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1 Clay minerals of Pliocene deposits and their potential use for the purification of polluted
2 wastewater in the Sohag area, Egypt.

3

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14

15 **Abstract**

16 In our study we investigated the clay fraction composition of Pliocene clay deposits in the
17 Sohag area, Egypt. Our goal was to obtain insights into the origin of the deposits, and to
18 assess their potential for use in inexpensive wastewater purification. Rationale for the latter
19 was that in Egypt both industrial wastewater and irrigation water are often polluted with
20 heavy metals (HMs), the load of which can be significantly reduced using the Pliocene clay.
21 We combined physico-chemical analyses with detailed X-ray diffraction (XRD)
22 mineralogical investigations and Specific Surface Area (SSA) measurements of samples from
23 16 locations in four areas containing Pliocene clay deposits. The grain size distribution of the
24 studied samples was dominated by silt (75-89 %) with lower quantities of clay (6-20 %) and
25 sand (2-15%). Neither grain size distribution nor the distribution of individual clay minerals
26 varied between the tested samples, suggesting they all originate from a single source area.
27 The effect of differential cation saturation (K^+ and Mg^{2+}) and differential heat treatments

28 (25°C, 300°C, and 550°C) on the XRD patterns of oriented aggregates of the clay-sized
29 fractions revealed 4 different clay mineral groups in the tested samples. The relative
30 abundances of the clay minerals were semi-quantified and revealed a dominance of smectite
31 (69-91% on average) with relatively low contents of kaolinite (9-29% on average) and minor
32 amounts of illite (1-7% on average) and chlorite (0- < 1%). This mineral assemblage
33 suggests chemical weathering and indicates warm climatic conditions of the source area
34 during the period of deposition. The higher CEC values of the Pliocene clay deposits (32.3-
35 65.4 cmol/kg also pointed to the occurrence of smectite in the soils. The SSA of the Pliocene
36 clay fractions (26.25-128.97 m²/g) correlated well with their exchangeable cation contents
37 (K⁺ and Ca²⁺, R² = 0.96 and 1.0 respectively) and micropore volumes (R² = 1.0). Micropore
38 volumes and SSA of the studied samples increased with the size of the exchanged cation: K⁺
39 > Ca²⁺ > Na⁺. The mineralogical composition suggests that Pliocene smectite-rich deposits in
40 the studied area have great potential to be used as raw material for inexpensive, local
41 purification of wastewater polluted with HMs.

42

43 **1. Introduction**

44

45 Clay materials (< 2 µm size) are an important, abundant and inexpensive natural resource
46 for many applications such as the process industries, agriculture, environmental remediation
47 and construction (Pedro, 1994; Murray, 1999; Murray, 2000; Sanfeliu et al., 2002; Gomes &
48 Silva, 2007). The main properties that make clay materials such an important resource are,
49 *inter alia*, their high specific surface area, adsorptive capacity, rheological properties,
50 chemical inertness and, depending on their chemical composition, absence of toxicity (Dixon
51 and Weed, 1989; Lin et al., 2002; Carretero et al., 2006).

52 Given their high adsorptive capacity, a very interesting application of clay materials is as
53 a low cost agent to remove heavy metals (HMs) from wastewaters, particularly in developing
54 countries such as Egypt, where more sophisticated techniques are often not widely available
55 (e.g., Srivastava et al., 1989; Ikhsan et al., 2005; Gu, et al., 2010; Refaey et al., 2014). In the
56 Egyptian Sohag area a large reserve of Pliocene clay deposits is present. In a recent pilot
57 study we showed that clay materials from several locations in this area offer great potential
58 for removal of HMs from polluted waters, both in the presence and absence of naturally-
59 occurring organic matter that might interfere with such an application (Refaey et al., 2014). A
60 next step towards application of clay materials from the Sohag area for wastewater treatment
61 is a thorough characterization of their clay mineral assemblage.

62 The clay mineral assemblage determines properties related to the retention of HMs, such
63 as cation exchange capacity (CEC) and specific surface area (SSA), but also properties like
64 swelling ability and plasticity that are crucial for the technical applicability of the clays in
65 wastewater cleanup. With respect to CEC, the clay mineral composition determines the
66 amount of permanent negative charge, and contributes to a larger or smaller extent to the
67 amount of variable charged sites present (McBride 1994). For instance, kaolins have only a
68 modest amount of permanent negative charge due to limited isomorphous substitution and only
69 a modest amount of residual charge at their edges and from exposed basal hydroxyls (Grim
70 1968; Bolland et al., 1976; Murray, 1999). On the other hand, due to extensive isomorphous
71 substitution, smectites and vermiculites have high permanent negative charge and thus are
72 responsible for most of the high CECs generally found in soils (Aparicio et al., 2010). The
73 SSA is mainly influenced by the grain size distribution, CEC, geotechnical characteristics and
74 types and amounts of clay minerals and is considered one of the most important parameters
75 that quantify interaction processes at the liquid-solid interface (e.g., Yukselen-Aksoy &
76 Kaya, 2010; Heister, 2014).

77 Clay mineral distribution in parent material of marine origin, like in the Sohag region in
78 Egypt, generally reflects varying climatic zones in the clastic source areas in addition to
79 means of transport (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969). It therefore has
80 also been used for paleoclimatic reconstructions (Singer, 1984; Chamley, 1989).
81 Characterization of Sohag region clay minerals therefore not only is important to assess their
82 technical applicability in local wastewater treatment, but will also shed light on the climatic
83 and environmental records of the sediments, yielding valuable insights in the history and
84 genesis of the region (El-Shahat et al., 1997).

85 Therefore, the main objectives of this study were: (i) discriminating the Pliocene
86 deposits from several locations in the Egyptian Sohag area on the basis of their textural and
87 mineralogical attributes, (ii) identifying and characterizing the different clay mineral types in
88 the context of their application in local wastewater treatment, and (iii) shedding light on the
89 paleoclimatic conditions that prevailed during formation of the sediments and their influence
90 on the sediment's composition. To this end, X-ray diffraction (XRD) analyses were applied
91 on air-dried, heated and glycerol-saturated oriented preparations with prior saturation with K^+
92 and Mg^{2+} .

93

94 **2. Materials and methods**

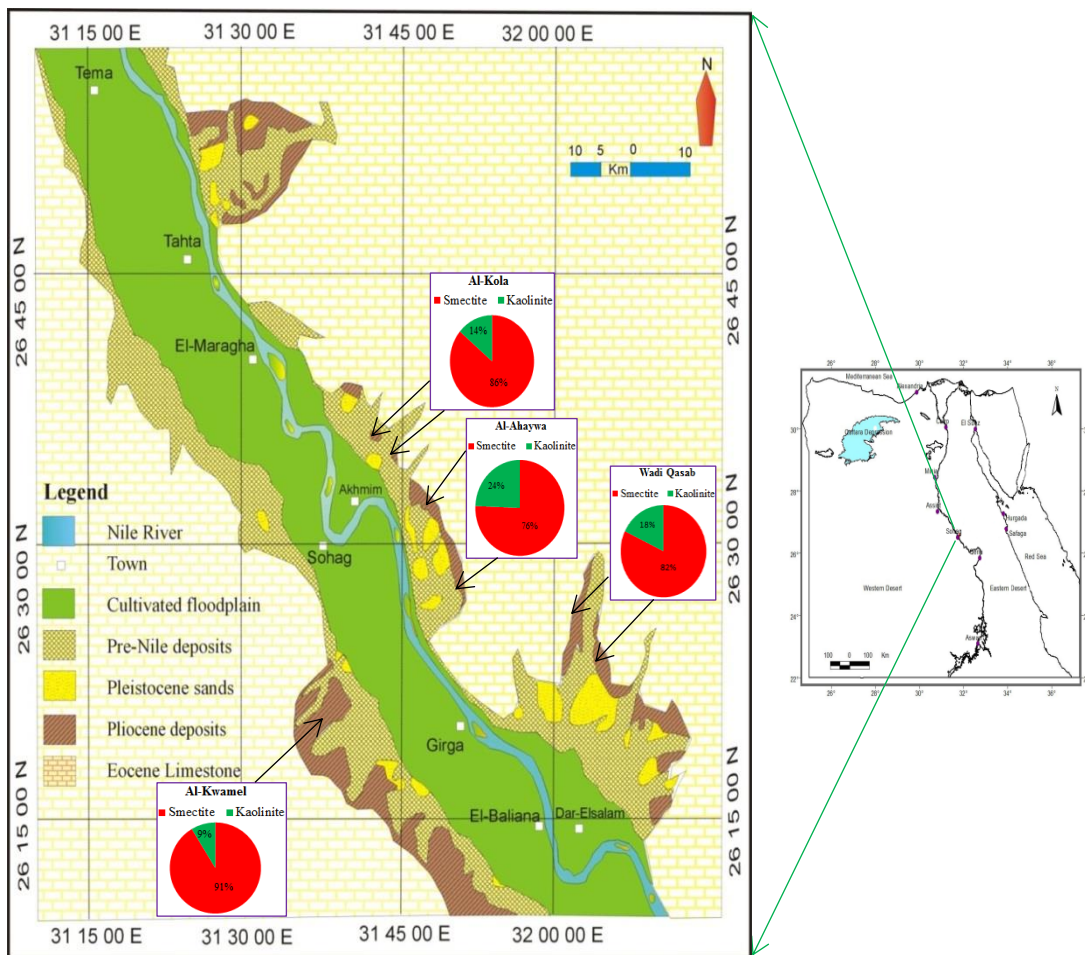
95

96 *2.1. Area of study and sedimentary successions*

97

98 The study area is presented in Fig. 1 and is referred to as the Sohag area given the
99 central location of this town in the study area. The area is bordered from both the east and
100 west by a higher relief Eocene limestone plateau. Fig. 1 presents a simplified geological map
101 of the area.

102 The Sohag area is located at East and West Sohag governorate, Egypt, in the middle
 103 part of the Nile Valley that is situated south of Cairo (460 km), represented by the Nile basin
 104 stretch extending between 26° 19' 87" to 26° 33' 08" N lat; 31° 39' 04" to 32° 03' 62" E
 105 long. The study area comprises various sediments ranging in age from Lower Eocene to
 106 Recent (Said, 1990; Omer, 1996; Omer and Issawi, 1998; Hassan et al., 2005) as shown in
 107 Fig. 1. The studied samples were collected from The Muneiha Formation (Pliocene) deposits
 108 that are characterized by their high fine earth fraction and smectite contents.
 109



110
 111 Fig. 1. Simplified geological map of Sohag area (TEGPC and CONOCO 1987) with indication of clay mineral
 112 assemblages at each sampling area.

113

114 The Muneiha Formation forms a single lithostratigraphic unit (Omer, 1996; Omer and
115 Issawi, 1998; Hassan et al., 2005), that is equivalent to the Madmoud Formation of Said
116 (1981). The Muneiha Formation includes estuarine fine clastic sediments formed as a result
117 of the rising and invasion of the Mediterranean Sea through a long gulf extending from Cairo
118 to Aswan in the Pliocene (Issawi et al. 1978; Hassan et al., 2005). This Formation was
119 divided into two main divisions (lower and upper members) based on its deposition
120 environment and facies (Omer, 1996). Fig. 2 represents the deposit. The lower part is
121 composed mainly of bedded to massive dark brown (chocolate) clay to dark grey marine clay
122 with thin interbeds of fine sand and silt (Fig. 2). The upper part is dominated by fluvial
123 sediments consisting of fining upward cycles. The sediments are sloped toward the cultivated
124 flood plain covered with the younger sediments and widespread in both the surface and
125 subsurface in the study area.

126

127 2.2. *Sampling*

128

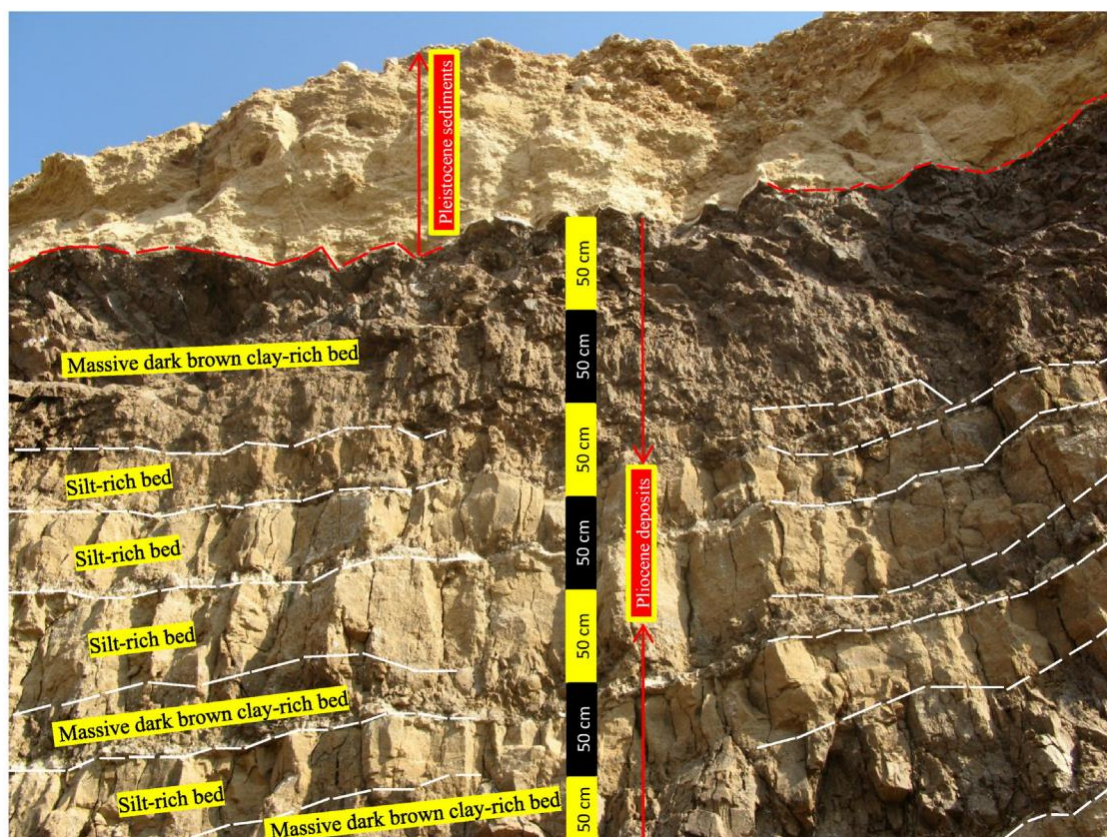
129 Sixteen samples were selected from the larger suite of twenty seven soils sampled from
130 the Muneiha formation in the Egyptian Sohag region.

131 The samples were collected from outcrops of this Pliocene deposit at the east and west
132 bank of the Nile River. The Pliocene clay deposits constitute the main outcrops in the studied
133 area. They lack diagnostic soil horizons and are capped by poorly consolidated sand, gravel,
134 and clay of Quaternary age. The wadi deposits, including the Pliocene deposits, in the Sohag
135 area are infertile and generally classify as Calcaric Fluvisols according to the FAO World
136 Reference Base for Soil Resources 2006 (Jones et al., 2013).

137 Selection of the sixteen samples was based on analyses of grain size distribution, texture
138 and clay mineral composition such that the samples represented a variation in physico-

139 chemical characteristics linked to potential use for large scale application purposes revolving
140 around treatment of wastewater. Specifically, multiple spatially distributed samples were
141 taken from the Al-Kwamel (KW; 5 samples), Al-Kola (KO; 3 samples), Al-Ahaywa (AH; 2
142 samples) and Wadi Qasab (WQ; 6 samples) areas. The samples from KW, KO, AH, and WQ
143 were collected along the surface of vertical exposures, i.e. both artificial and natural outcrops
144 in the field at heights of 1 to up to 10 m (see Fig. 2 for an example). The geographic
145 distribution of the sampling sites is displayed in Fig. 1. The samples were transported from
146 Egypt to The Netherlands in sealed plastic bags and stored at 4°C until analyzed.

147



148

149 Fig. 2. Outcrop field photograph of the Al-Kola area showing an alternation of Pliocene clay-rich beds with thin interbeds of
150 fine sand and silt laminae.

151

152 2.3. Physico-chemical characteristics of the Pliocene clay deposits

153

154 The samples were first air dried, then gently crushed by means of an agate mortar and
155 pestle to pass through a 2-mm sieve. Total carbon (TC) and total nitrogen (TN) contents in
156 the soils were determined with a C/N analyzer (Elementar Vario EL, Hanau, Germany). The
157 total content of Fe-oxyhydroxides was estimated as dithionite-citrate-bicarbonate extractable
158 iron (Fe_d) (AAS, Perkin Elmer, Waltham, Massachusetts, USA) using the method of Mehra
159 and Jackson (1960) and Holmgren (1967). Mn-oxide and short-range-order (oxalate
160 extractable) Fe- and Al- (hydr)oxide (Fe_o and Al_o) contents were measured using the method
161 of Searle and Daly (1977). Field water content was determined by drying soil samples at
162 105°C for 24 h. The soil pH_{H_2O} was also measured (1:2.5 v/v ratio). The CEC of the soils was
163 determined using the method of Hendershot and Duquette (1986). Major cations (Ca^{2+} , Mg^{2+} ,
164 and K^+ , and Na^+) and major anions (Cl^- , SO_4^{2-} , and PO_4^{3-}) were measured using an ICP-OES
165 (Perkin Elmer-Optima 3000XL) and San⁺⁺ Automated Wet Chemistry Analyzer-Continuous
166 Flow Analyzer (CFA), respectively.

167 Before determining the grain size distribution of the studied soils, they were treated with
168 1 M HCl and H_2O_2 (30%) to remove respectively carbonates and organic matter contents.
169 Grain size distributions were determined on the basis of sieving for the coarse component ($>$
170 $150\ \mu\text{m}$) and a SediGraph (model 5100 grain size analyzer) for the fine component ($<$ 150
171 μm) according to Stein (1985) and Jones et al. (1988). Silt and clay fractions ($<$ $63\mu\text{m}$) were
172 separated from the remaining portion by sieving. Then, the clay fraction ($<$ $2\ \mu\text{m}$) was
173 separated using the sedimentation-decantation technique according to Jackson (1969).

174 SSA measurements were performed at the Van 't Hoff Institute for Molecular Sciences,
175 University of Amsterdam, The Netherlands, using CO_2 at 273 K on Thermo Scientific Surfer
176 instrument. CO_2 gas adsorption was used. Given the higher temperatures it employs as
177 opposed to N_2 physisorption and it is considered more suitable for SSA determination of

178 sediments and soil material (e.g., Echeverría et al., 1999; Kwon & Pignatello, 2005;
179 Eusterhues et al., 2011).

180 Four samples (KW-2, KO-2, W-2, and AH-2) were selected for SSA measurement from
181 the soils sampled in the study area; representing one sample for each area. The selection was
182 such that the samples represented a variation in physico-chemical characteristics. The SSA
183 was calculated according to the Dubinin-Radushkevich equation (Dubinin & Radushkevich,
184 1947). Prior to the measurements, the samples were outgassed for at least 24 h at 200 °C in
185 vacuum to remove adsorbed water.

186

187 *2.4. Qualitative and semi-quantitative analysis of clay assemblages using XRD*

188

189 *2.4.1. Sample preparation for XRD analysis*

190

191 The separated clay fraction was divided into two parts; the first one was saturated with
192 K^+ and the second one with Mg^{2+} . Demineralized water and centrifugation were then used
193 (2575 x g) to remove excess salts after saturation (Whittig, 1965). Afterwards, the samples
194 were freeze-dried and kept for mineral identification.

195 To prepare oriented aggregates for XRD analysis about 25 mg from each freeze-dried
196 clay fraction sample was added to 10 ml demineralized water in a 25 ml volume tube and
197 mixed well ultrasonically (5 sec). The mixture was deposited gravimetrically on a porous
198 mounting medium (ceramic tile, 37.2 mm in diameter and 6.2 mm thick) connected to a
199 funnel under vacuum that provided the preferred orientation. After subsequent air-drying, the
200 samples were ready for XRD analysis. For each sample, five X-ray diffractograms were taken;
201 Mg-saturated samples were X-rayed in the air-dried and glycerol solvated states. The K-

202 saturated samples were X-rayed after air drying and heating to 300 and 550 °C for 2 h
203 (Bouchet et al., 1988).

204

205 2.4.2. *XRD analysis*

206

207 XRD analysis was performed at the Van der Waals-Zeeman Institute, University of
208 Amsterdam, The Netherlands, using a Philips (now PANalytical) PW 1830 instrument, with a
209 Philips PW 3710 control unit (Cu K_α radiation with wavelength 1.54056 Å produced at 50
210 mA and 40 kV). Minerals were identified by characteristic reflections as discussed in
211 Brindley and Brown (1980) and Moore and Reynolds (1997). The relative percentages (semi-
212 quantitative) of clay minerals were determined using empirically estimated weighting factors
213 of Biscaye (Biscaye, 1965). The low chlorite and illite contents in studied samples were
214 estimated from the relative peak height (Johns et al., 1954) because they could not to be
215 detected in the glycerol solvated states.

216

217 **3. Results**

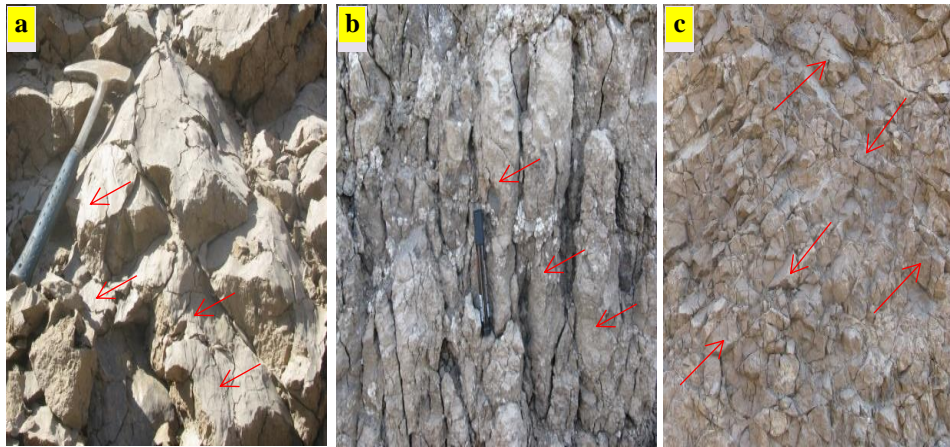
218

219 *3.1. Physico-chemical properties of Pliocene clay deposits*

220

221 Field observations showed that the Pliocene sediments have slickensides and desiccated
222 under formation of deep cracks in a roughly polygonal structure (Fig. 3a; b; c).

223



224

225 Fig. 3. a) Pliocene deposits upon swelling and shrinking in wet and dry conditions display slickenlines on slickensides
 226 (polished and striated) (WQ area), b) deep wide cracks forming wedge-shaped or parallel-sided aggregates (KO area), and c)
 227 polygonal patterns (AH area).

228

229 The studied samples had large CECs ranging from 32.3-65.4 cmol_c/kg (Table 1). The
 230 CEC, water content of air-dried samples and amount of clay fraction were strongly correlated
 231 (both $R^2 = 0.75$). Crystalline iron-oxide contents were small to moderate (3.7-17.6 g kg⁻¹),
 232 while soil organic carbon (SOC) contents were low in all samples (0-5.35 g kg⁻¹; Table 1).
 233 The pH was always slightly basic (Table 1). Na⁺ was the dominant exchangeable cation with
 234 the highest abundance of Na⁺ in sediments sampled from the KW area, while Ca⁺², Mg⁺² and
 235 K⁺ provided minor contributions (Table 1).

236 Table1. Selected physical and chemical properties of soil samples.

Samples	pH	EC	H ₂ O	CEC	SOC	CBD ext.	Oxalate ext.	Major cations				_Major anions_	
		μs cm ⁻¹	%	cmol _c kg ⁻¹		Fe-oxide	MnO ₂	Na ⁺	Ca ⁺²	Mg ⁺²	K ⁺	Cl ⁻¹	SO ⁺⁴
						g kg ⁻¹		g kg ⁻¹				g L ⁻¹	
KW-1	7.58	9.9	8.40	60.48	0.43	17.13	31.54	5.34	0.65	0.23	0.012	7.26	0.17
KW-2	7.53	8.8	8.88	64.23	0.28	14.63	35.08	5.44	0.33	0.11	0.010	6.50	0.45
KW-3	7.80	14.5	6.90	43.21	0.21	17.42	35.90	9.01	1.69	0.26	0.016	8.15	5.92
KW-4	8.21	3.1	4.02	32.28	5.35	3.67	5.64	1.48	0.17	0.02	0.006	2.06	0.47
KW-5	7.81	5.9	7.58	51.38	0.36	5.12	3.59	2.77	0.81	0.09	0.011	3.11	2.85
KO-1	7.77	3.3	8.43	56.72	0.00	17.64	23.30	1.22	0.43	0.16	0.014	2.26	0.36
KO-2	7.61	5.0	10.36	65.36	1.72	9.69	13.05	2.09	0.68	0.21	0.011	3.56	0.17
KO-3	7.20	7.9	9.99	51.26	0.69	14.34	17.06	2.77	2.32	0.60	0.017	5.35	3.47
WQ-1	7.50	5.8	9.44	58.76	1.24	17.46	12.12	2.41	0.97	0.08	0.022	4.18	0.09
WQ-2	7.38	9.3	9.44	62.52	0.00	17.53	33.22	3.60	2.44	0.18	0.026	6.54	0.12
WQ-3	7.61	3.0	7.14	48.08	0.35	8.83	4.74	1.14	0.34	0.08	0.019	2.46	0.10
WQ-4	7.30	4.1	7.27	47.53	0.41	16.05	5.07	1.31	0.74	0.16	0.030	3.38	0.19
WQ-5	7.67	4.1	7.47	50.09	0.00	4.49	70.51	1.28	0.72	0.14	0.032	2.89	0.11
WQ-6	8.05	1.3	8.90	55.40	0.30	11.54	51.66	0.49	0.10	0.05	0.008	1.67	0.43
AH-1	7.73	7.5	7.96	55.36	0.85	10.63	20.96	4.07	0.54	0.18	0.010	3.82	0.05
AH-2	8.07	3.9	8.22	59.07	0.80	9.18	10.75	2.09	0.13	0.05	0.004	3.16	0.15

237 # CBD ext. (Citrate Bicarbonate Dithionite extraction).

238

239 3.2. Grain size distribution

240

241 Table 2 presents the grain size distribution, i.e. percentages of clay, silt and sand in the
 242 various samples. The silt content along the study area did not vary greatly in the studied
 243 samples (Table 2). The silt fraction dominated over the other fractions in all studied samples
 244 (75-89%); the clay fraction varied from 6 to 20% and the sand content fluctuated between 2
 245 and 15% (Table 2). As a result, the grain size distribution of all studied samples classified as
 246 silt.

247 Table 2. Grain size distribution (% of total mass) of the studied samples.

Samples	Depths	Clays	V. F. silt	F. silt	M. silt	C. silt	V. C. silt	V. F. sand	F. sand	C. sand
		<2	2-4	4-8	8-16	16-31	31-63	63-125	125-250	500-1000
		~m µm								
Location 1										
KW-1	5.0	9.2	5.4	7.2	12.2	23.1	32.7	7.2	0.3	2.8
KW-2	3.0	17.6	8.9	12.5	16.6	22.6	17.6	2.6	0.1	1.5
KW-3	2.0	8.0	7.0	12.3	19.7	29.0	21.0	2.3	0.1	0.6
Location 2										
KW-4	4.0	6.3	7.8	12.5	19.1	19.8	22.7	9.1	0.7	2.0
KW-5	3.5	6.7	6.9	10.9	14.8	18.5	26.9	9.4	0.5	5.4
Location 3										
KO-1	3.0	7.2	6.5	9.3	15.8	27.6	27.0	5.5	0.3	0.8
KO-2	2.0	18.2	14.8	17.8	20.2	17.3	8.4	1.1	0.0	2.2
KO-3	1.0	14.7	12.5	17.8	21.2	19.2	12.7	1.3	0.1	0.5
Location 4										
WQ-1	4.0	11.3	10.2	14.2	20.6	22.6	17.6	3.6	0.2	0.0
WQ-2	1.0	14.7	15.0	21.5	24.1	16.5	6.6	0.4	0.1	1.0
Location 5										
WQ-3	4.0	7.2	6.4	8.9	15.9	23.6	28.5	7.2	0.4	2.0
WQ-4	3.0	12.9	9.3	15.1	21.0	23.8	14.4	1.3	0.2	2.1
WQ-5	2.0	14.8	13.0	17.7	19.4	18.5	11.8	2.7	0.3	2.1
Location 6										
WQ-6	2.0	18.5	9.9	14.4	21.2	19.7	13.4	2.2	0.0	0.7
Location 7										
AH-1	5.0	19.8	15.2	16.4	17.3	14.6	11.4	2.5	0.3	2.7
AH-2	1.0	18.3	14.9	15.7	18.5	16.9	10.0	1.8	0.2	3.8

248

249 # V.F. = Very fine; F. = Fine; M. = Medium; C. = Coarse; V.C. = Very coarse.

250

251 3.3. Clay mineral composition

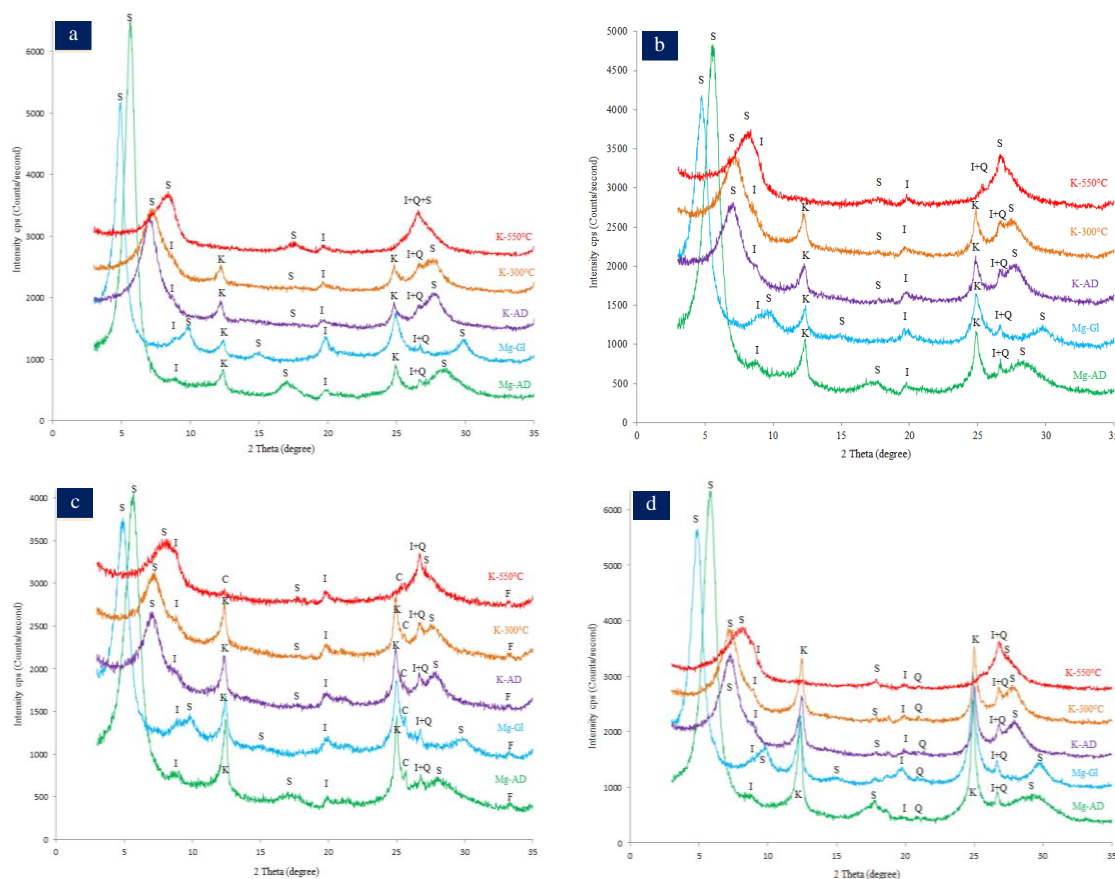
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253 3.3.1. Smectite

254

255 The XRD patterns of Mg- and K-saturated clay fraction patterns confirmed that smectite
 256 is present (Fig. 4). The basal spacing of smectite (001) in Mg-saturated expanded from ~16
 257 Å to ~18 Å after the glycerol solvation treatment. Upon treatment with K⁺, the ~16 Å of
 258 smectite contracted to ~12.5 Å at room temperature (25°C), slightly collapsed to ~12 Å
 259 following heating to 300°C, and highly collapsed to ~11 Å at 550°C (Fig. 4).

260



261

262 Fig. 4. Selected XRD patterns of oriented mounts of the < 2 μm size soil fraction in the KW (a), KO (b), WQ (c),
 263 and AH (d) areas. Lower panels (Green & blue): Mg-saturated slides in air-dried state (Mg-AD) and after glycerol solvation
 264 (Mg-Gl). Upper panels (violet, brown, and red): K-saturated slides in air-dried state (K-AD) after thermal treatment (K-
 265 300°C & K-500°C). S: smectite; K: kaolinite; I: illite; Q: quartz; C: chlorite; F: Fe-oxide

266

267 Second-, third-, and fourth-order basal reflections were identified in the XRD patterns of
 268 the untreated and glycerol solvation treated samples. Only the first-, second-, and third-order
 269 reflections were present in the heated samples (Fig. 4). The absence of reflection in the

270 glycerol solvated samples (Mg-GI-treatments) between 6 and 9°2 θ (Fig. 4), confirm that in all
271 samples smectite was well crystallized and did not contain interlayers of illite (Raigemborn et
272 al., 2014).

273 The correlation between CEC vs. water content ($R^2 = 0.75$) and CEC vs. amount of clay
274 fraction ($R^2 = 0.75$) in the studied samples (Tables 1 and 2) confirms once again the
275 predominance of smectite clays and strongly influences the ability of the smectite-rich
276 sediments to retain water in interlayer sites (e.g., Henry, 1997; Eisenhour & Brown, 2009).

277 Na⁺ was the dominant exchangeable cation in all studied samples (Refaey et al., 2014) and
278 this indicates that the type of smectite is Na-smectite (Weaver, 1956; Murray, 1999).

279 Furthermore, the Na/Ca ratio of tested samples in the KW (3.4-16.5), KO (2.1-3.1), WQ (1.5-
280 4.9), and AH (7.5-16) sites revealed a high expanding capacity of the Pliocene sediments
281 (Karakaya et al., 2011). The alternate swelling and shrinking of expanding smectite clays in
282 the study area resulted in deep cracks, slickensides and wedge-shaped structural elements
283 (Fig. 3a, b) during the dry season (Gray & Nickelsen, 1989; Youssef, 2008; Ismaiel, 2013).
284 The large content of Na⁺ over Ca²⁺ and Mg²⁺ cations in the studied sediments which occupy
285 most of the wadi terraces and part of the wadi floors in the low desert zone of the study area
286 probably was responsible for swelling and cracking in the foundations in the new planning
287 area (Mitchell, 1976; Youssef, 2008).

288

289 3.3.2. *Kaolinite*

290

291 Reflection peaks of kaolinite at ~7.15 Å and ~3.57 Å remained unchanged when the
292 samples were subjected to solvation with glycerol (Mg-saturated) and upon heating to 300 °C
293 but they disappeared upon heating to 550 °C (K-saturated) as a result of the destruction of the

294 structure. Such behavior is characteristic of kaolinite (Moore and Reynolds, 1997; Refaey et
295 al., 2008; Hong et al., 2012; Tsao et al., 2013).

296 Kaolinite in the WQ and AH areas displayed narrow and sharp peaks (Fig. 4c, d),
297 indicating that it was highly crystalline (Brindley and Brown, 1980). Less narrow but well-
298 defined peaks (Fig. 4a, b) were also present at infrequent levels in the KW and KO areas,
299 suggesting a slightly poorer degree of crystallinity (Arslan & Aslan, 2006).

300

301 3.3.3. *Illite and chlorite*

302

303 Illite and chlorite were scarce or absent in most of the studied samples. The presence of
304 illite was confirmed in the current study by reflection peaks at 10.13, 4.53, and 3.33 Å d-
305 spacing, which remained unchanged when the samples were subjected to heating treatments
306 (300 °C and 500 °C). Furthermore, the 3.33 Å (003) reflection of illite was developed with
307 quartz (010). The K⁺ content in all tested soil samples was the lowest among all exchangeable
308 cations, which is in line with the scarcity of illite as a mineral constituent of the clay fractions
309 (Hower and Mowatt, 1966; Inoue and Utada; 1983; Brusewitz, 1986; Velde, 1986; Refaey et
310 al., 2014).

311 Chlorite minerals were detected only in the WQ and AH areas as a very weak peak
312 appeared in the position of the kaolinite peak after heating treatment to 550°C (Fig.4 c). Also,
313 a weak peak was recognized as a shoulder at 3.46 Å that showed no change upon glycerol
314 solvation and heating to 550°C (Fig.4 c).

315

316 3.3.4. Non-clay minerals

317

318 Non-clay minerals such as quartz and hematite were recognized as weak reflection peaks
319 at 4.21 and 2.69 Å d-spacing respectively, indicating that only trace amounts of non-clay
320 minerals were present. To exclude the possibility of the quartz peaks having originated from
321 the ceramic tile itself, we compared X-ray analyses of the tile with and without sample
322 material present. None of the characteristic peaks found for the empty tiles (results not
323 shown) appeared in the analyses when sample material was present.

324

325 *3.4. Qualitative and semi-quantitative description of experimental XRD patterns*

326

327 The intensity of the clay mineral peaks changed notably in the different sampled areas,
328 indicating variations in relative proportions of clay species of the studied samples (Fig. 4). On
329 the one hand, in all studied samples smectite had the highest, sharpest and most symmetrical
330 peaks (001 reflection) indicating predominance of smectite over the other clay minerals in the
331 assemblage. On the other hand, the illite and chlorite mineral groups, as well as the non-clay
332 minerals such as quartz and Fe-oxide (hematite/goethite), were present as weak peaks
333 indicating trace amounts (Fig. 4). There was no indication of the presence of any regularly
334 stratified mixed-layer clay. Therefore, all expandable clay is treated here as highly
335 expandable smectite.

336 The clay mineral assemblages of the Pliocene clay deposits showed an overall similar
337 composition with smectite as the most abundant class, followed by moderate amounts of
338 kaolinite and scarce amounts of illite and chlorite (1-7% and < 1% abundance respectively)
339 (Table 3). Therefore, representative XRD patterns were selected to illustrate clay mineral
340 assemblages with different treatments as shown in Fig. 4. The average of the smectite content
341 as determined by the Biscay method (Biscay, 1965) and the peak intensity methods (Johns et
342 al., 1954) in the KW, KO, WQ, and AH areas was 91, 80, 74, and 69 %, whereas the

343 proportion of kaolinite equaled 9, 18, 24, and 29 %, respectively (Table 3). The smectite
 344 proportional percentages in all studied areas increased in the order KW > KO > WQ > AH.

345

346 Table 3. Relative clay mineral abundance in the clay fraction of sediment samples based on the peak height
 347 (method according to Johns et al., (1954) and Biscay (1965)).

348

Method	Clay fraction mg g ⁻¹	Peak height method (Johns et al., 1954)				Biscay's method (1965)							
		Smectite Rel. %	Smectite mg g ⁻¹	Kaolinite Rel. %	Kaolinite mg g ⁻¹	Illite Rel. %	Illite mg g ⁻¹	Chlorite Rel. %	Chlorite mg g ⁻¹	Smectite Wt. %	Smectite mg g ⁻¹	Kaolinite Wt. %	Kaolinite mg g ⁻¹
KW-1	92	94	86	4	4	2	2	-	-	89	82	11	10
KW-2	176	87	153	10	18	3	5	-	-	90	158	10	18
KW-3	80	85	68	12	10	3	2	-	-	94	75	6	5
KW-4	63	93	59	7	4	1	1	-	-	94	59	6	4
KW-5	67	89	60	10	7	2	1	-	-	90	60	10	7
KO-1	72	77	55	18	13	5	4	-	-	86	62	14	10
KO-2	182	72	131	22	40	6	11	-	-	87	158	13	24
KO-3	147	71	105	24	35	5	7	-	-	85	125	15	22
WQ-1	113	68	77	25	28	7	8	-	-	84	95	16	18
WQ-2	147	62	91	35	52	3	4	-	-	82	121	18	27
WQ-3	72	68	49	28	20	4	3	-	-	84	61	16	12
WQ-4	129	59	76	35	45	5	6	<1	-	81	104	19	25
WQ-5	148	66	98	30	44	4	6	<1	-	81	120	19	28
WQ-6	185	67	124	29	54	4	7	<1	-	81	150	19	35
AH-1	198	60	119	38	75	2	4	<1	-	75	148	25	49
AH-2	183	66	121	30	55	4	7	<1	-	76	139	24	44

349

350 # Rel. % = relatively peak height % of each clay mineral; Wt. % = relative weight percentages of each clay mineral.

351

352 3.5. The SSA of the clay fraction

353

354 The SSAs in the representative samples of KW-2, KO-2, W-2, and AH-2 were 34.0, 47.8,
 355 129.0, and 26.2 m²/g respectively, whereas the micropore volumes were 6.02, 8.48, 22.86 and
 356 4.65 cm³/g respectively. The results show SSA to be related to the type of exchangeable
 357 cations, in the following order: K⁺ > Ca²⁺ > Na⁺. In all samples, strong correlations were
 358 observed of the SSA with the amount of K⁺ (R² = 0.96), Ca²⁺ (R² = 1.0), and micropore
 359 volumes (R²=1.0).

360

361 4. Discussion

362

363 4.1. Origin and genesis of clay minerals

364

365 The grain size distribution and clay mineral assemblage in the Sohag area can give an
366 important first idea about the palaeoclimate conditions and weathering processes at the source
367 area (Velde & Meunier 2008; Agha et al., 2013). The fact that the grain size distribution of
368 the studied samples exhibited no large variation in sand, silt, and clay fraction contents nor
369 distribution of individual clay minerals suggests that the sediments derived from one source
370 area. Moreover, the high amounts of silt in comparison to sand in all studied samples (Table
371 2) suggest that the sediments were deposited from suspension and were formed under
372 uniform conditions of slow moving water (Ghandour et al., 2004).

373 During the Pliocene, East Africa was characterized by seasonal, arid and warm
374 environments (Jacobs et al., 1999). The Late Pliocene climate, specifically in Egypt, was arid
375 to semi-arid with seasonal runoff that resulted in a prevalence of grasslands (e.g., Griffin,
376 2002; Swezey, 2009; Talbot & Williams, 2009; Agha et al., 2013). A study by El-Shahat et
377 al. (1997) of Pliocene sediment from the North western desert, Egypt, indicates an initial
378 provenance of metamorphic and acidic igneous rocks from the Red Sea highlands. The
379 weathered regolith of the Red Sea basement rocks must have been eroded by several
380 tributaries that fed a master stream (Paleo-Nile) during the late Pliocene pluvial (Said, 1981;
381 El-Shahat et al., 1997). The genesis of smectite is favored by dry seasons alternating with less
382 pronounced wet seasons (Singer, 1984), poorly drained environments (Schaeztl & Anderson,
383 2005) as well as low-lying topography such as in marine environments (Odoma et al., 2013).
384 All these features, in particular the dominance of smectite, also indicative of chemical
385 weathering (Raigemborn et al., 2014), are present in the study area. This suggests the
386 Pliocene deposits in the Sohag region were deposited in a marine environment under arid to
387 semi-arid climatic conditions (Salman et al., 2013), in particular in a warm climate with
388 alternating pronounced dry and less pronounced wet seasons (Lewis & Berry, 1988;

389 Ghandour et al., 2004; Ehrmann, et al., 2007). In general, the presence of abundant smectite
390 in the studied area is generally linked to a transgression of the sea in the Pliocene (Tantawy et
391 al., 2001).

392 In addition, the presence of kaolinite as second abundant clay mineral is indicative of
393 chemical weathering of acidic igneous and metamorphic rocks or their detrital weathering
394 products under tropical to subtropical humid climatic conditions (Hendriks, 1985; Marzouk,
395 1985; Chamley, 1989; Refaey et al., 2008). The lower abundance of kaolinite relative to
396 smectite in the present study, especially in the KW area (West bank of Nile River; Fig. 1),
397 situated at lower altitude than the other sampling sites (East bank of Nile River), further
398 confirms the earlier mentioned deposition from suspension as a primary sedimentation
399 mechanism. Kaolinite tends to concentrate in relatively near-shore shallow water settings, in
400 line with its tendency to flocculate as coarser grains than smectite that tends to settle as finer
401 particles in deeper offshore settings (Raucsik & Merenyi, 2000; Thiry, 2000).

402 The absence of mixed layer minerals (Illite-smectite) implies that the origin of clay
403 minerals in the Pliocene deposits is of detrital origin where there is no evidence for the
404 influence of burial diagenesis which lead to conversion of smectite to illite (Hoffman &
405 Hower, 1979; Chamley, 1989; Ghandour et al., 2004). Furthermore, it is implausible that the
406 clay mineral assemblages in the studied area originated from deep burial diagenetic alteration
407 due to the lower overburden thicknesses in the studied area (Agha et al., 2013). Nor was any
408 evidence for hydrothermal alteration observed during field sampling.

409

410 *4.2. Implications for HM retention*

411

412 It is well known that smectites have higher CEC values than kaolinites (e.g., Babel &
413 Kurniawan, 2003; Aparicio et al., 2010; Hong et al., 2012). In the KW and KO areas, soil

414 KW-2 and soil KO-2 had the highest CEC values in line with their having the largest clay
415 fraction and highest proportion of smectite compared to kaolinite (Table 1, 2). However, in
416 the WQ and AH areas, soil WQ-2 and soil AH-2 had the highest CEC values (Table 1) in
417 spite of the fact that they did not have the largest absolute clay content of the samples from
418 the area (Table 2). Therefore, in the KW and KO areas, in contrast to the WQ and AH areas,
419 it is the clay mineralogical composition rather than the absolute amount of clay that
420 determined the CEC. This observation is in line with the results from other studies and is
421 linked to the previously mentioned large difference in CEC between smectites and kaolins,
422 which in soils with appreciable kaolinite contents overrides absolute amounts of clay
423 minerals as dominant factor (e.g., Rice et al., 1985; Youssef, 2008; Parfitta et al., 2008;
424 Usman, 2008). As a result of these differences in CEC, although our previous study showed
425 the capacity for HM (Cu, Ni and Zn) adsorption was high in all soils, a higher affinity was
426 found in the soils from the KW and KO than from the WQ and AH areas (Refaey et al.,
427 2014).

428 The measured SSA values (26.25-128.97 m²/g) of the Pliocene clay fraction all fell
429 within the normal range (33-130 m²/g) for pure Na⁺, K⁺, Ca²⁺, and Mg²⁺-smectite as
430 determined by gas adsorption (Volzone & Ortiga, 2004; Kaufhold et al., 2010). Compared
431 with the KW-2, KO-2, and AH-2 samples, the WQ-2 sample showed a significantly higher
432 SSA and micropores volume in line with its higher K⁺ and Ca²⁺ contents (Volzone & Ortiga,
433 2004, Ayari, et al., 2007). This can be explained by the fact that the ionic radius of the
434 exchangeable cations has a strong effect on the CO₂ gas adsorption and consequently on the
435 value of SSA in the interlayer positions of this sample (Rutherford et al., 1997; Volzone &
436 Ortiga, 2004). Also in line with previous findings, the measured SSAs and micropore
437 volumes of our samples both decreased in the following sequence: K-clay > Ca-clay >> Na-
438 clay (e.g., Rutherford et al. 1997; Volzone & Ortiga, 2004; Afsin et al., 2009). The large

439 primary surfaces of the investigated clays explain the previously observed large adsorption
440 capacity of the deposits in the study area for the Cu, Ni, and Zn (Refaey et al., 2014).

441

442 *4.3. Application in the region*

443

444 Pliocene smectite-rich deposits in the studied area can be used as a potential raw
445 material for purification of wastewater from toxic HMs because of their very fine particle size
446 and physical and chemical properties, including SSA, that are related to their clay
447 mineralogical composition. Particular for the Sohag region, discharge of large amounts of
448 wastewater (sewage) used as irrigation water for wood production as well as the use of high
449 amounts of fertilizers in new reclamation areas causes infiltration and accumulation of many
450 pollutants to ground water reservoirs, including HMs (Ayman & Mohamed, 2011). The
451 Pliocene clay deposits in the study area might be used to reduce the load of HMs as well as
452 organic pollutants from such sources. Furthermore, crude water purification using Pliocene
453 clay deposits may extend the applicability of the treated water from wood production alone to
454 include the irrigation of crops (Rashed & Soltan, 2002).

455 In addition to potential use in regional wastewater (pre)treatment, the studied Pliocene
456 deposits could be utilized as liners (barrier) in landfills to control the seepage of HM
457 containing leachate into the surrounding environment (Abollino et al., 2003; Talaat et al.,
458 2011), a particular problem in the desert areas of the Sohag region. The suitability of soil
459 material as liners relates to its particle size distribution, Atterberg limits, swelling potential,
460 CEC and hydraulic conductivity (Taha & Kabir, 2005). Specifically for landfill liners,
461 preferred value ranges for such parameters that have been specified in the literature include:
462 percentage of clay ($< 2\mu\text{m}$) ≥ 20 , percentage of fines ($< 75\ \mu\text{m}$) $\geq 50\%$, CEC $\geq 10\ \text{meq}/100\text{g}$,
463 plasticity index (PI) $\geq 12\%$, activity ≥ 0.3 (Rowe et al., 1995; Daniel 1998; Taha & Kabir,

2005). The studied Pliocene clay deposits from the Sohag area contain clay percentages between 8-20% and percentages of fines between 81-98% (Table 1) . In particular the more clay rich samples (i.e. locations KO, WQ and AH) thereby come close to the mentioned preferred values with respect to clay percentages, while always exceeding the threshold values for the percentage of fines. Moreover, a study by Youssef (2008) of the Pliocene deposits in the studied area revealed that these deposits had the following Atterberg limits: liquid limit (LL)=44-62%, plastic limit (PL)=26-38%, plasticity index (PI)=14-36% and activity (AC)=0.41-0.72. These index properties fall within the mentioned preferred value range and are indicative of a high shrinkage limit that will result in little volume change of the material when used as landfill liners (Taha & Kabir, 2005). Note that the high AC value of the studied Pliocene deposits is indicative of the low hydraulic conductivity as well as of the high SSA of the clay fraction (Benson et al., 1994; Taha & Kabir, 2005). In addition, the high CEC and SSA values of Pliocene deposits will result in a greater amount of inorganic contaminants being removed from the leachate when used as liner or in water treatment (Kayabali 1997; Taha & Kabir, 2005). Altogether this makes that the studied clay deposits, in particular the ones with the higher clay percentages, seem well suited for regional application as cheap landfill lining . Our present study can serve as a foundation on which to build further explorations into such regional applications.

In general, the present work supports the potential of the studied sediments as a natural and inexpensive material for removing toxic HMs that was tentatively established in our previous study (Refaey et al., 2014), and established the underlying mechanisms of such applications. Specifically, Originally, we recommended materials from the KW area for treatment of wastewater rich in HMs such as Zn and Ni, as they showed a high affinity for these materials. On the other hand, we proposed clay-rich materials from the KO, WQ and AH areas to be most effective in the treatment of wastewater rich only in Cu (Refaey et al.,

489 2014) which is known to form strong inner-sphere complexes with surface of Fe-
490 (hydro)oxides in sediments even when the smectite content is less. However, the new
491 information obtained from the present study shows that, given the significantly higher SSA
492 and microporosity of the WQ-2 sample, material from this area warrants extra research
493 attention to be used as starting point for further exploration in waste water treatment, not only
494 for HM removal but possibly also for toxic gas adsorption (Volzone, 2007).

495

496 5. Conclusions

497

498 The grain size distribution of the studied samples was dominated by silts (75-89 %) with
499 lower quantities of clays (6 -20 %) and sands (2-15%). XRD analysis demonstrated that the
500 clay mineral composition of the Pliocene clay deposits studied was composed almost
501 exclusively of smectites and kaolinite, with the former always being the most abundant class
502 of clay minerals. The presence of a large amount of smectite in association with a low
503 quantity of kaolinite minerals in our study suggests an origin from chemical weathering
504 conditions under warm and semi-arid conditions. Furthermore, the absence of mixed layer
505 clays confirmed that the tested sediments were derived from transported weathered materials.
506 The physico-chemical properties of the studied sediments as well as the type and amount of
507 smectites indicate that they have a high capacity to immobilize large amount of dissolved
508 HMs. The present study has shown that there are strong relationships between the SSA and
509 soil chemical properties such as exchangeable cations where K^+ and Ca^{2+} -rich clay fraction
510 tends to have higher SSA and micropore volume values. This makes the studied sediments
511 potentially useful in high-value-added markets, e.g., as environmentally friendly and
512 inexpensive raw material for waste water treatment. To further examine such application,
513 additional research should focus on unraveling the mechanisms of such interactions,

514 specifically in quasi-realistic operational and field settings such as in column experiments.
515 Particularly interesting is the exploration of the material from the WQ area giving its
516 significantly higher SSA and microporosity than material from the other areas.

517

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519

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527

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