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New methodological approach for deep penetrating geochemistry and environmental studies part 2: field determination of Co(II) /Ni(II) and Pb(II) /Zn(II) of on-site soil extractions by electrochemical stripping techniques

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1 **New methodological approach for deep penetrating**
2 **geochemistry and environmental studies**
3 **Part 2 : Field determination of Co(II)/Ni(II) and Pb(II)/Zn(II) of on-**
4 **site soil extractions by electrochemical stripping techniques**

5
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14 **Abstract**

15 In the framework of deep penetrating geochemistry for mineral exploration, we
16 report a field electroanalytical method using disposable screen-printed working
17 electrodes able to quantify metal pathfinders in partial extracts of soil samples at the
18 nanomolar level on site. Four metal pathfinders (Co, Ni, Pb, Zn) were chosen due to their
19 geological interest and suitability of electrochemical detection. Square Wave Anodic
20 Stripping Voltammetry (SW-ASV) was developed for the simultaneous detection of
21 Pb(II) and Zn(II) providing limits of detection (LODs) of 1.2 nM and 5.3 nM respectively.
22 A linear scan-cathodic stripping voltammetry (LS-CSV) methodology was developed for
23 the joint detection of Co(II) and Ni(II) yielding LODs of 1.8 nM and 3.5 nM respectively.
24 Method validation was carried out on 14 upper B-horizon soil samples during a field
25 survey. Two wet extraction procedures were applied for soil samples - a strong extraction
26 using HNO₃ and a weak extraction with CaCl₂. Excellent agreement between
27 electroanalytical methods and ICP-MS was found for Pb(II) while a small
28 underestimation was observed for Zn(II). For Co(II) and Ni(II), the LS-CSV
29 measurements in the HNO₃ extractions were impossible due to the change from low pH
30 to pH to 7.15 which induces precipitation of the Fe and Al. For the CaCl₂ extractions, the
31 Co(II)/Ni(II) results obtained by LS-CSV were in excellent agreement with ICP-MS
32 measurements.

33

34 **Keywords:** Geochemical exploration, Field survey, Cobalt, Nickel, Lead, Zinc, Cathodic

35 stripping voltammetry, anodic stripping voltammetry, screen-printed carbon electrodes.

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41 Deep-penetrating geochemistry is employed to reveal geochemical vectors towards
42 concealed mineralization using the metal concentrations of surface samples taken of
43 upper soil horizons, plant tissues and snow (Cameron *et al.* 2004), (Dunn 2007),
44 (Hamilton 2007), for example. These techniques have gained their place in geochemical
45 prospecting due to effectiveness in exploration target evaluation and generation.
46 Availability of commercial large-scale analytical facilities and their ability to measure
47 very low concentrations has made deep exploration geochemistry a mainstream green-
48 field technique for mineral exploration in many parts of the world. Accurate
49 quantification of metal contents from soil samples is performed extracting weakly bound
50 metal ions with partial extractions and analyzing them with inductively coupled plasma
51 mass spectrometry (ICP-MS). Analytical work conducted by a laboratory requires a
52 process including sample preparation, sample transportation to the laboratory, organizing
53 the logistics and finally the arrival of the data. This process may take from weeks to
54 months.

55 Electrochemical sensors are ideal for field applications due to their portability, low
56 detection limits and low cost. They have been used with good results for detecting trace
57 metals in ocean waters, often located in laboratories on ships (Omanović *et al.* 2015). The
58 key advantage of electrochemical sensors is that they also work well for samples with
59 high salt concentration, while providing detection limits in the nanomolar range
60 (Companys *et al.* 2017) whereas ICP-MS determination requires an extra step of desalting
61 to perform the analysis. In general, field laboratory and portable analytical methods is an
62 asset for exploration geochemical surveys such as demonstrated with portable X-ray
63 fluorescence spectroscopy for total antimony concentrations for soil samples, e.g.
64 (Lemièrre *et al.* 2020). An additional benefit is a rapid turnaround, allowing immediate
65 follow-up based on results of previous sampling days that would aid in confirming the
66 deep penetrating geochemical anomalies with *e.g.*, with additional denser sampling
67 designs. However, to detect an exogenic labile geochemical signal from upper soil
68 samples originating from a concealed deposit is not possible without weak partial
69 extractions. Electrochemical determination of elemental concentrations would be
70 beneficial in measuring these low concentration solutions.

71 The challenge with electrochemical probes as compared with ICP-MS is to deal with
72 the smaller number of metal ions analyzed per measurement; 2 to 3 versus 20 to 25,
73 respectively. In addition, the time per measurement for most electrochemical probes is
74 roughly 15 to 60 minutes per sample for one or two metals while the ICP necessitates 2

75 to 5 minutes per sample for 20 metals. In summary, the electrochemical field probes can
76 quickly provide measurement data with less complicated logistics pertaining to sample
77 handling. However, they offer a smaller number of detected metals with fewer samples
78 measured per day when compared with the ICP.

79 Electrochemical methods are generally based on the measurement of an electric
80 current generated by an oxidation-reduction reaction of the targeted metal as function of
81 an applied potential. These currents, which are proportional to the metal ion concentration
82 in solution, are measured using a three-electrode system (working, reference and auxiliary
83 electrodes).. Different metal ions can normally be identified by their position in the
84 applied potential axis (x-axis) which is related to their respective reduction potentials
85 (Bard and Faulkner 2000). For trace metallic contaminant analysis in environmental
86 matrices, stripping potentiometry techniques are the most suitable owing to their low
87 detection level and low susceptibility to interferences from adsorption of organic
88 compounds at the electrode surface. They are comprised of two stages: firstly, the target
89 metal ions are preconcentrated on the working electrode (deposition step) and secondly
90 the metal is quantified (measuring step). It is the preconcentration step, if carried out in
91 very small volume-to-surface ratio electrodes, that enables detection of very low metal
92 concentrations, easily in the nanomolar range (Rocha *et al.*, 2010).

93 The purpose of this work is to develop field electroanalytical methods to quantify the
94 trace metal on-site in upper B-horizon soil samples extracted with nitric acid extraction
95 and calcium chloride extraction and to validate their performance with the ICP-MS
96 measurements. The electrochemical field probes being developed here represent a true
97 analytical challenge since they employ screen-printed working electrodes for which new
98 methodologies must be developed. A two-stage strategy was implemented focusing first
99 on development of the electroanalytical methods for some metal pathfinders in the
100 laboratory, and secondly to validate those latter ones together with the newly assembled
101 field electrochemical probe during a field survey. The method validation was carried out
102 on fourteen B-horizon soil samples by comparing the same extracted solution measured
103 on-site by our electroanalytical techniques with the ICP measurements by a certified
104 laboratory.

105 Two techniques were chosen for the electrochemical method development: 1) anodic
106 stripping voltammetry which reduces metal ions directly at the electrode (Borrill *et al.*
107 2019) and 2) cathodic stripping voltammetry where metal quantification is aided by

108 addition of a complexing agent (van den Berg 1991), thus enabling the quantification of
109 a wide variety of metal ions with low detection limits. Four metal ions were chosen for
110 testing the electroanalytical methods during this field trip: cobalt (Co(II)) and nickel
111 (Ni(II)) using linear scan cathodic stripping voltammetry, LS-CSV(Pérez-Peña *et al.*
112 1994) and zinc (Zn(II)) and lead (Pb(II)) using square wave anodic stripping voltammetry
113 SW-ASV(Nor and McNeal 1993).

114 **1. Methods**

115 **1.1 Reagents**

116 All solutions were prepared with Ultra-pure water (18.2 M Ω , ELGA LabWater). One
117 hundred μ M, 10 μ M and 1 μ M standard solutions of Co(II), Ni(II), Zn(II), Pb(II) were
118 obtained from dilutions of the certified metal standard *TraceCERT*[®] 1000 mg/L solutions
119 (supplied by Fluka). The 0.18 mM Hg(II) solution (pH adjusted to 1.9) employed for the
120 working electrode preparation was made from the certified mercury standard
121 *TraceCERT*[®] 1000 mg/L solution (Fluka). The ionic strength was set with a solution of
122 1 M NaNO₃ prepared from solid powder (*TraceSELECT*[™], \geq 99.999% from Fluka),
123 while NaOH 1 M standard (Merck Titripur[®]) or HNO₃ 65% (p.a Merck Suprapur[®])
124 solutions were used pure or diluted to adjust pH. H₂SO₄ (> 95%, Sigma-Aldrich),
125 NH₄CH₃COO, NH₄SCN, HCl (all pro analysis Merck) were used for the cleaning of the
126 working electrode and re-oxidation of the mercury film. A 3-(N-
127 morpholino)propanesulfonic acid (MOPS) (>99.5%, Sigma) and dimethylglyoxime
128 (DMG) (>99%, Sigma) were used as buffer and complexing agent, respectively. MOPS
129 and DMG solutions were prepared from solids. The preparation of the DMG solution at
130 0.1 M required dissolution in ethanol (Merck Suprapur[®]), and MOPS solution at 0.1 M
131 required dissolution in ultra-pure water. Nitrogen (>99.999% pure) for the
132 electrochemical experiments was purchased from Air Liquide in France and from Linde
133 AG in Finland.

134

135 **1.2 Instrumentation**

136 The field electrochemical system was a PalmSens 4 potentiostat/galvanostat
137 controlled by PsTrace 5.5 electrochemical software (PalmSens BV, Houten, The
138 Netherlands). This instrument is compact (15.7×9.7×3.5 cm, 500 grams) and can be
139 powered either by a computer USB port or by a normal power source. (Palmsens 2022)

140 The PsTrace 5.5 software supports a variety of voltammetric and galvanometric
141 techniques (including linear sweep voltammetry and square wave voltammetry) and
142 controls a magnetic stirrer (Micro-stirrer VELP Scientific, Usmate, Italy or HANNA
143 Instruments, Lingo Tanneries, France) connected to the instrument permitting the
144 realization of a certain number of double step (or stripping) techniques. Dissolved oxygen
145 can chemically reoxidize the metal deposited in the mercury during the stripping step thus
146 interfering with the measurement. Therefore, a nitrogen bottle (99.999% purity) was used
147 to provide the nitrogen necessary to eliminate the oxygen from the cell.

148 For quantitative work, a 50 mL disposable polystyrene beaker was used as the
149 electrochemical cell. Polystyrene is the most appropriate material to perform metal ion
150 quantification since there are no losses of ions to the container walls (Pinheiro and Bosker
151 2004). The use of a disposable electrochemical cell permits a faster execution of each
152 measurement as it eliminates the need to clean the cell prior to use.

153 All electrochemical measurements were performed using a 3-electrode system,
154 comprised of a Ag/AgCl reference electrode (DRIFEF-5SH from World Precision
155 Instruments, Sarasota, FL, USA), an auxiliary electrode in the form a 2 mm glassy carbon
156 rod (ref. 6.1247.000, supplied by Metrohm, Switzerland) and the screen-printed carbon
157 electrodes modified with thin mercury films (SPC-TMFE) as the working electrode (see
158 section 2.3 and 2.4).

159 Temperature and pH were measured using a combined pH electrode Sentix 41-3 with
160 a PT 1000 temperature probe connected to a pH 197 pH meter (all from WTW, Weilheim,
161 Germany).

162 1.3 Fabrication of the screen-printed carbon electrode

163 Screen-printing was carried out at Dublin City University with a semi-automated
164 DEK 248 (DEK Printing Machines Ltd., Weymouth, UK). A nylon screen with a mesh
165 thickness of 77 T (filaments per cm) was employed. Electrodes were screen-printed onto
166 a pre-shrunk polyethylene terephthalate (PET) substrate (175 μm thickness). Carbon
167 paste ink (C10903D14, Gwent Electronic Materials Ltd. Pontypool, UK) was applied and
168 cured at 150°C for 15 min. Two consecutive prints of the carbon were performed. A non-
169 conductive dielectric layer was applied to define the electrode area (3 mm diameter) and
170 cured in the UV curing machine (UV Process Supply, Inc., Cortland, Chicago, IL, USA)
171 for 3 cycles. UV lamp intensities of 300 watts per inch were used for insulating layer-
172 curing procedures.

173

174 1.4 Working electrode modification with Hg

175 The preparation, use and post-treatment of thin-mercury film screen-printed working
176 electrodes (SPC-TMFE) are described hereafter:

- 177 • In order to remove impurities from the carbon electrode surface, the electrode was
178 first placed in a 0.2 M H₂SO₄ solution and a linear scan applied between (-1.20 V
179 - +1.50 V (vs. Ag/AgCl)) at 0.10 V/s (Morrin *et al.* 2003). Following this, a
180 second electrochemical treatment was applied consisting of 50 successive cyclic
181 voltammograms (-0.80 V - +0.80 V (vs. Ag/AgCl)) at 0.10 V/s in NH₄CH₃COO
182 1 M/HCl 0.5 M (Rocha *et al.* 2007).
- 183 • For the electrodeposition of the Hg film to the carbon electrode surface, the
184 electrode was immersed in a 0.18 mM Hg(NO₃)₂ solution and a potential of -1.30
185 V (vs Ag/AgCl) was applied for 420 s. Following this, a square wave voltammetry
186 was carried out from -1.30 V to -0.20 V (amplitude 25 mV, step 4 mV, frequency
187 25 Hz) to verify the presence of the Hg film before using (Rocha *et al.* 2007).
- 188 • At the end of the electrode lifetime, the Hg film was completely removed from
189 the carbon surface by re-oxidation so that it could be properly disposed according
190 to safety regulations ensuring that no mercury trace was left in the field. Mercury
191 re-oxidation was carried out in 5 mM of NH₄SCN (pH 3.4) solution using Linear
192 Sweep Voltammetry (LSV) from -0.10 V to +0.80 V (scan rate of 0.005 V/s)
193 (Rocha *et al.* 2007).

194 1.5 Cathodic stripping voltammetry for detection of Co(II) and Ni(II)

195 LS-CSV (Pérez-Peña *et al.* 1994) encompasses two steps. First, a deposition or pre-
196 concentration step is carried out leading to the adsorption of complexed metal ions, in this
197 case, Co- and Ni-DMG at the SPC-TMFE surface. Following this, a cathodic stripping
198 step was applied, during which adsorbed complexes at the electrode surface are reduced.
199 Peak height was used as the quantitative response to detectable metal ion concentrations.
200 Two experimental methods were used; one using oxygen purge (in the field survey) and
201 another in presence of oxygen (reported in the Further developments, section 4.3). To
202 eliminate the oxygen interference in the measurements, the sample solution was purged

203 with N₂ for 15-20 min. A constant flow of N₂ was maintained above the sample solution
204 during all measurements.

205 Two methods were carried out successively for metal quantification:

206 The first method consisted of quantifying both Co(II) and Ni(II) together. A 30 s
207 deposition step under an applied deposition potential (E_d) of -0.65 V in a stirred solution
208 was carried out followed by a reduction step where a linear scan was applied between -
209 0.75 and -1.60 V, (9 V/s scan rate; 0.004 V potential step). In the second experiment,
210 Co(II) only was quantified. To achieve this, a pre-treatment was used after the deposition
211 step, imposing a potential of -0.93 V for 1 s to reduce Ni(II) and remove it from the
212 surface, just prior to the measuring step, so that Co(II) only was measured. Immediately
213 after the measurement, the potential applied to the electrode was kept at -1.60 V to
214 minimize adsorption of the metal-DMG complexes at the electrode surface. All
215 measurements were performed in triplicate.

216 For the second method dealing with unpurged solutions, an additional step was introduced
217 between deposition and reduction of metal ions. This step consists of applying a constant
218 potential of -0.75 V for 45 s (no stirring), so that much of the oxygen in the electrode
219 diffusion layer is consumed, thus significantly decreasing the oxygen interference in the
220 signal during the reduction step.

221 1.6 Square wave anodic stripping voltammetry for detection of Pb(II) 222 and Zn(II)

223 The ASV measurement comprised a deposition and a re-oxidation step: the
224 deposition step was performed at -1.20 V for a fixed time (under stirring for 45 s or 90 s
225 as specified), while the reoxidation step was carried out using square wave voltammetry
226 from -1.20 to -0.20V, (frequency 25 Hz, a potential amplitude 0.025 V, potential step
227 0.004V). Peak height was used as the quantitative response to detection metal ion
228 concentrations. Between each measurement, a continuous potential was applied in order
229 to prevent ion adsorption at the electrode surface. The sample solution was purged with
230 N₂ for 15-20 min. A constant flow of N₂ was maintained above the sample solution during
231 all measurements. All measurements were performed in triplicate.

232

233 1.7 Soil sample analysis using standard addition

234 1.7.1 LS-CSV Co(II)/Ni(II)

235 The measurement solution comprised a specified volume of sample (between 0.1 and
236 16 mL), to which 2 mL NaNO₃ (1 M), 300 µL DMG (0.1 M) and 2 mL MOPS (0.1 M)
237 were added and the pH was adjusted to 7.15 using HNO₃ or NaOH. Finally, Ultra-Pure
238 water was added to obtain the final volume of 20 mL. Even if normally the determination
239 of Ni and Co using DMG is generally performed at pH above 8.5, in this work we have
240 tested the protocol at different pH values and found that the lowest value before the signal
241 decreasing was 7.15. The objective was to minimize reagent consumption in the field.
242 The standard addition method of calibration was carried out comprising the sample
243 measurement followed by three metal aliquot additions to the sample (in triplicate).

244 1.7.2 SW-ASV Pb(II)/Zn(II)

245 The measurement solution comprised a specified volume of sample (between 0.1 and
246 5 mL), to which 0.4 mL HNO₃ (1 M) was added. Note that a good part of this acid will
247 be consumed by the organic matter present in the soil extract. Ultra-Pure water was then
248 added to obtain a final volume of 20 mL in the electrochemical cell. The pH was adjusted
249 to 3.5 using HNO₃ (1 M) if necessary. The standard addition method of calibration was
250 carried out comprising the sample measurement followed by three metal aliquot additions
251 to the sample (in triplicate).

252 In both LS-CSV Co(II)/Ni(II) and SW-ASV Pb(II)/Zn(II) cases reverse-axis standard
253 addition analysis (Goncalves *et al.* 2016) is used to compute the concentration from the
254 y-intercept and thus obtain the error estimation and the LOD from the respective standard
255 error ($LOD=3s_b$, where s_b is the intercept error). An LOD is thus obtained for each
256 standard addition measurement therefore the overall LOD presented in this work is an
257 average of all measured samples.

258 2. Study area and sampling

259 2.1 Experimental site and sample collection

260 Soil sample collection took place in June-July 2019 at the Rajapalot Au-Co project
261 area, 30 km west of Rovaniemi city in the Peräpohja Belt in northern Finland. During the
262 field campaign, the target metals were measured in two different solution extracts from
263 freshly collected soil samples (De Junet *et al.* in press). 14-point locations were sampled
264 on and around the Raja Au-Co prospect (66.45° N, 24.75° E). The site is characterized
265 by old growth boreal forests on well-drained coarse-grained glacial sediments, over which
266 soil samples were collected, and peatlands. The Au-Co mineralization has been

267 investigated by bedrock drilling by the exploration permit holding company Mawson Oy.
268 The sampled mineral soils are Podzols (IUSS Working Group WRB 2015) and their upper
269 B-horizon (spodic) samples were acquired at depths between 12 and 45 cm and collected
270 in plastic bags. The map of the sampling site with the sample points is presented as Figure
271 1 in (De Junet *et al.* in press) roughly 1/3 of them located on the known mineralized bodies
272 and the rest on the background. Further details on the mineralization type and associated
273 enriched elements and the main physical and chemical properties of soil materials are
274 summarized in the Supplementary Data 1 of Part 1 (De Junet *et al.* in press).

275 2.2 Soil sample preparation and extractions

276 The standard protocol when measuring trace metals in soil samples implies as an
277 initial step a liquid-solid extraction procedure on dried soil samples. As drying a soil
278 sample is time-consuming and thus not compatible with on-site measurement, the liquid-
279 solid extraction was tested on freshly collected (wet) soil samples.

280 To validate this wet extraction procedure, we compared ICP results obtained for the
281 on-site fresh soil extractions carried out during the Rajapalot survey and the dried soil
282 extractions performed in the laboratory. This work was presented in detail in Part 1 (De
283 Junet *et al.* in press).

284 After collecting the upper soil B-horizon, samples were transported to the field
285 laboratory where the soils were sieved to finer than 2 mm particle size fraction. The <2
286 mm particle size grinding and sieving was chosen instead of the usual <0.065 mm particle
287 size used in Scandinavia for dry soils, since the later would be too long when applied to
288 wet soils in the field. Two extraction media were investigated for use: 0.43 M HNO₃ nitric
289 acid and 0.01 M CaCl₂ calcium chloride. In each extraction, 3.0 g of soil were weighed
290 on a technical balance (precision 0.1 g) and transferred to a 50 mL Falcon® tube in which
291 either 30 mL of 0.01 CaCl₂ or 0.43 M HNO₃ was added. These suspensions were shaken
292 for two hours in a rotator mixer (Intelli-Mixer™ RM-2L, ELMI, Riga, Lithuania);
293 decanted for 30 minutes and filtered using a Acrodisc® 25 mm w/0.45 µm syringe filter
294 with Supor™ STRL membrane (manufactured by Pall Corporation, Port Washington,
295 New York, USA) and distributed in equal parts into two plastic containers where one was
296 reserved for electrochemical analysis and the other for ICP-MS analysis. The samples
297 were stored at 4 °C. Each soil extraction was carried out in triplicate. To check for
298 possible metal contaminations, blank samples (containing extractant but no soil) were
299 also carried through each procedure and analyzed by ICP-MS at ALS laboratory (Prague,

300 Czechia). The details of the ICP-MS analysis can be found in Part 1 of this manuscript
301 (De Junet *et al.* in press).

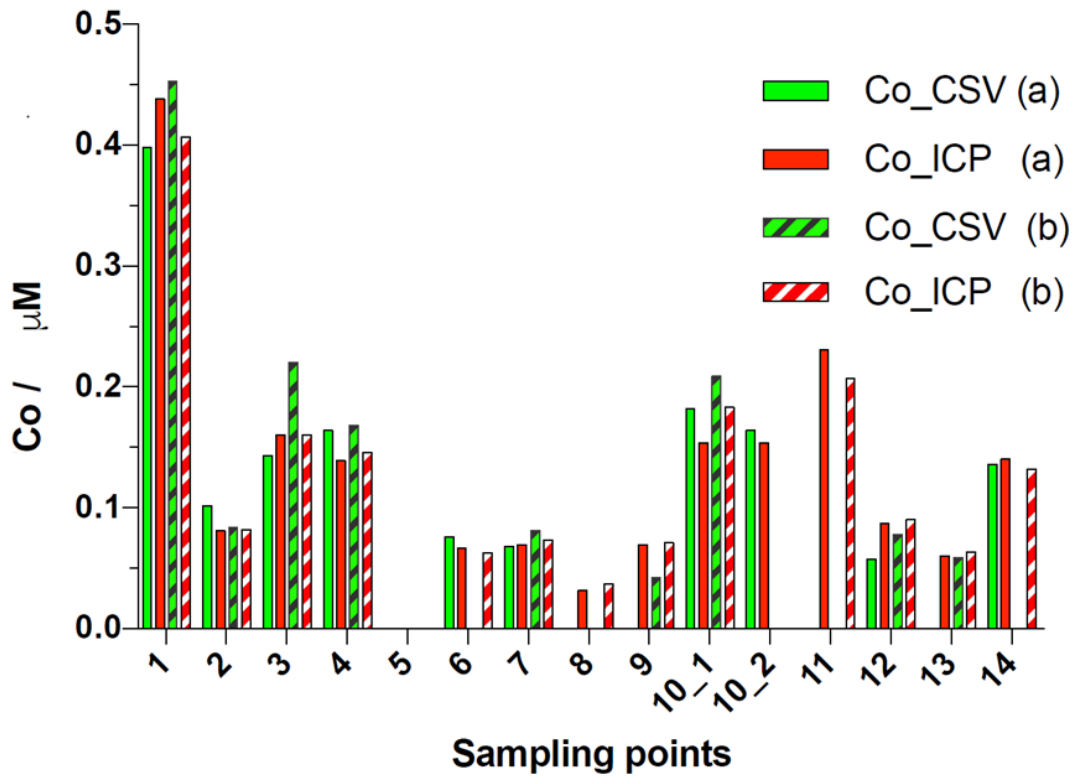
302 **3. Results and discussion**

303 3.1 LS-CSV Co(II) and Ni(II)

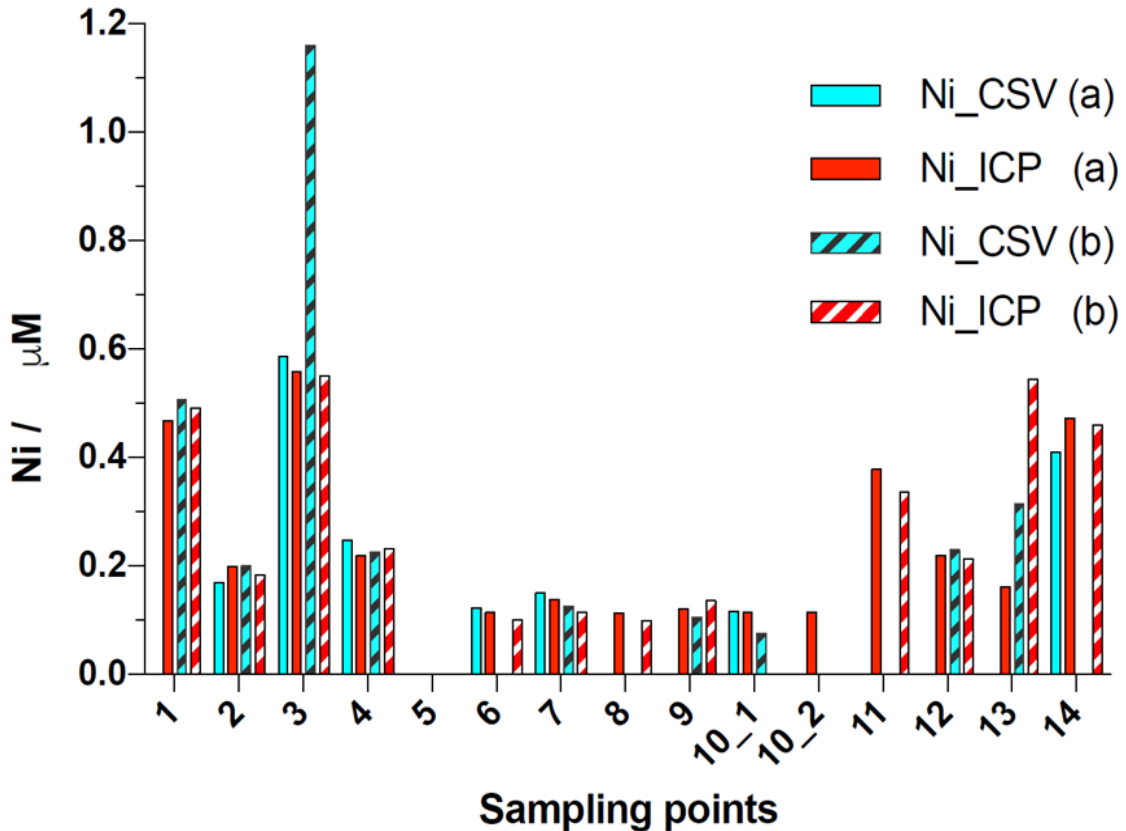
304 A previously reported LS-CSV method (Herrera-Melián *et al.* 1994) for the detection
305 of Co(II) and Ni(II) using a hanging mercury drop electrode was adapted and optimized
306 for our working electrode (section 1.4). Average LODs of 1.8 nM for Co(II) and 3.5 nM
307 for Ni(II) and a linearity limit of 25 nM for both metals were measured. Examples of
308 voltammograms and standard addition plots are given in Section A of the Supplementary
309 Data. In cases where the sample concentrations surpassed this linearity limit during the
310 on-site quantification, we applied a quadratic regression to relate the electrochemical
311 measured signal with the metal concentration values instead of a classical linear function,
312 such that a larger range of metal concentrations could be measured. For large
313 voltammetric waves an overlap of the Co(II) and Ni(II) peaks was observed. For Co(II)
314 quantification this was overcome by selectively eliminating the Ni(II) peak as described
315 in section A of the Supplementary data Figs. S1 and S2. However for Ni(II)
316 quantification, selective removal of Co(II) was not possible. Therefore, peak separation
317 (see in SD: Figure S3) was performed using Fytik software (Wojdyr 2010).

318 Within the field survey, it was not possible to analyse HNO₃-extracted samples due
319 to their low pH. The required pH for the LS-CSV analysis was 7.15 and pH adjustments
320 using 1 M NaOH caused the formation of brownish precipitate. This precipitate was likely
321 iron-based since the ICP measurements showed a range of concentrations between 0.2
322 and 5.1 mM Fe in the 14 samples analysed. When precipitate was removed from the
323 sample via filtration, no Co(II) or Ni(II) were detected in the supernatant indicating that
324 those ions likely also co-precipitated.

325 During the field survey 27 CaCl₂ extracted samples were measured over six days.
326 Among the sample extracts, five presented such high metal ion content that it led to an
327 electrode saturation (insufficient dilution of the sample) and three samples could not be
328 measured due to electrode contamination. Thus, 19 Co(II) and 17 Ni(II) samples were
329 successfully analyzed.



330 **Figure 1:** Cobalt concentrations obtained by LS-CSV and ICP-MS for the soil B horizon CaCl₂
 331 extractions, where data annotated (a) and (b) in the legend are the replicates.



332 **Figure 2:** Nickel concentrations obtained by LS-CSV and ICP-MS for the soil B horizon CaCl₂
 333 extractions where data annotated (a) and (b) in the legend are the replicates.

367 Figures 1 and 2 report the analyzed Co(II) and Ni(II) concentrations for the CaCl₂
368 extraction as determined by LS-CSV and by ICP-MS measurements. Figure 1 shows that
369 for Co(II), LS-CSV measurements were in broad agreement with ICP-MS. Fig 2. also
370 displays good agreement for Ni(II) analyses, with the exception of two sampling points
371 (3b, 13b). It is likely that 3b is an outlier, as the replicate (3a) agrees very well (<5%)
372 with both ICP measurements. On the other hand, only a single LS-CVS analysis was
373 performed for sampling point 13, the two ICP measurements (13a and 13b) are
374 significantly different from each other, and the single LS-CSV result does not agree with
375 either ICP-MS analysis.

376 During the method development, we found out that a working electrode could be
377 used for four consecutive samples before observable performance degradation. During
378 the field laboratory work a new working electrode was thus made (at a rate of roughly 1
379 per hour) for every four samples, which constrained the number of samples analyzed in a
380 day.

381

382

383 3.2 SW-ASV Zn(II) and Pb(II)

384 The SW-ASV method development for simultaneous quantification of Zn(II) and
385 Pb(II) using the SPC-TMFE supported by the screen printed electrodes with a deposition
386 time of 90s (see section 3.6) yielded an average detection limit of 5.3 nM for Zn(II) and
387 1.2 nM for Pb(II). The linearity limit was 300 nM for Zn(II) and 50 nM for Pb(II).
388 Examples of voltammograms and reverse standard addition plots are given in Section B
389 of the Supplementary Data.

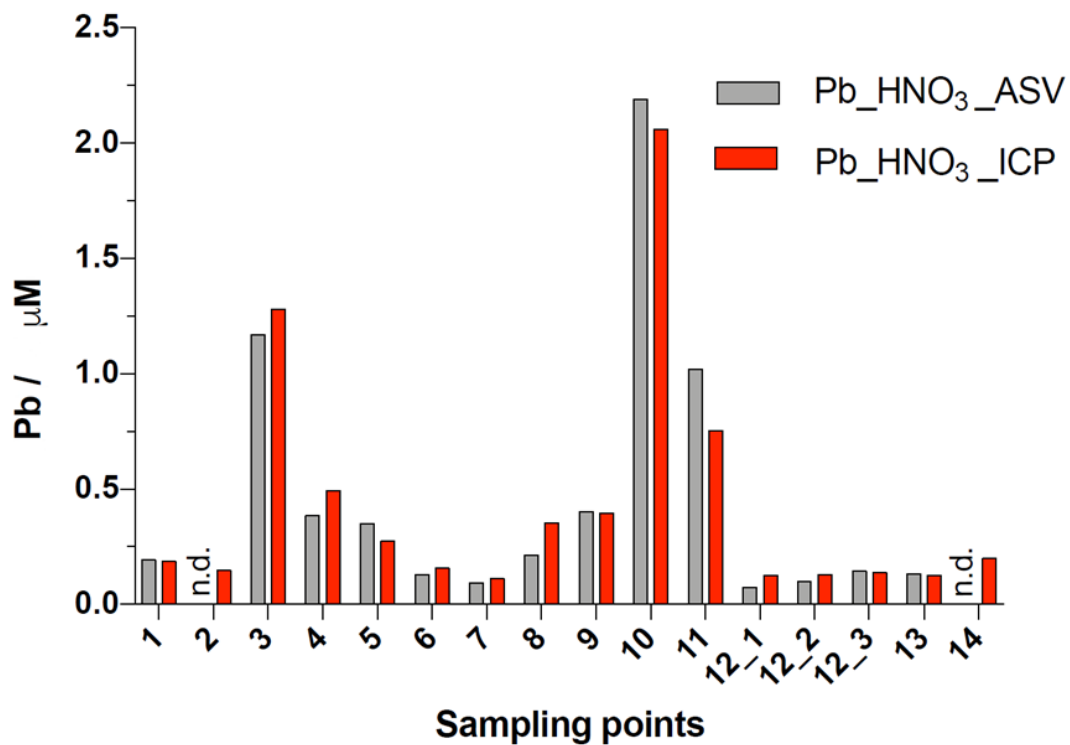
390 During the field survey, thirty-three samples were measured in six working days. For
391 five of these samples the measurements were not successful probably due to a working
392 electrode malfunction, since all of them were measured with the same electrode in the
393 same day. Thus, twenty-eight out of thirty-three samples were successfully analyzed for
394 Zn(II) and Pb(II). Figures 3 and 4 summarize the results obtained from the
395 electrochemical measurements and the ICP-MS data for the samples issue from the HNO₃
396 extractions, for Zn(II) and Pb(II) respectively.

397 [Figure 3](#) shows the excellent agreement between Pb(II) concentrations
398 measured by electrochemical and the ICP measurements. In [Figure 4](#) it can be
399 observed that all data except one were below the ICP detection limit provided by ALS-

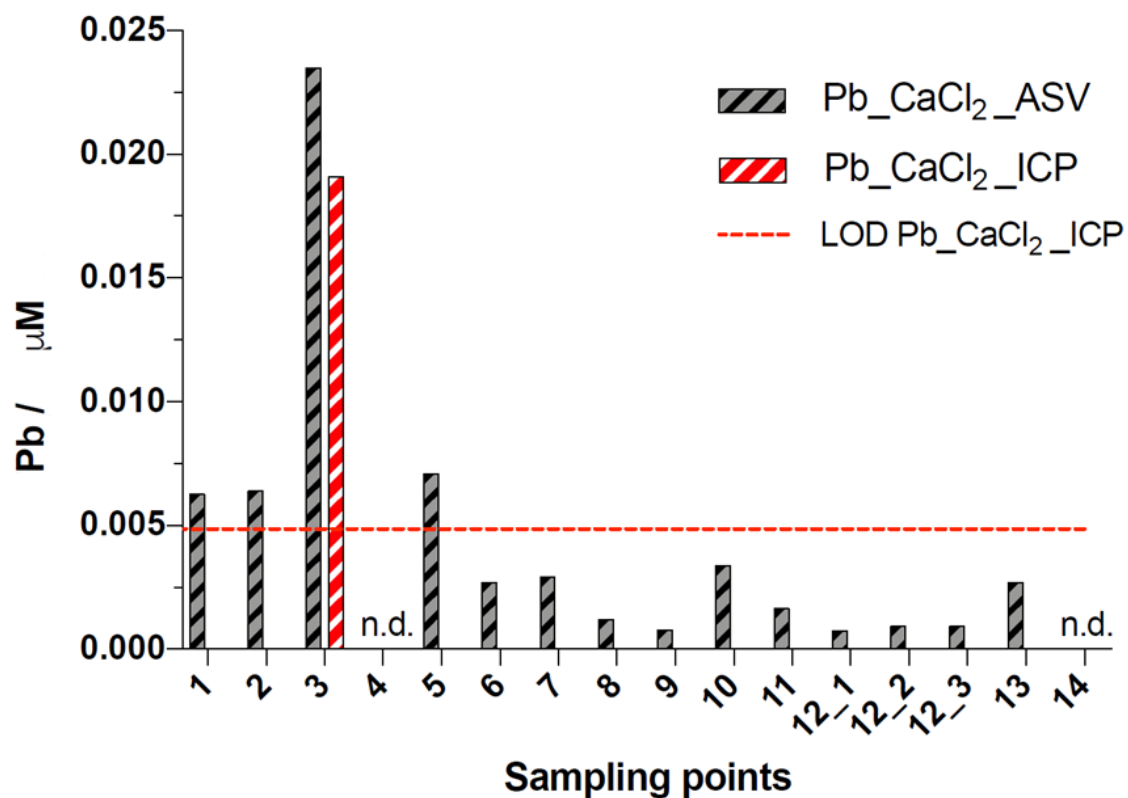
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400 Prague (0.005 μM). Instead the field probe was able to measure all the samples
 401 confirming the excellent detection limit for Pb with this technique.



402 **Figure 3:** Lead results obtained by SW-ASV and ICP-MS for the soil B horizon HNO₃ extractions

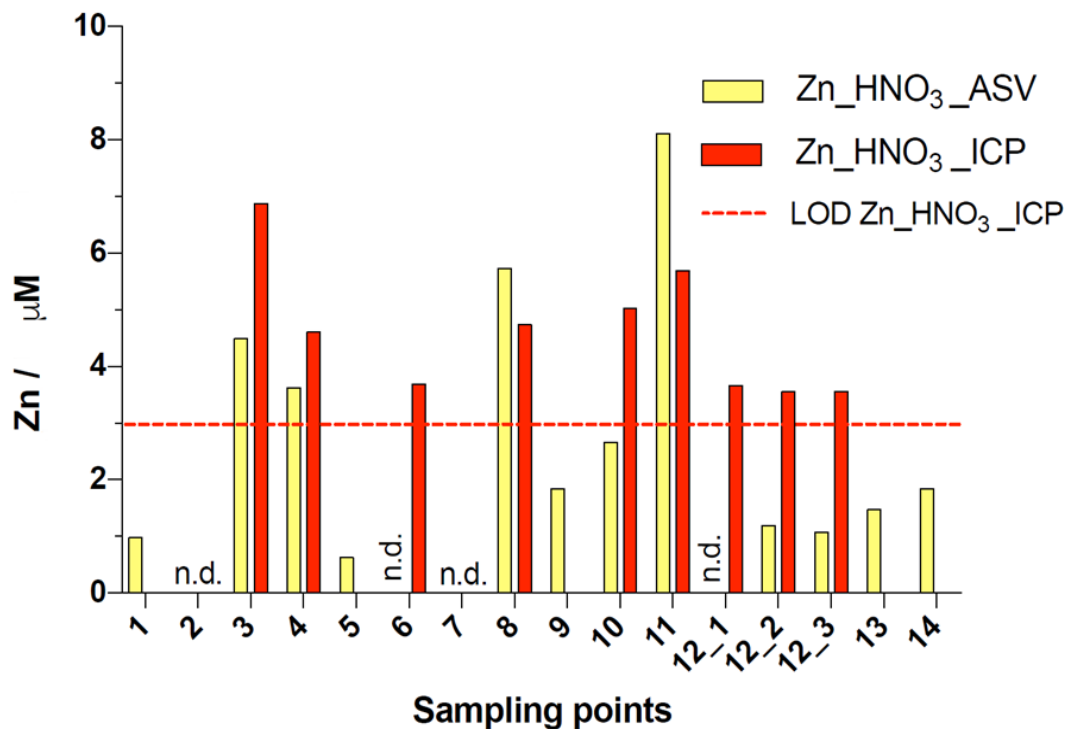


403

423 **Figure 4:** Lead results obtained by SW-ASV and ICP-MS for the soil B horizon CaCl₂ extractions.
 424 The red line gives the LOD for the ICP measurement. The red dotted line represents the detection
 425 limit for the ICP measurement provided by ALS-Prague (0.005 μM).

426 [Figure 5](#) and 6 illustrate the comparison of Zn(II) measurements with the
 427 developed electrochemical method and ICP for the HNO₃ and CaCl₂ extracted soil
 428 samples. Apparently, ALS-Prague used different calibrations for the ICP results provided
 429 in [Figure 5](#) and [Figure 6](#) yielding different LOD of 3 and 0.6 μM and
 430 thus a limit of quantification (LOQ) of 9 and 1.8 μM respectively. This is unfortunate for
 431 our comparison purposes since all reported ICP values except number 4 in Figure 6 lie
 432 between the LOD and LOQ. ALS provided ICP concentration values but, in reality, the
 433 correct way to report these measures is to state that the Zn concentrations are ranging
 434 between the LOD and LOQ. Note that the detection limits for the LS-ASV measurements
 435 are two orders of magnitude lower than those reported for the ICP measurements (5.3
 436 nM).

437 Within these limitations, we observe in Figure 5 that there are five ICP concentrations
 438 below the LOD (1, 5, 9, 13, 14) and another five between LOD and LOQ (3, 4, 8, 10, 11)
 439 in agreement with the electrochemical concentrations. For the two samples 12_2 and
 440 12_3, disagreements are noticed since the electrochemical measurements were well
 441 below the reported ICP LOD values.



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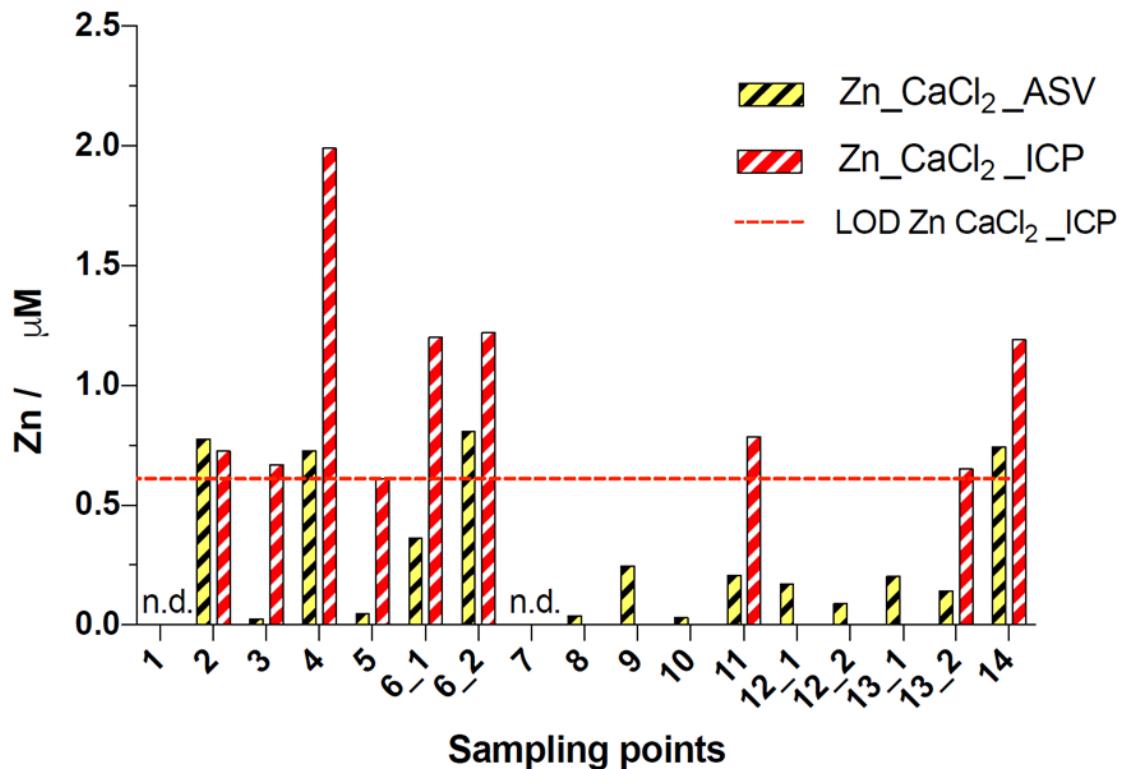
471 **Figure 5:** Zinc results obtained by SW-ASV (green) and ICP (black) for the soil B horizon HNO₃
472 extractions. The red line gives the LOD for the ICP measurement. All samples were measured by
473 ICP, thus, a non-reported value is below the LOD. The n.d. notation corresponds to a failed
474 electrochemical measurement. The red dotted line represents the detection limit for the ICP
475 measurement provided by ALS-Prague (3 µM).

476 Figure 6 shows that there are six ICP concentrations below the LOD (8, 9,
477 10, 12_1, 12_2, 13_1) and another three between LOD and LOQ (2, 6_2, 14) in agreement
478 with the electrochemical concentrations. We observe disagreements in five samples (3, 5,
479 6_1, 11, 13_2) where ICP detected zinc while the electrochemical measurement is well
480 below the reported ICP LOD. Finally for sample 4, there is a significant difference
481 between ICP and electrochemical values.

482 Results in Figure 6 suggest that electrochemical measurements provide lower
483 concentrations levels than the ICP analysis. A possible explanation for this
484 underestimation would be the presence of a considerable amount of Cu(II) ions in
485 solution; between 1.7 and 5.4 µM for the HNO₃ extraction and up to 1.2 µM for the CaCl₂
486 extraction were measured by ICP-MS. It is well known that formation of intermetallic
487 complexes inside the mercury electrode due to the presence of Cu(II) can affect the Zn(II)
488 quantification (Brett *et al.* 1997).

489 We already investigated a possible solution to this problem by changing the detection
490 technique from SW-ASV to Stripping Chronopotentiometry (SCP) that is less sensitive
491 to copper interference (Rocha *et al.* 2007). To that point, a work was published recently
492 that described a new SCP methodology to quantify Pb(II) and Zn(II) in river water
493 samples (Hackel *et al.* 2021). Very low LODs were reported for Pb(II) (0.06 nM) and
494 Zn(II) (1.9 nM) and the methodology was validated by comparison with ICP-MS results
495 (all above the LOQ). Again we observed an excellent agreement for Pb(II) while using
496 SCP the problem was not solved for Zn(II) since the results were 30% to 50% lower than
497 the ICP-MS, as observed in this work. In the near future, we will carry out further
498 investigations into the origin of these discrepancies.

499



500 **Figure 6:** Zinc results obtained by SW-ASV and ICP-MS for the soil B-horizon CaCl₂ extractions.
 501 The red line gives the LOD for the ICP measurement. All samples were measured by ICP, thus,
 502 a non-reported value is below the LOD. The n.d. notation corresponds to a failed electrochemical
 503 measurement. The red dotted line represents the detection limit for the ICP measurement provided
 504 by ALS-Prague (0.6 μM).

505

506 3.3 Further developments

507 During the field survey, the most significant logistical challenges were related to the
 508 use of a nitrogen bottle in order to purge the solutions. It was difficult to find a local
 509 supplier and to transport the bottle to the on-site laboratory. Therefore, the main priority
 510 is now to eliminate the need to purge the solutions.

511 Regarding the Zn(II)/Pb(II) analysis deprived of oxygen degassing, we tested a filter
 512 (Etienne *et al.* 2020; Le *et al.* 2020) which eliminates the dissolved oxygen at the vicinity
 513 of the working electrode during the stripping step of the SCP procedure (Rotureau *et al.*
 514 2021). This system is not yet ready for the field. Further development is required to
 515 include a second potentiostat for operation and miniaturization of the coupling of the
 516 metal sensing electrode and the oxygen filter.

517 Preliminary to the Co(II)/Ni(II) field measurements, we tested a method in the
 518 laboratory to carry out unpurged quantification of Co(II) and Ni(II) using a hanging
 519 mercury drop electrode (HMDE). This method was originally proposed by (Herrera-

520 Melián *et al.* 1994) for seawater. Upon testing this method in our working electrode (SPC-
521 TMFE) we observed that the detection limit was considerably worse than at the HMDE.
522 We also ascertain that nitrogen purging was effective in decreasing this detection limit;
523 therefore, it was necessary to continue purging during the field survey.

524 We decided to modify the LS-CSV method by introducing a new step. A potential of
525 -0.75V was applied for 45s without stirring between the deposition and the reduction
526 steps. During this step, a large part of the oxygen lying near the electrode is consumed,
527 thus significantly decreasing the oxygen interference of the baseline. This modified
528 methodology without purging yielded a detection limit of 3.5 nM for Co(II)(1.8 nM
529 purged) and 6.1 nM for Ni(II) (3.5 nM purged), which are sufficient for most natural
530 waters and more than adequate for soil extracts. A preliminary test of this methodology
531 has been made using a snow sample from the winter 2019 campaign at Rajapalot. Co(II)
532 concentrations of 3.7 ± 0.6 nM were in good agreement with the 3.1 ± 0.4 nM measured
533 with ICP-MS.

534 **4. Conclusions**

535 Two field probes were used to measure Co(II)/Ni(II) with Linear Scan Cathodic
536 Stripping Voltammetry (LS-CSV) and Zn(II)/Pb(II) with Square Wave Anodic Stripping
537 Voltammetry (SW-ASV) of two different extracts, namely HNO₃ 0.43M and CaCl₂
538 0.01M. Extraction was made of freshly collected B-horizon soil samples. The field probe
539 measurements were validated with ICP-MS quantifications performed on the same
540 samples by a certified laboratory. The main conclusions of our work are summarized
541 below:

- 542 a) There was an excellent agreement between LS-CSV and ICP for Co(II)/Ni(II)
543 measured from the CaCl₂ extraction;
- 544 b) HNO₃ extraction cannot be used for determination of Co(II)/Ni(II) by LS-CSV,
545 due to the amount of iron and aluminum in the extract solution that precipitate and
546 adsorb the Co and Ni ions;
- 547 c) Electrochemical Pb(II) quantifications were in a good agreement with ICP-MS
548 measurements for the HNO₃ extraction while for the CaCl₂ extraction were well
549 below the ALS reported ICP detection limit;
- 550 d) SW-ASV underestimated Zn(II) concentrations in comparison to the ICP
551 measurements for both the CaCl₂ and HNO₃ extractions. This is most likely due to
552 formation of intermetallic complexes with copper.

553 During the field survey we also observed that numbers of samples analyzed daily
554 will probably be sufficient to handle the number of soil samples collected especially if
555 the latter are pretreated daily in the field.

556 However, for other samples such as river water the number of samples that can be
557 analyzed daily may be even higher. In this case the measurement rate of four metals in
558 twenty samples with two field probes and two operators a day is much more labor
559 intensive than ICP-MS measurements are. The solution to increase the productivity lies
560 on the automatization of the field electrochemical probe especially regarding the sample
561 changing and the ability to measure multiple metals by an operator.

562 After the field survey a major problem of purging the samples was addressed for the
563 quantification of Zn(II)/Pb(II) using an oxygen filter and for the quantification of
564 Co(II)/Ni(II) by a methodology change. Besides avoiding the need of carrying a nitrogen
565 bottle in the field, unpurged quantifications will also increase the number of samples
566 analyzed daily.

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571 geochemical exploration techniques for target scale mineral exploration in Europe. The
572 objective is met by developing the analytical aspects in determining the elemental
573 concentrations in different surface sources (soil horizons, plant tissues, snow) and the
574 statistical data analysis aspects for reliable interpretation of the elemental spatial anomaly
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577 European Union’s Horizon 2020 Research and Innovation Program under the Grant
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579 **Supplementary Data**

580 A. Illustrations of LS-CSV voltammograms, peaks deconvolution procedure by Fityk
581 software and reverse-axis standard addition analysis for Co(II) and Ni(II) quantification
582 B. Illustrations of SW-ASV voltammograms and reverse-axis standard addition analysis
583 for Pb(II) and Zn(II) quantification

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672 **Figures**

673 Figure 1: Cobalt concentrations obtained by LS-CSV and ICP-MS for the soil B horizon
 674 CaCl₂ extractions, where data annotated (a) and (b) in the legend are the replicates. ... 12
 675 Figure 2: Nickel concentrations obtained by LS-CSV and ICP-MS for the soil B horizon
 676 CaCl₂ extractions where data annotated (a) and (b) in the legend are the replicates. 12
 677 Figure 3: Lead results obtained by SW-ASV and ICP-MS for the soil B horizon HNO₃
 678 extractions..... 14
 679 Figure 4: Lead results obtained by SW-ASV and ICP-MS for the soil B horizon CaCl₂
 680 extractions. The red line gives the LOD for the ICP measurement. The red dotted line
 681 represents the detection limit for the ICP measurement provided by ALS-Prague (0.005
 682 μM). [15+4](#)
 683 Figure 5: Zinc results obtained by SW-ASV (green) and ICP (black) for the soil B
 684 horizon HNO₃ extractions. The red line gives the LOD for the ICP measurement. All
 685 samples were measured by ICP, thus, a non-reported value is below the LOD. The n.d.
 686 notation corresponds to a failed electrochemical measurement. The red dotted line
 687 represents the detection limit for the ICP measurement provided by ALS-Prague (3
 688 μM). 15
 689 Figure 6: Zinc results obtained by SW-ASV and ICP-MS for the soil B-horizon CaCl₂
 690 extractions. The red line gives the LOD for the ICP measurement. All samples were
 691 measured by ICP, thus, a non-reported value is below the LOD. The n.d. notation
 692 corresponds to a failed electrochemical measurement. The red dotted line represents the
 693 detection limit for the ICP measurement provided by ALS-Prague (0.6 μM). 17

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