in this time. The
258 moisture content of the sediment as it was sampled was 42%, and the organic matter
259 content was 17% (in dry basis). Specific gravity and permeability of the sediment were
260 2.35 and $6.45 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$, respectively. pH and EC ($\mu\text{S} \cdot \text{cm}^{-1}$) were 3.35 and 2427
261 respectively. The content of the toxic metals and elements in sediment were (in dry
262 basis) Al: 6.67%; As: $1030 \text{ mg} \cdot \text{L}^{-1}$; Fe: 5.68%; and Mn: $751 \text{ mg} \cdot \text{L}^{-1}$ (Table 2). The
263 second visit to the study area was in March 2018; in this moment, rain water had
264 accumulated in the pond and the overflow was discharged into a nearby stream (Fig.
265 SM-1c).

266

267 **4.2. Leachability of arsenic and heavy metals in sediment**

268 Leaching tests are becoming very important to assess the risk of release of potential
269 pollutants from a variety of solid materials. Column extraction experiments and
270 sequential extraction analysis were performed to determine the leachability and
271 availability of arsenic (As) and heavy metals in the pond sediment. Column extraction
272 tests are easy to perform and they help to investigate the leachability under simulated
273 field conditions using deionized (DI) water. The effluent was flushed through the
274 sample and collected at intervals of one pore volume up to a maximum of 5 pore

275 volumes. pH, ORP and conductivity of the leachate were measured. The results showed
276 that the leachate was very acidic, in fact, the acidity increased with the pore volumes
277 flushed (pH=3.42-2.67). Electric conductivity (EC) values slightly increased
278 (2207-3675 $\mu\text{S}\cdot\text{cm}^{-1}$) along the test, mainly due to the decrease of the pH. Organic
279 matter content was slightly decreased to 14.8% from the original organic content of the
280 sediment (17%).

281 The column tests proved that various metals, mainly Al, Fe and Mn were mobilized and
282 removed from the solid matrix by flushing DI water (Fig. 2). Arsenic was not mobilized
283 with DI water and only minor As amounts were found in the leaching effluent. 2.5% of
284 Al and 1.5% of Fe were removed from the sediment. Those percentages are relatively
285 low, but considering the initial concentration of Fe and Al in the sediment, it can be
286 stated that there was an important mobilization of Fe and Al. Unlike, Mn was
287 completely removed from the sediment with DI water, confirming its easy extractability
288 and therefore, the risk of mobilization of Mn from the sediment in the mine pond.

289

290 **4.3. Metal fractionation in sediment**

291 Sequential extraction analyses may provide vital information about chemical and
292 biological availabilities, origins, and mode of occurrence of toxic heavy metals (Sungur
293 et al., 2014; Sungur, 2016). This method enables understanding of the potential sources
294 and the mobility of heavy metals (Reddy et al., 2001; Cook and Parker, 2006; Karaca et
295 al., 2017). In the sequential extraction procedures, several extracting solutions are used
296 sequentially on the same sample (Rauret, 1998). Fig. 3 shows the fractionation of Al, As,
297 Fe and Mn in the sediment, using the method described by Tessier et al. (1979). As it

298 can be seen in the figure, more than 95% of the elements are associated to the most
299 immobile fraction (V-residual), and only minor fractions (4.5% of Mn, 1,3% of Fe,
300 0.25% of As, and 0.12% of Al) can be found in fractions I to IV. Mn showed the highest
301 concentration in fractions I and III, and Fe showed a significant concentration in
302 fraction III. Al and As only showed very small amounts in fractions I-IV. Considering
303 the high concentration of Fe and Al in the sediment, those minor amounts in fractions I
304 to IV might represent a significant concentration of toxic elements in the pond water in
305 contact with the sediment. The fractionation results are in agreement with the leaching
306 column test (Fig. 2). The most mobile metal, Mn, was completely released from the
307 sediment solid matrix, whereas Al, Fe and As were more difficult to mobilize. The low
308 solubility of As in water is another reason for the low mobilization of this toxic element
309 (García-Sánchez et al., 2010)

310

311 **4.4. Electrokinetic treatment of sediment**

312 The electrokinetic treatment of a sediment specimen was carried out in the experimental
313 setup composed of a central tube and two electrode chambers on both ends. The
314 electrode chambers were filled with DI water. The pH was not controlled in the
315 electrode solutions, so the pH increased in the cathode up to pH 12 and decreased in the
316 anode to pH 2 due to the electrolysis of water (Ricart et al., 1999). A constant 1
317 $\text{DCV}\cdot\text{cm}^{-1}$ was applied for 18 d. The electric current intensity registered along the test
318 showed a peak intensity in the beginning of the test (27 mA) and then continuously
319 decreased until 2.5 mA at the end of the test. The decreasing of the current intensity is
320 due to the transportation of ions from the sediment to the electrode chambers. The lower
321 concentration of ions into the solid matrix to carry the electric current resulted in the

322 continuous decrease of the intensity. This transportation was mainly by electromigration
323 of cations and anions towards the cathode and anode respectively. The other transport
324 mechanism is electroosmosis. The electroosmotic flow (EOF) was collected in the
325 cathode at an almost constant flow of $0.4 \text{ mL} \cdot \text{h}^{-1}$ from the day 3 to the end of the test.
326 This constant electroosmotic flow contributes to the removal of cationic metal species
327 towards the cathode.

328 At the end of the electrokinetic test, the sediment specimen was extruded from the
329 central tube of the electrokinetic cell and divided into 5 equal portions, namely S1-S5
330 from anode to cathode. pH, EC, salinity and moisture content were measured in the
331 sediment and in the electrode solutions (Supplementary material, Fig. SM-2). Arsenic
332 and metal concentrations were determined in the sediment portions and electrode
333 solutions (Fig. 4) as well as the fractionation of the target species at the end of the test
334 (Fig. 5).

335 The pH profile of the sediment specimen increased from anode to cathode. The initial
336 pH of the sediment was very acid (pH = 3.35, Table 2) but the electrolysis of water
337 during the electrokinetic treatment tended to acidify the sediment specimen on the
338 anode side, and increased the pH on the cathode side. A similar trend can be observed
339 for EC and salinity. The acidification of the specimen resulted in higher electric
340 conductivity due to the higher mobility of the H^+ ions. Moreover, low pH favored the
341 solubility of many metallic species, resulting in higher ionic concentration, higher EC
342 and salinity. The low EC and salinity in the S5 on the cathode side suggested an
343 effective removal of contaminating metals (Fig. 4). The moisture content along the
344 sediment specimen after the electrokinetic treatment was uniform ranging from 44 to
345 46%, very similar to the initial moisture content (42%, Table 2).

346 Fig. 4 shows the distribution of the selected metals (Al, Fe and Mn) and As in the
347 sediment specimen after the electrokinetic test. The profile of concentrations in the
348 portions of sediment from anode (portion S1) to cathode (portion S5) confirmed the
349 migration of the elements as positive ions towards the cathode. The formation of
350 cationic metallic species was expected considering the low pH in the specimen. Thus,
351 both electromigration and electroosmosis contributed to the transportation of the toxic
352 elements out of the solid matrix. A detailed analysis of the results in Fig. 4 let us to
353 conclude that Al can be removed by electrokinetics, whereas the removal of As an Fe
354 was negligible. Fe can be linked to the crystalline structure of mineral making its
355 removal impossible by electrokinetics. Arsenic was not removed. This may be related to
356 the complex chemistry of As that forms multiple species, some of them not soluble,
357 depending on the pH and ORP of the medium (García-Sánchez et al., 2010). The
358 removal of As can only be achieved by using solubilizing agents that stabilized the
359 Arsenic as a cation or anion forming stable complexes. The use of DI water in the
360 electrode chambers was not enough for the solubilization of As.

361 Mn showed a very different behavior compared to the other elements. As observed in
362 Fig. 4, there is a clear trend in the mobilization and transportation of Mn from anode to
363 cathode. Mn was solubilized in portion s1 due to the low pH, and it was transported by
364 electromigration towards the cathode. Mn precipitated in portions S4 and S5, due to the
365 higher pH (Fig. SM-2). Based on these results, it is hypothesized that the complete
366 removal of Mn from the sediment specimen can be achieved at longer treatment time
367 and controlling the pH in the cathode to avoid the premature precipitation of Mn into
368 the sediment.

369 The fractionation of Al, As, Fe and Mn in the sediment at the end of the electrokinetic

370 test showed a mobilization of the metals and As from the fraction V to the fractions I-IV,
371 especially for Fe and Mn (Fig. 5). The mobilization of As affected mainly the portions
372 S1 and S2. The As mobilization is linked to the acidification of the sediment specimen.
373 These results confirmed that the electrokinetic treatment is able to mobilize the toxic
374 elements from the solid matrix. The fractionation tests suggested that longer treatment
375 time in the electrokinetic treatment would result in better removal of metals and As. The
376 removal could be enhanced neutralizing the alkaline environment on the cathode side
377 and using facilitating agents to keep in solution the As and metals.

378

379 **5. Conclusions**

380 This study investigated the geological conditions of Biga Peninsula. There are
381 metamorphic rocks, ophiolitic melange, plutonic rocks, subvolcanics, volcanic rocks
382 and volcanoclastics along with marine and terrestrial sediments in the region. This
383 variety of rocks and the associated minerals resulted in many interesting metallic ores
384 and coal for commercial exploitation. The former and present mining activities in the
385 Biga peninsula represent a major threat for the environment and public health. This
386 study focus in arsenic and metallic contaminants that can be found in the mine soil,
387 wastes and pond sediments. The mining activity left behind an uneven surface that
388 accumulates the rain water forming mining ponds. The water in the ponds is
389 contaminated after being in contact with the mine soil and pond sediments. This water is
390 a vector for the contaminants that are dispersed in the surroundings and may enter the
391 food chain.

392 The sediments sampled in a mine pond in a former mine area close to Sebepli village

393 (Gönen, Turkey) showed a very low pH and high concentrations of As, Al, Fe and Mn.
394 These toxic elements can be leached from the solid matrix in a column test with DI
395 water. Electrokinetic remediation was tested as a technology for the removal of those
396 toxic elements from the sediment. The results proved that electrokinetics is useful in the
397 removal of Al and Mn. As was partially mobilized but it is hypothesized that the use of
398 facilitating agents is necessary for its effective removal. As a conclusion, we can state
399 that longer treatment time, neutralization of the alkaline environment in the cathode,
400 and the use of facilitating agents will be necessary for the remediation of mine pond
401 sediments.

402

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406

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518 associations of NW Anatolia and their tectonic significance. J. Geodyn. 31,
519 243-271.
- 520

521 Table 1. Geological characteristics of Biga peninsula

Rock formations	Characteristics and rocks	References
1. Paleozoic metamorphic rocks		
Kazdağ metamorphic complex	Oldest basement rocks in the region. Rocks: gneiss, amphibolite, mica schist, quartzite and marbles.	Bingöl et al., 1975. Duru et al., 2004,
Meta-ultramafic rocks (meta-ophiolite)	Rocks: meta-dunite, meta-serpentinite, amphibolite and meta-gabbro lithologies.	Duru et al., 2004. Erdoğan et al., 2013,
Çamlıca Metamorphics	Meta-sedimentary rocks. Mica schist, phyllite and quartz mica schist.	Okay et al., 1990,
2. Karakaya complex and Jurassic-Cretaceous Sediments		
Jurassic-Cretaceous sediments	Sandstone, limestone and cherty limestone.	Altınlı and Saner, 1971,
Çetmi ophiolite melange	Spilitized basic volcanic rocks, serpentinites and limestone blocks with mudstones.	Okay et al., 1990,
3. Cenozoic magmatic rocks		
Plutonic rocks	a) Karabiga pluton: granite, monzogranite and syeno-granite. b) Kuşçayırı granite: granite and granodiorite. c) Evciler pluton: granite, granodiorite and monzonite. d) Kestanbol pluton: quartz monzonite and granite. Small amounts of quartz syenite and syenite with syenite porphyry.	Yılmaz et al., 2001. Delaloye and Bingöl, 2000. Karacık, 1995.
Volcanic and subvolcanic rocks	Calc-alkali volcanism in Eocene to late-Miocene. Alkali volcanism in late-Miocene to Pliocene. Rocks: andesite, trachy-andesite, basaltic andesite, dacite, rhyolite.	Genç, 1998.
4. Cenozoic sedimentary rocks		
Maastrichtian-Early Eocene	Only present in limited areas in the northern section of the Biga Peninsula.	
Middle Eocene-Oligocene	Generally uplifted and eroded, only observed in very limited areas.	Siyako et al., 1989.
Miocene	Bituminous shale and lignite formations occur.	
Plio-Quaternary	Fluvial pebblestone, sandstone lithologies and lacustrine limestones were deposited.	

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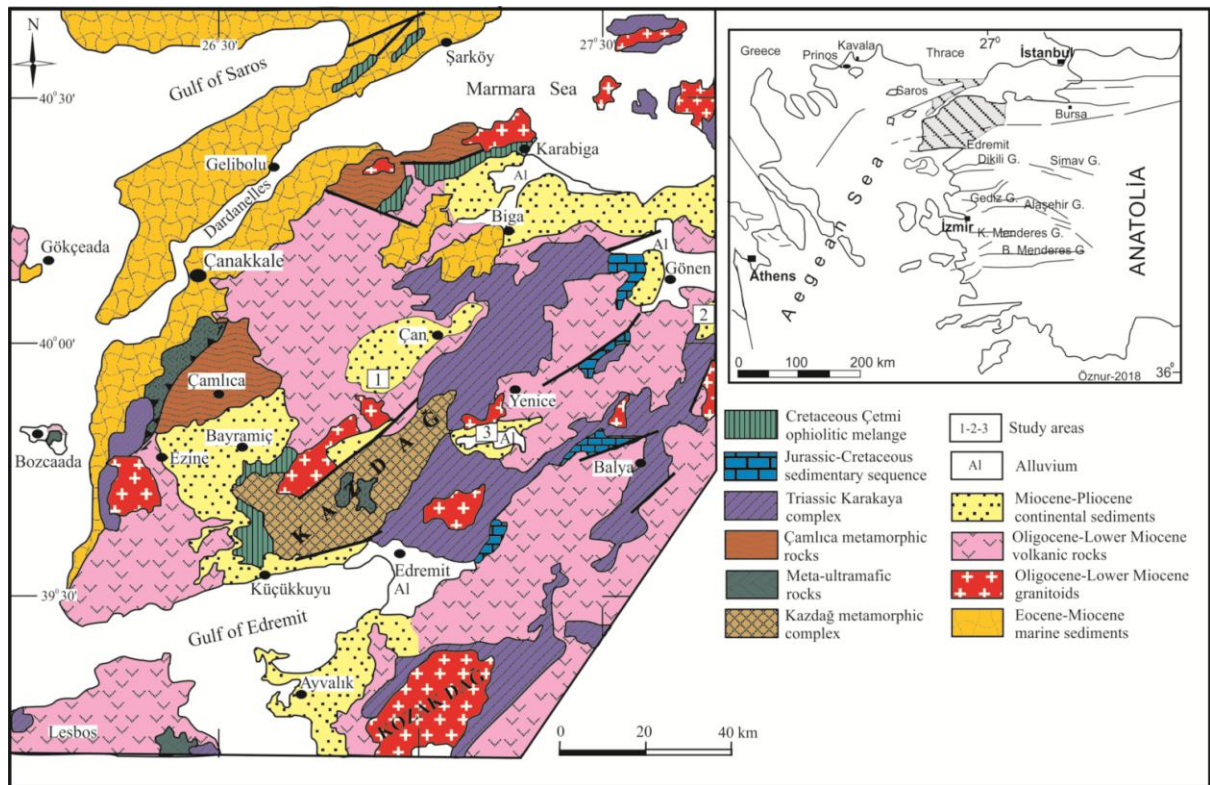
525 Table 2. Characterization of sediment sample

Parameters	Sediment	Test Method
pH	3.35	
ORP (mV)	35	ASTM D1293
EC ($\mu\text{S cm}^{-1}$)	2427	
Salinity (% _o , NaCl equivalent)	1.15	
Water content (% _o , wt.)	42	ASTM D2216
Specific gravity (g cm^{-3})*	2.35	ASTM D854
Organic content (%)*	17	ASTM D2974
Permeability (cm s^{-1})	$6.45 \cdot 10^{-6}$	ASTM D2434
Grain size		ASTM D422
Gravel (%)	0	
Sand (%)	12	
Silt+clay (%)	88	
Metal content*		
Al (%)	6.67	
Fe (%)	5.68	USEPA Method 3050
As ($\text{mg} \cdot \text{L}^{-1}$)	1030	
Mn ($\text{mg} \cdot \text{L}^{-1}$)	751	

526 *Dry basis

527

528 Figure 1

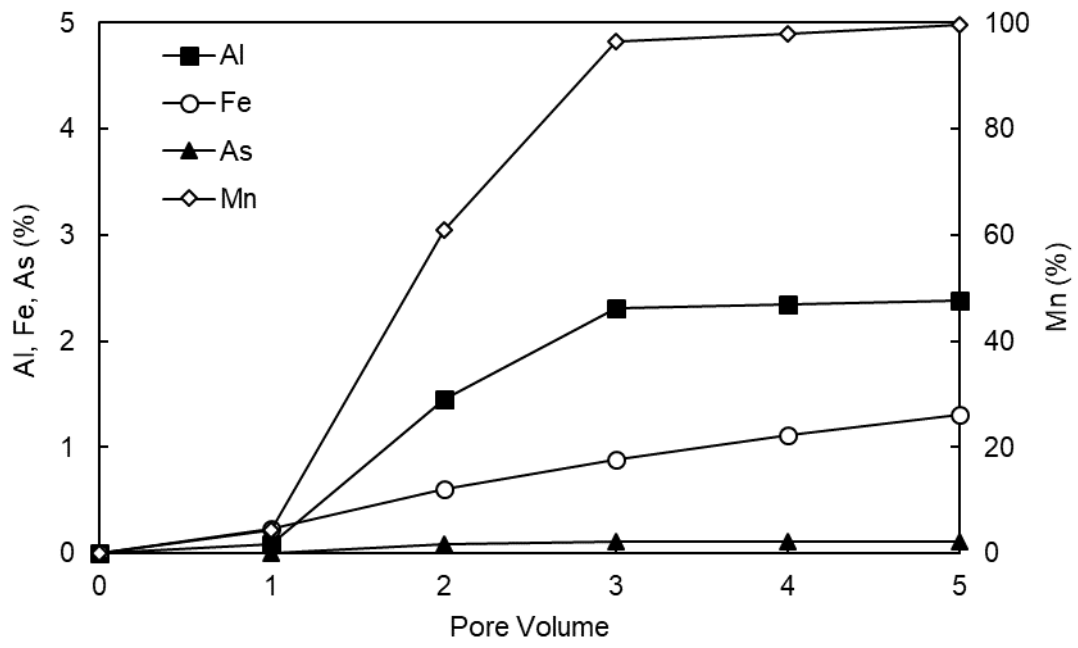


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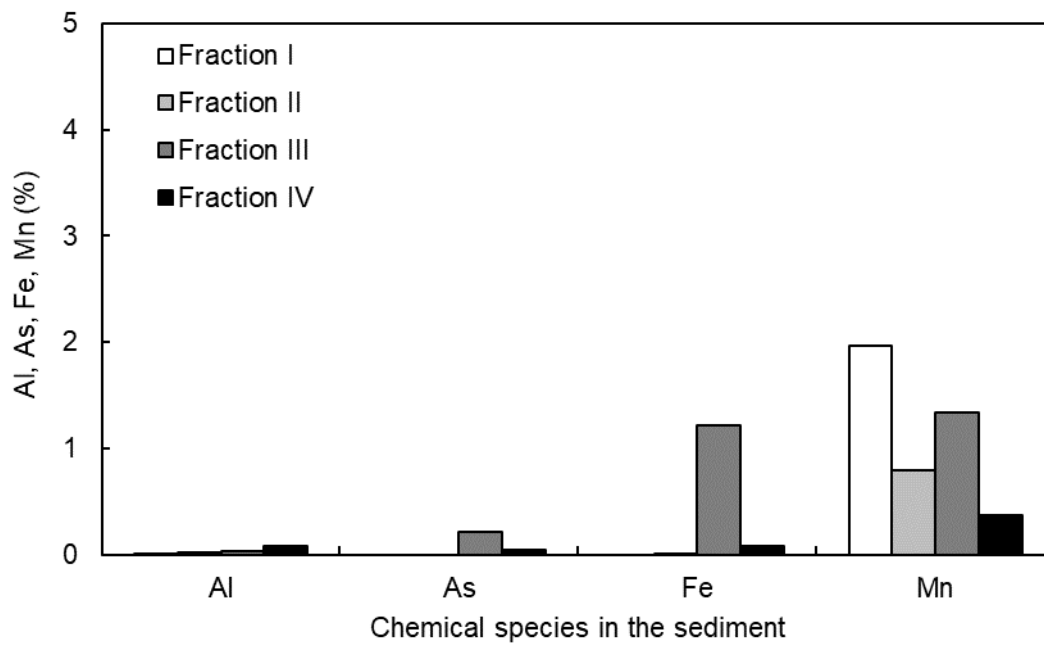
532 Figure 2



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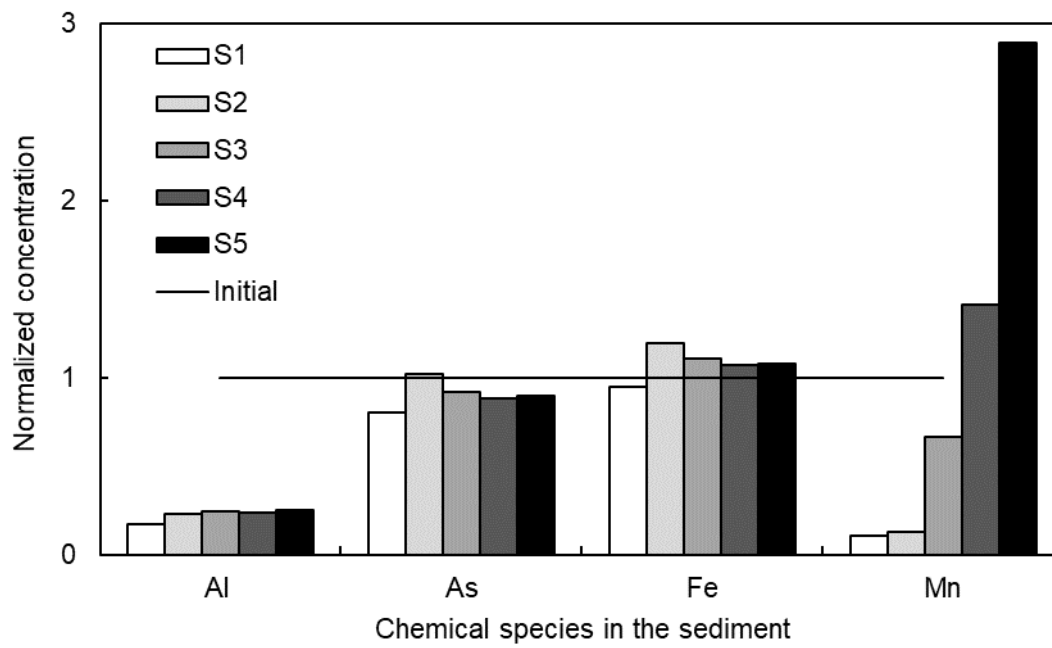
535 Figure 3



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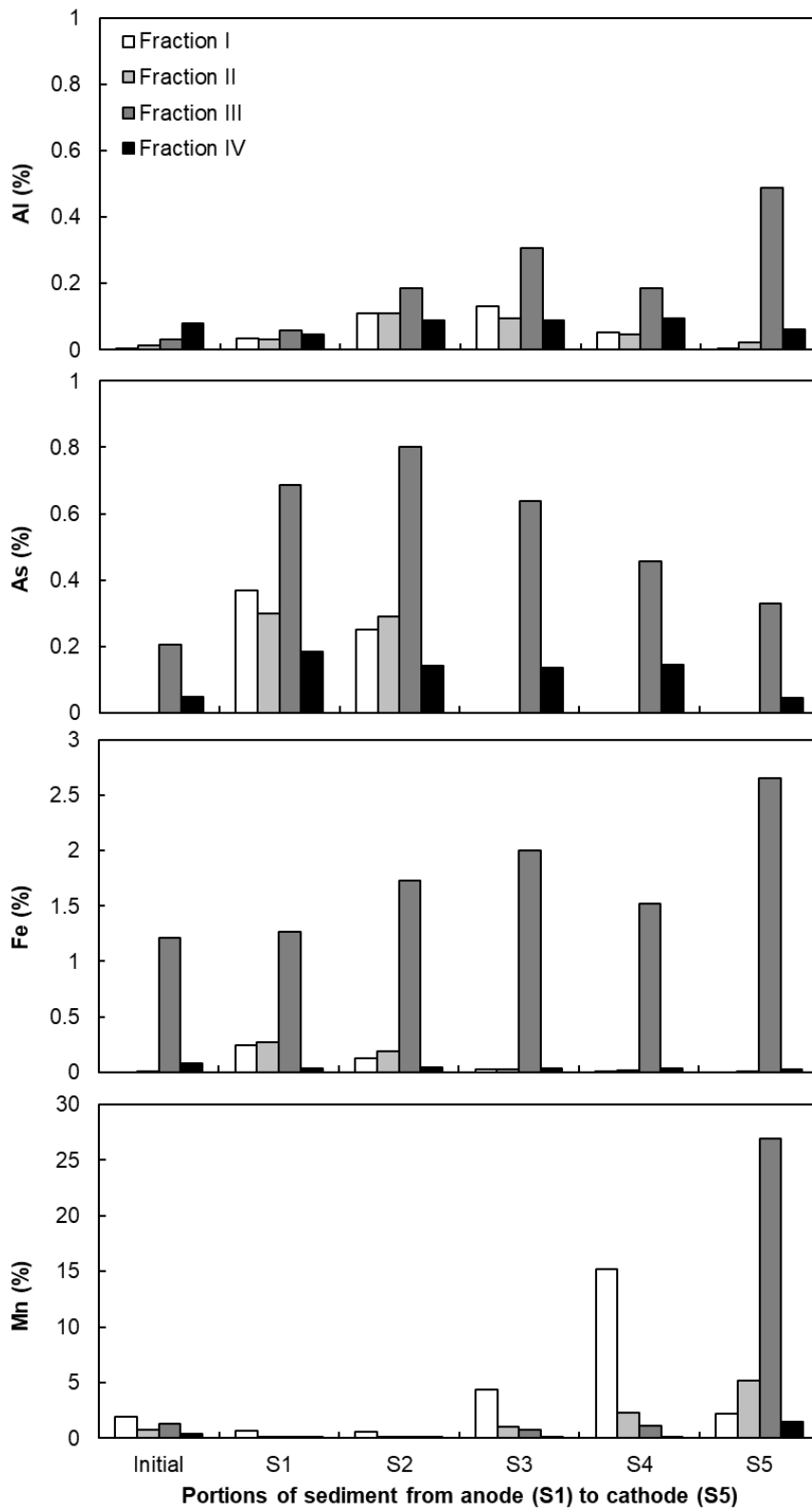
538 Figure 4



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541 Figure 5



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544 FIGURE CAPTIONS

545 Fig. 1. Location and Geological map of the Biga peninsula (NW Turkey) and
546 surrounding area (Simplified from Okay et al., 1990; Duru et al., 2004; MTA, 2001).

547 Fig. 2. Column extraction tests of Al, Fe, As and Mn from the sediment with DI water
548 (Pore volume is the volume of effluent referred to the void volume of the sediment
549 specimen).

550 Fig. 3. Fractionation of Al, As, Fe, and Mn in sediment specimen with the Tessier et al.
551 (1979) method.

552 Fig. 4. Arsenic and metal normalized concentrations (C/C_0) in the sediment specimen
553 after the electrokinetic treatment. Portions of sediment specimen were labeled from S1
554 (the closest to anode) to S5 (the closest to cathode).

555 Fig. 5. Fractionation of Al, As, Fe, and Mn in sediment specimen after the electrokinetic
556 treatment. Portions of sediment specimen were labeled from S1 (the closest to anode) to
557 S5 (the closest to cathode).

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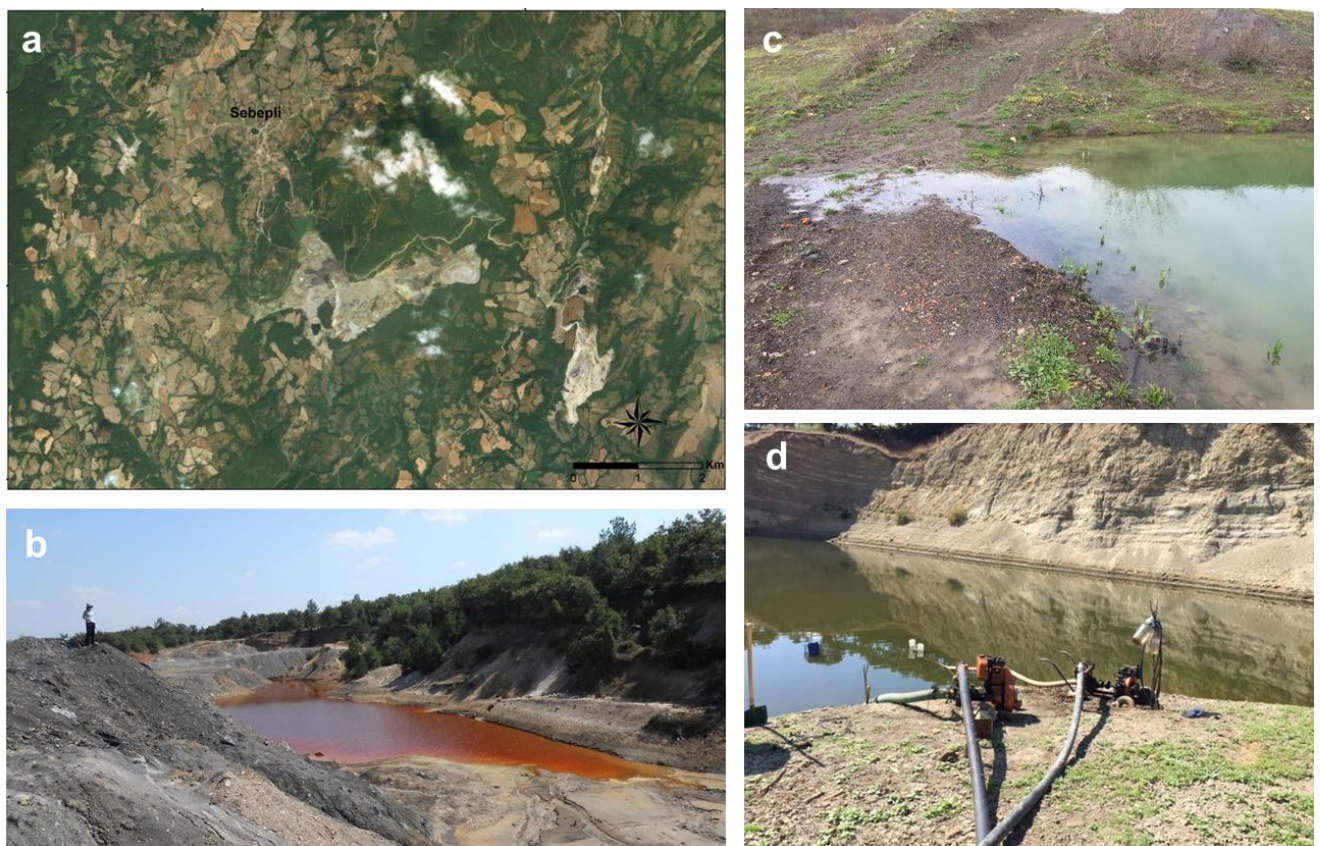
559 SUPPLEMENTARY MATERIAL

560 Fig. SM-1. Abandoned mines and derelict mine ponds in the Biga Peninsula. a)
561 Abandoned mine close to Sebepli village (Gönen). b) Acidic lake and floor sediments in
562 Çan-Çanakkale. c) Overflow of the mine pond to a local river (Yenice-Gönen). d) Use
563 of water pond for land irrigation (Yenice-Gönen).

564 Fig. SM-2. Physicochemical characteristics of the sediment after the electrokinetic
565 treatment. Portions of sediment specimen were labeled from S1 (the closest to anode) to
566 S5 (the closest to cathode).

567

568 Figure SM-1



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