Water Analysis via Portable X-ray Fluorescence Spectrometry

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ABSTRACT

Rapid, in-situ elemental water analysis would be an invaluable tool in studying polluted and/or salt-impacted waters. Analysis of water salinity has commonly used electrical conductance (EC); however, the identity of the elements responsible for the salinity are not revealed using EC. Several studies have established the viability of using portable X-ray fluorescence (PXRF) spectrometry for elemental data analysis of soil, sediment, and other matrices. However, the accuracy of PXRF is known to be affected whilst scanning moisture-laden soil samples. This study used PXRF elemental data in water samples to predict water EC. A total of 256 water samples, from 10 different countries were collected and analyzed via PXRF, inductively coupled

plasma atomic emission spectroscopy (ICP-AES), and via a digital salinity bridge. The PXRF detected some elements more effectively than others, but overall results indicated that PXRF can successfully predict water EC via quantifying Cl in water samples (validation R^2 and RMSE of 0.77 and 0.95 $\log \mu\text{S cm}^{-1}$, respectively). The findings of this study elucidated the potential of PXRF for future analysis of pollutant and/or metal contaminated waters.

INTRODUCTION

Environmental quality assessment is of paramount importance as the world's population approaches eight billion people in the coming decades. Non-polluted soil and water for food production are among the most basic of human necessities. However, industrial development has resulted in widespread pollution and salinization of both soil and water resources (e.g., Pen-Mouratov et al., 2008; Weindorf et al., 2013a; Rengasamy, 2006; Trujillo-González et al., 2016). For example, Auchmoody and Walters (1988) documented the impact of brine spills on soils and vegetation in the Allegheny National Forest of Northwestern Pennsylvania, noting that "brine spills and accidental discharges pose serious environmental threats." Similarly, Vidakovic-Cifrek et al. (2002) note that calcium bromide and calcium chloride are commonly prepared high density brines used in oil exploration and production. However, they concede that accidental releases of such salts can and do pollute adjacent groundwater and soil. Also, many pollutant laden surface waters concern the suspension of metals bound to soil particles which are carried into waterways as suspended solids. As recently as 2015, a major Pb contamination crisis affected the public water supply of Flint, Michigan, USA. Globally, saline and sodic soils constitute 397.1 and 434.3 million ha (UN-FAO, 2016) while polluted soils are found at hundreds of thousands of sites worldwide. For example in Europe, heavy metals from smelting

activities account for 34.8% of polluted soils (IASS, 2012). This pollution, in turn, represents a significant threat to human health (Brevik and Sauer, 2015).

Soil and water salinity are intrinsically linked as the former relies on slurries or saturated pastes whereby salts precipitated in soil dissolve into solution and are measured in the aqueous phase. Traditional analysis of water salinity has commonly used electrical conductance. For decades, the Solubridge (a rudimentary, analog salinity bridge) was the preferred technology (Salinity Laboratory Staff, 1954), whereas more recently, the use of digital conductivity meters has become commonplace. Conductivity meters rely on the fact that dissolved cations and anions in aqueous solution effectively bolster the transmission of electric current (Rhoades, 1996). Thus, the more dissolved salt present in aqueous samples, the greater the electrical conductivity (EC). However, salinity meters only provide information on the total dissolved solutes found in water; they do not identify the types of cations/anions which contribute to the salinity of the sample. Elemental identification/quantification has been reliant first upon flame photometry, then atomic absorption spectroscopy (AAS) (Wright and Stuczynski, 1996), and finally inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Soltanpour et al., 1996). Colorimetry and other wet chemistry techniques may also be used for the identification and qualitative estimation of certain elements (e.g., Kuo, 1996). However, recent advances in portable X-ray fluorescence (PXRF) spectrometry have provided a field portable instrument capable of making elemental determinations *in-situ* in minutes.

Applied to soil and environmental science, several methods have been established for PXRF use in soil, sediment, and other matrices; among them Method 6200 (US-EPA, 2007), a recently established method by the Soil Survey Staff (2014), and a method by the Soil Science Society of America (Weindorf and Chakraborty, 2016). Specific applications of PXRF for soil and

environmental quality analysis include quantification of cation exchange capacity (Sharma et al., 2015), soil reaction (pH) (Sharma et al., 2014), enhanced soil horizonation (Weindorf et al., 2012), plant essential nutrients (McLaren et al., 2012), and the spatial variability of pollutants (Paulette et al., 2015; Clark and Knudsen, 2014). However, three studies in particular indicate the possible utility of PXRF for elemental determination in water samples. Weindorf et al. (2013b) used PXRF for the determination of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with Ca and S as proxy elements for gypsum content. Using simple linear regression, PXRF-determined S and Ca predicted total gypsum content, as determined by thermogravimetry, with R^2 of 0.91 and 0.88, respectively. Similarly, Swanhart et al. (2014) used Cl as a proxy for saturated paste soil salinity and found a calibration R^2 of 0.83, with and even stronger R^2 of 0.90 using multiple elements and multiple linear regression. As both of these represent salts present in soil, there is reason to believe that PXRF may be effective in determining water salinity using single or multiple elements as proxies (e.g., Cl, Ca, S, K). Finally, Eksperiandova et al. (2002) used PXRF for the analysis of waste water by combining the water with gelatin and agar. Evaluating low levels of metals ($<400 \text{ mg L}^{-1}$) in solution, they obtained reasonably good determination via PXRF (relative standard deviation up to 0.08%). As such, we conducted preliminary PXRF scans of several brine well water samples from North Dakota and found reasonable predictability of EC; data which established the precedent for the larger study presented herein.

In fairness, the PXRF does present certain limitations (Weindorf et al., 2014) which need to be considered for aqueous sample assessment. Moisture is known to denude the fluorescent energy of various elements, potentially interfering with accuracy (Weindorf et al., 2014). Also suspended sediments, themselves rife with abundant elements, would likely bias PXRF results. However, the use of specialized films (e.g., Prolene[®] thin-film) with maximum fluorescence

transmissivity and filtration/centrifugation of samples to remove any suspended sediments would seem logical means toward overcoming such limitations.

Given the number of polluted and/or salt impacted waters found worldwide, the evaluation of PXRF as a rapid analytical technique for aqueous samples appears timely. If proven accurate for the assessment and quantification of dissolved solutes, it could be an important step toward consideration of more advanced aqueous chemistries inclusive of pollutants (e.g., heavy metals) and suspended solids. As such, the objective of this research was to evaluate the potential of PXRF in predicting water EC. We hypothesize that PXRF will successfully detect elements which can be used to predict water salinity and show strong correlation to electrical conductivity data across a wide range of salinity concentrations.

MATERIALS AND METHODS

Sample collection

A total of 256 water samples were collected from 10 different countries (Belgium, Bolivia, Brazil, Curacao, Honduras, Italy, Mexico, Romania, Trinidad, United States) in 2015 and 2016. Samples from within the United States were collected from Alaska, Arizona, California, Colorado, Florida, Minnesota, Nevada, New Mexico, Oklahoma, Texas, Tennessee, Utah, and Wyoming. Table 1 shows the distribution of sample collection. Waters collected were as follows: lake (71), swimming pool (7), river (64), sea (3), tap (84), and well (27). Each sample was placed in a new 120 ml plastic bottle, sealed, and refrigerated at 4°C prior to analysis. Samples were transported to the Pedology laboratory at Texas Tech University (Lubbock, TX, USA) for analysis.

Laboratory analysis

Prior to analysis, samples were allowed to return to room temperature (20°C). Most samples contained no visually observable suspended solids (Fig. 1a); for those few samples that did, filtration and centrifugation was undertaken prior to analysis. Electrical conductance was measured with a TraceableTM expanded range digital conductivity meter (Fisher Scientific, Hampton, NH, USA). The conductance probe was thoroughly washed with deionized water between samples. Performance of the salinity bridge was assured via assessment of standard conductance solutions.

Prior to PXRF analysis, each sample was placed in a Series 1400 plastic sample cup (Chemplex Industries, Palm City, FL, USA), then covered with Prolene[®] thin-film (Chemplex Industries, Palm City, FL, USA) (Fig. 1a). A Delta Premium (DP-6000) PXRF (Olympus-Innov-X; Waltham, MA, USA), was used to conduct the analyses. Prior to scanning the PXRF was calibrated with a standard 316 metal alloy target placed in front of the aperture. Once a calibration check with the alloy was successful, the instrument was positioned into a proprietary test stand (Fig. 1b) for scanning; the test stand shields the operator from any errant X-radiation. Samples were positioned on the sample stage such that the water was placed directly over the PXRF aperture. The PXRF was operated in *Soil Mode*, a configuration capable of scanning ~25 different elements. In *Soil Mode*, we configured each of the three beams to scan for 30 sec such that one complete scan of a given sample was completed in 90 sec. Beams one and two were both operated at 40 KeV, whilst beam three was operated at 15 KeV. Two types of data were downloaded from the instrument following scanning: 1) elemental data (as reported by the software as configured), and 2) raw spectral data reporting counts and fluorescent energy (KeV) for each scan. The former is a simpler approach for “off the shelf” application, while the latter provides data for advanced spectral analysis. While the PXRF can detect multiple elements

simultaneously, concentrations below the detection limit are problematic as they cause discontinuity in the number of samples across the dataset. In this study, many elements were uniquely identified in different water samples, but only Ca, Cl, and K were reported continuously across all samples.

Samples were also subjected to inductively coupled plasmas atomic emission spectroscopy (ICP-AES) analysis via a Genesis model instrument (Spectro Analytical Instruments, Irvine, CA, USA) (Soltanpour et al., 1996). Elemental data reported via ICP-AES included: Al, As, B, Cd, Ca, Cl, Cu, Fe, K, Pb, Mg, Mn, Mo, Na, Ni, P, S, Se, and Zn.

Separately, two different calibration curves were constructed using reagent grade KCl and NaCl mixed with deionized water. Concentrations were set as follows: 0.001%, 0.01%, 0.05%, 0.10%, 0.50%, 1%, 2%, and 5%. These standard solutions were evaluated for electrical conductance, and for elemental concentration via both PXRF and ICP.

Statistical analysis

In this study, water EC predictive models were built with PXRF sensed elements using R 2.11.0 (R Development Core Team, 2014). The normality of EC residuals was checked by the Shapiro-Wilk test. Notably, EC values were positively skewed (Pearson skewness coefficient 4.53), while Box–Cox conversion (Box and Cox, 1964) using log transformed EC values were able to conform the data to a normal distribution. Further, the three PXRF measured elements (Cl, K, and Ca) were log transformed. Principal component analysis (PCA) was executed via R version 2.11.0 using the ‘prcomp’ function to visualize the clustering of water samples from different sources. Optimal number of principal components (PC) was decided from a *screeplot*.

Piecewise linear regression (PLR) was employed to model water EC using three PXRF measured elements (Cl, K and Ca). A few observations with missing values were deleted *a priori* and the rest (n=252) were randomly split into training set (176 samples, ~70%) and test set (76 observations, ~30%). PLR, also known as segmented regression, partitions the explanatory variable into intervals and fits line segment to each interval. The boundaries between the intervals are called the breakpoints. Like nonlinear regression, PLR is particularly useful to model an abrupt change of relationship between a response and a predictor. However, since the linear model is fitted for each interval, the fitted PLR model can be easily presented by equations and is therefore highly interpretable. In this study, we used the PLR with only one breakpoint for PXRF-measured Cl, K, and Ca. The location of the breakpoint, intercept, and slopes were chosen to minimize the sum of squared errors (SSE). In this study, the PLR was executed by using the *segmented* package (version: 0.5-1.4) in R, produced by Muggeo (2008). Model predictability was compared via R^2 , RMSE, Akaike information criterion (AIC) and Bayesian information criterion (BIC) values (Akaike, 1973). In general, the best models show the smallest AIC and BIC values.

PXRF spectral analysis

Furthermore, PXRF spectra were baseline corrected and smoothed using a Savitzky–Golay first order polynomial via Unscrambler®X 10.3 (CAMO Software Inc., Woodbridge, NJ). PXRF K α emission lines of Cl (2.62 KeV), K (3.31 KeV), and Ca (3.69 KeV) were separated using only Beam 3 (15 KeV) under *Soil Mode*. We followed the method proposed by Sacristán et al. (2015) and calculated the full width at half maximum (FWHM) and the maximum height ($H_{\max}$) of Cl, K, and Ca peaks using Origin pro (OriginLab, MA, USA) for their subsequent use to predict water EC.

RESULTS AND DISCUSSION

Water chemistry

Summary statistics of different parameters of assayed water samples are presented in Table 2. As expected, results exhibited substantial variation in the EC of analyzed water samples, from very low ($1.33\mu\text{S cm}^{-1}$) to extremely high ($157,600.00\mu\text{S cm}^{-1}$), with a mean value of $7,837.55\mu\text{S cm}^{-1}$ (Table 2). Notably, this study was based on a factory calibrated PXRF instrument in ‘Soil Mode’ which showed several folds higher elemental concentration for Cl, K, and Ca than ICP-based results despite exhibiting reasonable agreement between PXRF and ICP results (Table 3; Fig. 2). This variation was perhaps due to the soil mode calibration which is not targeted to a water matrix. Moreover, higher elemental enrichment in water may have led to excessive self-absorption. Thus, it can be concluded that there is need for reliable standards focusing on water matrix to reduce this variation.

Principal Component Analysis

Principal component analysis was applied to the PXRF reported Cl, K, and Ca concentrations (Fig. 3). The first two leading PCs constituted over 95% of the elemental variation (Fig. 3a), implying that using a PC1 vs PC2 plot was adequate to describe the variations among three PXRF variables (Fig. 3b). While PC1 was dominated by the PXRF-Cl (loading coefficient: 0.91), PC2 was dominated by the difference between PXRF-Ca and PXRF-K. The PC1 vs PC2 plot produced certain clustering of data, so that differentiation between water sources was readily apparent. For instance, while samples from sea showed close clustering, lake and well water samples were highly spread out along PC1, indicating that lake and well samples had large variations among PRXF-Cl ($51\text{-}56,739\text{ mg kg}^{-1}$ and $48\text{-}300\text{ mg kg}^{-1}$ for lake and well samples,

respectively). While comparing lake and well water samples, lake samples had relatively large PC2 scores, indicating a larger difference between PRXF-Ca and PRXF-K. Moreover, pool samples had relatively low PRXR-Cl contents, since they exhibited smaller values along PC1. Notably, tap water samples appeared well-mixed with lake samples. KCl-standard samples were clustered together, while NaCl-standards were relatively spread out. In general, well water samples appeared to be away from most of the other samples from different sources. Importantly, the PC score plot indicated the compositional differences between water samples from different sources.

Regression model results

By observing the scatter plots with added fitted line(s) from the models (Fig. 4), the use of 2-segmented PLR for calibrating soil EC with PXRF elements seemed prudent since most of the time soil or water-elemental associations represent intricate groupings of linear segments of variable slope. Overall, the EC was estimated with good accuracy with PXRF-Cl (calibration $R^2 = 0.77$, calibration RMSE= $0.89 \log \mu\text{S cm}^{-1}$) (Table 3), which has been noted before elsewhere (Swanhart et al., 2014). Validation results very much followed the calibration outcomes with identical coefficient of determination (0.77) and close validation RMSE ($0.95 \log \mu\text{S cm}^{-1}$), implying high enrichment of chloride salts in water samples. Whilst the water EC prediction results were not as high as that obtained for soil EC using PXRF-Cl (Swanhart et al., 2014), the results were encouraging, considering the matrix interference, denudation of the fluorescent energy of various element by water, and that ~10% of the water Cl contents were either close or less than the detection limit of PXRF (60-100 ppm), enhancing the standard error of measurements. Contrariwise, no reasonable agreements were found between EC and PXRF-K (calibration $R^2 = 0.41$, calibration RMSE= $1.41 \log \mu\text{S cm}^{-1}$) and Ca (calibration $R^2 = 0.41$,

calibration RMSE= $1.40 \log \mu\text{S cm}^{-1}$), possibly due to matrix effects. Furthermore, PXRF-Cl model was considered preferable with deference to model accuracy (Table 4), due to its comparatively lower AIC (468.74) and BIC (484.59) values. Owing to PXRF's inability to directly quantify Na^+ because of its small, stable electron cloud, acceptable agreement between PXRF-Cl and water EC justified the possible incidences of halite (NaCl) in water samples (Aldabaa et al., 2015).

Plots of measured vs. PXRF predicted EC values are presented in Fig. 5. In general, all models showed overestimation at lower EC values and underestimation at higher values. Several of these overestimations occurred because of the relative scarcity of observations with low EC values. The equations for all three PLR models are presented in Table 5.

Limitations with PXRF spectra analysis

Fig. 6 represents stacked and some log-transformed isolated examples of baseline corrected and smoothed XRF emission lines of Cl (2.62 KeV), K (3.31 KeV), and Ca (3.69 KeV). Notably, while comparing all three stacked XRF spectra indicating different elemental concentrations of Cl, K, and Ca, most of them could not be distinguished from each other despite wider ranges of elemental concentrations in water samples (Table 2). Without log-transformation, most of the data were actually in the bottom of the plot. For example, in PRXF-K (Fig. 6b), 95% of the samples had the peak value < 253 . Note that, on log-transformed PXRF-Cl, Ca, and K spectra, only PXRF-Ca bumps produced FWHM values while most of PXRF-Cl bumps were unable to generate FWHM values due to their multi-modal shape. Besides, most of the PXRF-K bumps were monotonic and thus unsuitable to deduce the FWHM values. Moreover, using $H_{\max}$ representing changes in elemental concentrations, no better correlation was obtained than using elemental results (data not shown). Thus, the postulation of Sacristán et al. (2015) that using

247 $H_{\max}$ or FWHM could be a fast and easy quantification method without complex data processing
248 and matrix effects, may not be generalized and warrants more studies to find the suitable spectral
249 preprocessing methods.

250 The results from this study implies that there is substantial potential of employing PXRF for
251 rapid water salinity quantification or at least for screening purposes which require moderate
252 precision. The predictability can be enhanced with increasing variability in Cl concentrations in
253 the water samples. Given these results, PXRF shows potential as an effective approach for rapid,
254 on-site assessment of heavy metals and/or other pollutants in waters. Clearly, this is the next line
255 of approach warranting investigation. It is widely known that “heavier” elements are more easily
256 quantified by PXRF owing to a larger electron cloud. In soils, limits of detection for such
257 elements can be as low as $\sim 5 \text{ mg kg}^{-1}$. Another modification which warrants further investigation
258 is longer scanning time. However, the increased accuracy by such extended scanning times must
259 be considered against the alacrity gained by using PXRF. Finally, as this line of inquiry
260 proceeds, fine tuning of PXRF fluorescence energy spectra can be undertaken in support of
261 developing a “Water Mode” on the PXRF instrument for future testing. Such a configuration
262 would intrinsically consider the low density matrix of the water being scanned such that other
263 elemental signatures could potentially be parsed from the fluorescent energy.

264 The authors concede that water salinity assessment via electrical conductivity may be just as
265 easy as the use of PXRF. However, PXRF does provide actual elemental concentration (Cl)
266 which may be useful in identifying certain types of salt(s) dissolved in solution; information not
267 provided by simple electrical conductivity assessment. That notwithstanding, the key novelty of
268 this study is the fact that water samples can be scanned via PXRF with significant statistical
269 relationships to standard laboratory techniques. To our knowledge, this represents the first such

study of PXRF assessment of water samples. Clearly, more work needs to be done. But the potential of PXRF for future analysis of pollutant and/or metal contaminated waters has been established by protocols presented in the context of the present study.

CONCLUSIONS

This present study was a proof of concept demonstration and presented an easy and convenient PXRF protocol for quantifying water EC with Cl, K, and Ca. Results show that combining 2-segmented PLR models with PXRF-Cl produced acceptable prediction accuracy for water EC while no realistic agreements were observed between water EC and PXRF-K and Ca. This was possibly due to matrix effects represented by absorption and secondary fluorescence. The poor EC predictability while using PXRF spectral parameters like FWHM and $H_{\max}$ underlies the need for better spectral PXRF preprocessing methods and factory calibration of PXRF, possibly to include the development of a “*water mode*.” However, the results obtained are encouraging and point to the potential of PXRF for future rapid analysis of water samples in-situ. Study of its potential for quickly screening water samples for heavy metals and/or other pollutants is warranted.

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294 **REFERENCES**

295 Akaike, H., 1973. Information theory and the extension of the maximum likelihood principle. In:
296 Petrov, V.N., Csaki, F. (Eds.), 2nd International Symposium on Information Theory.
297 Akademiai Kiadó, Budapest. pp. 267--281

298 Aldabaa, A.A.A., Weindorf, D.C., Chakraborty, S., Sharma, A., Li, B., 2015. Combination of
299 proximal and remote sensing methods for rapid soil salinity quantification. *Geoderma*
300 239-240, 34-46.

301 Auchmoody, L.R., Walters, R.S., 1988. Revegetation of a brine-killed forest site. *Soil Science*
302 *Society of America Journal* 52, 277-280.

303 Box, G.E.P., Cox, D.R., 1964. An analysis of transformations. *J. R. Stat. Soc. Series B Stat.*
304 *Methodol.* 26, 211–252.

305 Brevik, E.C., Sauer, T.J., 2015. The past, present, and future of soils and human health studies.
306 *SOIL* 1, 35-46. doi:10.5194/soil-1-35-2015.

307 Clark, J.J., Knudsen, A.C., 2014. Extent, characterization, and sources of soil lead contamination
308 in small-urban residential neighborhoods. *Journal of Environmental Quality* 42, 1498-
309 1506.

310 Eksperiandova, L.P., Blank, A.B., Makarovskaya, Y.N., 2002. Analysis of waste water by x-ray
311 fluorescence spectrometry. *X-Ray Spectrometry* 31(3), 259-263.

312 Institute for Advanced Sustainability Studies. 2013. Soil contamination: A severe risk for the
313 environment and human health. IASS special publication. 5 p.

314 Kuo, S., 1996. Phosphorus. In: Sparks et al. (Eds.), *Methods of soil analysis – Part 3, Chemical*
315 *methods*. Soil Science Society of America, Madison, WI. p. 869-919.

316 McLaren, T.I., Guppy, C.N., Tighe, M.K., 2012. A rapid and nondestructive plant nutrient
317 analysis using portable X-ray fluorescence. *Soil Science Society of America Journal* 76,
318 1446-1453.

319 Muggeo, V.M.R., 2008. Segmented: an R package to fit regression models with broken-line
320 relationships. *R News* 8(1), 20–25.

321 Paulette, L., Man, T., Weindorf, D.C., Person, T., 2015. Rapid assessment of soil and
322 contaminant variability via portable x-ray fluorescence spectroscopy: Copșa Mică,
323 Romania. *Geoderma* 243-244, 130-140.

324 Pen-Mouratov, S., Shukurov, N., Steinberger, Y., 2008. Influence of industrial heavy metal
325 pollution on soil free-living nematode population. *Environmental Pollution* 152, 172-183.

326 R Development Core Team. 2014. R: a language and environment for statistical computing. R
327 Found. Stat. Comput. Vienna, Austria (Available online with updates at
328 <http://www.cran.r-project.org>, Verified on January 6, 2016).

329 Rengasamy, P., 2006. World salinization with emphasis on Australia. *Journal of Experimental*
330 *Botany* 57, 1017-1023.

331 Rhoades, J.D., 1996. Salinity: Electrical conductivity and total dissolved solids. In: Sparks et al.
332 (Eds.), Methods of soil analysis – Part 3, Chemical methods. Soil Science Society of
333 America, Madison, WI. p. 417-435.

334 Sacristán, D., Viscarra Rossel, R.A., Recatalá, L., 2016. Proximal sensing of Cu in soil and
335 lettuce using portable X-ray fluorescence spectrometry. *Geoderma* 265, 6–11.

336 Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils.
337 Agricultural Handbook No. 60. US Department of Agriculture, Washington, DC.

338 Sharma, A., Weindorf, D.C., Man, T., Aldabaa, A., Chakraborty, S., 2014. Characterizing soils
339 via portable x-ray fluorescence spectrometer: 3. Soil reaction (pH). *Geoderma* 232-234,
340 141-147.

341 Sharma, A., Weindorf, D.C., Wang, D.D., Chakraborty, S., 2015. Characterizing soils via
342 portable x-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). *Geoderma*
343 239-240, 130-134.

344 Soil Survey Staff. 2014. Soil survey field and laboratory methods manual. Soil Survey
345 Investigations Report No. 51, Version 2. USDA-NRCS, Lincoln, NE.

346 Soltanpour, P.N., Johnson, G.W., Workman, S.M., Jones, J.B., Miller, R.O., 1996. Inductively
347 coupled plasma emission spectrometry and inductively couple plasma-mass
348 spectrometry. In: Sparks et al. (Eds.), Methods of soil analysis – Part 3, Chemical
349 methods. Soil Science Society of America, Madison, WI. p. 91-139.

350 Swanhart, S., Weindorf, D.C., Chakraborty, S., Bakr, N., Zhu, Y., Nelson, C., Shook, K., Acree,
351 A., 2014. Soil salinity measurement via portable x-ray fluorescence spectrometry. *Soil*
352 *Science* 179(9), 417-423.

353 Trujillo-González, J.M., Torres-Mora, M.A., Keesstra, S., Brevik, E.C., Ballesta, R.J., 2016.
354 Heavy metal accumulation related to population density in road dust samples taken from
355 urban sites under different land uses. *Science of the Total Environment* 553, 636-642.

356 United Nations – Food and Agricultural Organization. 2016. Extent of salt-affected soils.
357 Available at [http://www.fao.org/soils-portal/manejo-del-suelo/manejo-de-suelos-](http://www.fao.org/soils-portal/manejo-del-suelo/manejo-de-suelos-problematicos/suelos-afectados-por-salinidad/more-information-on-salt-affected-soils/es/)
358 [problematicos/suelos-afectados-por-salinidad/more-information-on-salt-affected-soils/es/](http://www.fao.org/soils-portal/manejo-del-suelo/manejo-de-suelos-problematicos/suelos-afectados-por-salinidad/more-information-on-salt-affected-soils/es/)
359 (verified 10 Mar. 2016).

360 Vidakovic-Cifrek, Z., Pavlica, M., Regula, I., Papes, D., 2002. Cytogenetic damage in shallot
361 (*Allium cepa*) root meristems induced by oil industry “high-density brines”. *Archives of*
362 *Environmental Contamination and Toxicology* 43, 284-291.

363 Weindorf, D.C., Chakraborty, S., 2016. Portable X-ray fluorescence spectrometry analysis of
364 soils. Hirmas, D. (Ed.), *Methods of soil analysis*. Soil Science Society of America,
365 Madison, WI. p. 1-8. doi:10.2136/vzj2015.09.0132.

366 Weindorf, D.C., Paulette, L., Man, T., 2013a. In-situ assessment of metal contamination via
367 portable x-ray fluorescence spectroscopy: Zlatna, Romania. *Environmental Pollution* 182,
368 92-100.

369 Weindorf, D.C., Herrero, J., Castañeda, C., Bakr, N., Swanhart, S., 2013b. Direct soil gypsum
370 quantification via portable x-ray fluorescence spectrometry. Soil Science Society of
371 America Journal 77, 2071-2077.

372 Weindorf, D.C., Bakr, N., Zhu, Y., 2014. Advances in portable X-ray fluorescence (PXRF) for
373 environmental, pedological, and agronomic applications. Advances in Agronomy 128, 1-
374 45.

375 Weindorf, D.C., Zhu, Y., Haggard, B., Lofton, J., Chakraborty, S., Bakr, N., Zhang, W.,
376 Weindorf, W.C., Legoria, M., 2012. Enhanced pedon horizonation using portable x-ray
377 fluorescence spectroscopy. Soil Science Society of America Journal 76(2), 522-531.

378 Wright, R.J., Stuczynski, T., 1996. Atomic absorption and flame emission spectrometry. In:
379 Sparks et al. (Eds.), Methods of soil analysis – Part 3, Chemical methods. Soil Science
380 Society of America, Madison, WI. p. 65-90.

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Figure1

Fig. 1.

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Figure6

Fig. 6.

Table 1. Locations where water samples were collected both within the United States and internationally.

Country	<i>n</i>	State	<i>n</i>
Belgium	1	Alaska	5
Bolivia	5	Arkansas	9
Brazil	10	Arizona	35
Curacao	3	California	1
Honduras	3	Colorado	17
Italy	10	Florida	6
Mexico	8	Minnesota	1
Romania	8	Mississippi	5
Trinidad	1	New Mexico	40
United States	207	Nevada	14
Total:	256	Oklahoma	8
		Tennessee	1
		Texas	30
		Utah	28
		Wyoming	7
		Total:	207

Table 2. Summary statistics of water EC, PXRF sensed elements and ICP measured elements.

Parameter	<i>n</i>	Minimum	Maximum	Mean	Std. deviation
EC ($\mu\text{S cm}^{-1}$)	252	1.33	157600.00	7837.55	24046.46
ICP Cl (mg kg^{-1})	252	0.10	3688.79	413.33	957.03
PXRF Cl (mg kg^{-1})	252	45.00	56739.00	1968.07	7625.02
ICP K (mg kg^{-1})	252	0.31	846.45	69.90	179.09
PXRF K (mg kg^{-1})	252	113.00	22901.00	331.15	1557.70
ICP Ca (mg kg^{-1})	252	4.55	1105.17	84.03	131.45
PXRF Ca (mg kg^{-1})	252	104.00	1410.00	224.85	174.34

Table 3. Pearson's correlation matrix of PXRF sensed elements and ICP measured elements.

Variables	ICP Cl (mg kg ⁻¹)	PXRF Cl (mg kg ⁻¹)	ICP K (mg kg ⁻¹)	PXRF K (mg kg ⁻¹)	ICP Ca (mg kg ⁻¹)	PXRF Ca (mg kg ⁻¹)
ICP Cl (mg kg ⁻¹)	1^a					
PXRF Cl (mg kg ⁻¹)	0.69	1				
ICP K (mg kg ⁻¹)	0.71	0.61	1			
PXRF K (mg kg ⁻¹)	0.34	0.22	0.20	1		
ICP Ca (mg kg ⁻¹)	0.32	0.24	0.32	-0.031	1	
PXRF Ca (mg kg ⁻¹)	0.33	0.29	0.22	0.006	0.60	1

^aValues in bold are different from 0 with a significance level alpha=0.05

Table 4. Water EC model statistics using PXRF measured elements as predictors.

Predictor (log transformed)	Model^a	Calibration R^2	RMSE_{cali}^b (log $\mu\text{S cm}^{-1}$)	Validation R^2	RMSE_{vali}^c (log $\mu\text{S cm}^{-1}$)	AIC^d	BIC^e
PXRF Cl (mg kg ⁻¹)	PLR	0.77	0.89	0.77	0.95	468.74	484.59
PXRF K (mg kg ⁻¹)	PLR	0.41	1.41	0.31	1.66	630.65	646.50
PXRF Ca (mg kg ⁻¹)	PLR	0.41	1.40	0.18	1.81	628.67	644.52

^aPLR, piecewise linear regression.

^bRMSE_{cali}, root mean squared error of calibration.

^cRMSE_{vali}, root mean squared error of validation.

^dAIC, Akaike information criterion.

^eBIC, Bayesian information criterion.

Table 5. Water EC calibration model equations (n=176) using PXRF measured elements as predictors.

Predictor (log transformed)	Model ^a	Calibration model equation
PXRF Cl (mg kg ⁻¹)	PLR	$\log(\text{EC}) = -1.070 + 1.620 \cdot \log(\text{PXRF-Cl}) - 0.820 \cdot \log(\text{PXRF-Cl}) \cdot \mathbf{1}[\log(\text{PXRF-Cl}) > 5.379]^b$
PXRF K (mg kg ⁻¹)	PLR	$\log(\text{EC}) = -13.780 + 4.132 \cdot \log(\text{PXRF-K}) - 2.899 \cdot \log(\text{PXRF-K}) \cdot \mathbf{1}[\log(\text{PXRF-K}) > 5.434]$
PXRF Ca (mg kg ⁻¹)	PLR	$\log(\text{EC}) = -11.078 + 3.442 \cdot \log(\text{PXRF-Ca}) - 6.104 \cdot \log(\text{PXRF-Ca}) \cdot \mathbf{1}[\log(\text{PXRF-Ca}) > 6.084]$

^aPLR, piecewise linear regression.

^b $\mathbf{1}(x > a)$ is an indicator function. If x is not greater than a , $\mathbf{1}(x > a)=0$, otherwise (i.e. $x > a$) $\mathbf{1}(x > a)=1$.

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HANDHELD XRF ANALYZERS
Limits of Detection

Low-Density Sample Types - (soils, powders, liquids)

Not Measured	<1 %	<0.5 %	<200 ppm
<50 ppm	<20 ppm	<10 ppm	<5 ppm

Periodic Table of Elements															
Elemental Data (Symbol, Atomic Number, Atomic Weight)															
H	He														
Li	Be	B	C	N	O	F	Ne								
Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
Lanthanides 57-71															
Actinides 89-103															

Prediction of water salinity via elemental concentration:

- Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Calcite: CaCO_3
- Halite: NaCl
- Sylvite: KCl
- Etc....