

# Speciation of Elements via a Sequential Extraction Procedure in Municipal Wastewater Biosolids from Three Rural WWTP in East Texas (USA)

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**Abstract** In this data article, the bioavailability of elements in municipal wastewater sludge (also known as biosolids) in samples collected from three treatment plants in East Texas, USA was evaluated. Although detailed speciation of the metals were assessed by using inductively coupled plasma optical spectroscopy (ICP-OES), and were discussed in the research article titled “Evaluating bioavailability of elements in municipal wastewater sludge (Biosolids) from three rural wastewater treatment plants in East Texas (USA) by a sequential extraction procedure” [1], this report presents the absolute raw concentrations and fractionations of the 26 metals from the biosolids (Nacogdoches Wastewater Sludge, Lufkin Wastewater Sludge, and Neches Compost sludge; NWWS, LWWS, NCS) produced from three wastewater treatments plants in East Texas. This data is important and useful for understanding the bioavailability of each of the elements in biosolids generated from activated wastewater treatment plants.

**Keywords:** *Sludge/biosolids, element bioavailability, wastewater treatment plants, metal speciation, ICP-OES*

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## 1. Introduction

Metals in soils and various other matrices can exist in various bioavailable forms [2]. The speciation of each metal depends on a variety of factors including pH, the metal itself, and the type of soils [3]. The bioavailable fractions are important in the assessment of metal translocation from soils to roots and to other plant parts. The use of continuous applications of composted wastewater sludge to soils may lead to bioaccumulation into various trophic levels along the food chain.

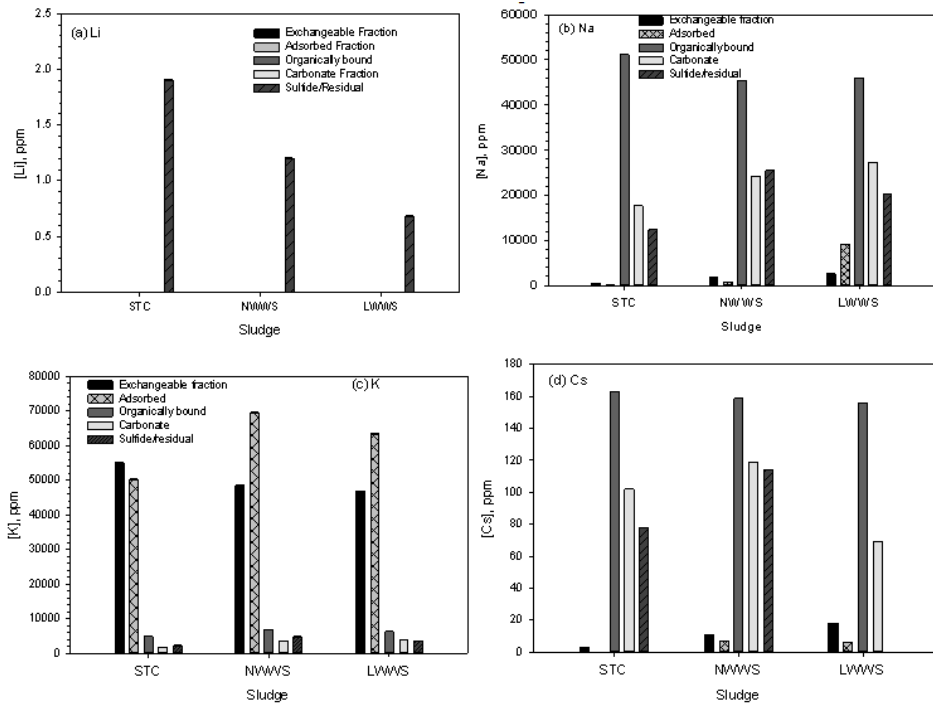
Various methods have been used to speciate metals into different forms in soils. The popular Tessier method [4] is often used to fractionate metals into five fractions, namely, exchangeable, carbonates, Fe–Mn oxides, organic, and sulfide/residual. The other methods such as Community Bureau of Reference (BCR) [5], Sposito’s method [6], Maiz, Galan, Geological Society of Canada (GCS) procedures [7,8] are also utilized for speciation. Other analytical procedures used have modified these methods. A majority of these methods often make use of a five-step process which fractionate metals into the exchangeable, adsorbed, organically bonded, carbonate and the sulfide/residual fractions [9,10]. Each of these methods have strengths and weaknesses, based on their objectives. Yet broadly, they are precise and accurate, and reflect on

the concentrations and fractionations of the metals. In this data note a modified Tessier method was used to provide the absolute concentrations of metals in composted wastewater sludges. Previous reports gave the relative percentage occurrences of each metal or element [9]. Herein, graphical presentations of the actual measured amounts not reported before are provided. In addition, the multivariate statistical method, Principal Component Analysis (PCA) was utilized to showcase correlations between the various elements.

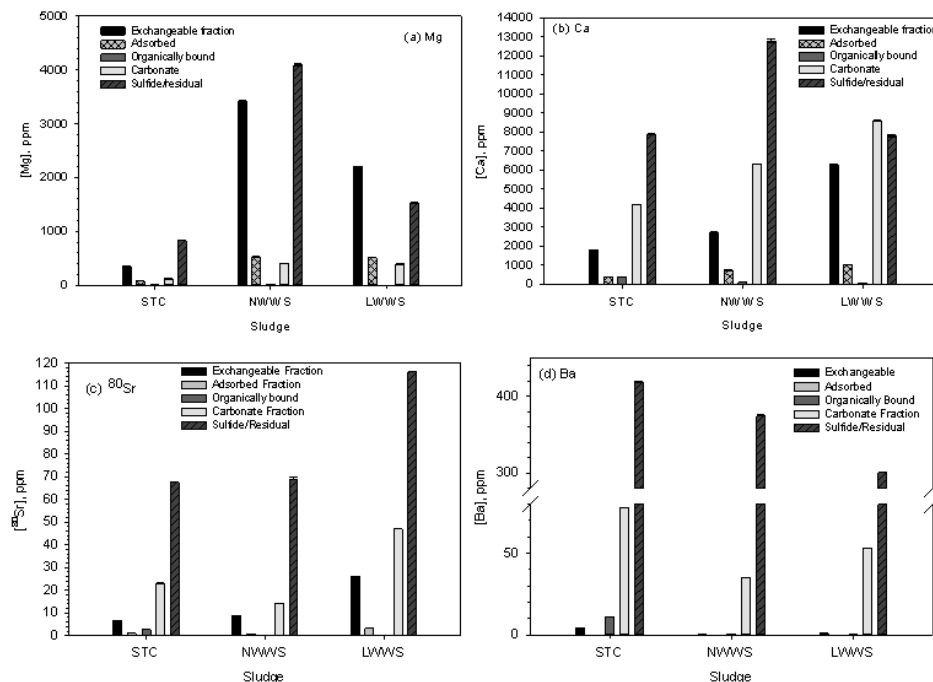
Three wastewater treatment plants in deep East Texas, namely, Nacogdoches Wastewater treatment plant (NWWTP), Lufkin Wastewater Treatment Plant (LWWTP) and Neches compost facility (NCF) produce composted sludges. In particular, NCF, produce a biosolid commercially sold under the trade name Soil Therapy Compost (STC). The objectives of this research compliments data reported before [9]. Therefore, this report documents concentrations and speciation of the metal concentrations in the biosolid wastewater sludge and composted wastewater sludge (CWS). The raw concentrations and fractionations of 26 metals (macroelements: Ca, Fe, K, Mg, Na, P, S, Li, Cs; microelements: As, B, Ba, Cd, Co, Cu, Hg, Mn, Mo, Pb, Se, V, Zn, Ni, Al, Cr, Sr) from the three biosolids (NWWS, LWWS, NCS) are presented in this article. This data is important and useful for understanding the bioavailability of the each of the elements in biosolids

generated from the activated wastewater treatment plants. The elemental metal concentrations data are valuable for referencing, inter-elemental comparative compositions, and differentiation between sludge samples from sites around the world. Further, this information is useful for comparisons to other sludge samples from various treatment plants. Finally, the values of this data are important in the following ways. Firstly, the data provides

important information for identification of elemental compositions in sludge samples in activated wastewater treatment plants. Secondly, the bioavailability patterns for each element are important for assessing appropriate amounts in sludges suitable for use when applied to various soil amendments. Thirdly, this data is useful to soil scientists, and environmental scientists. The data is useful in metal-soil-plant modeling studies.



**Figure 1.** Sequential fractionation of Group 1A metals, Li (a), Na (b), K (c), and Cs (d) in Soil Therapy Compost (STC), Lufkin wastewater sludge (LWWS) and Nacogdoches wastewater sludge (NWWS). (From Ref. # [9]). These figures are modified from Ref. [9] and represent absolute abundances of elements



**Figure 2.** Sequential fractionation of Group 2A metals, Mg (a), Ca (b), <sup>80</sup>Sr (c), and Ba (d) in soil therapy compost (STC), Nacogdoches wastewater sludge (NWWS) and Lufkin wastewater sludge (LWWS). From Ref. # [9]. These figures are modified from Ref. [9] and represent absolute abundances of elements

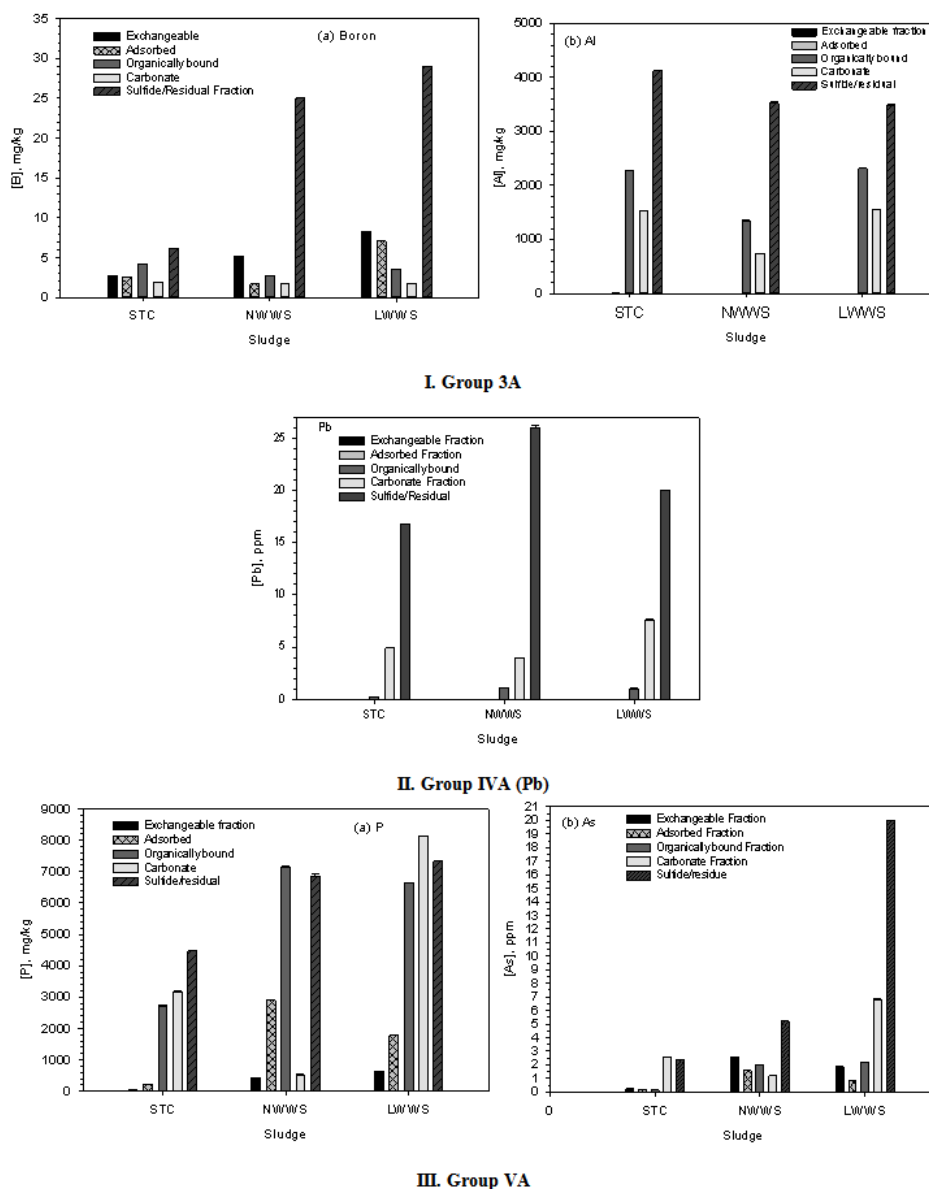
## 2. Materials and Methods

The experimental methods and procedures that allowed the data in this article are described in references [1,11,12,13] and other citations therein. Here, only the protocol for ICP-OES and ICP-MS (inductively coupled mass spectrometry and speciation data is provided.

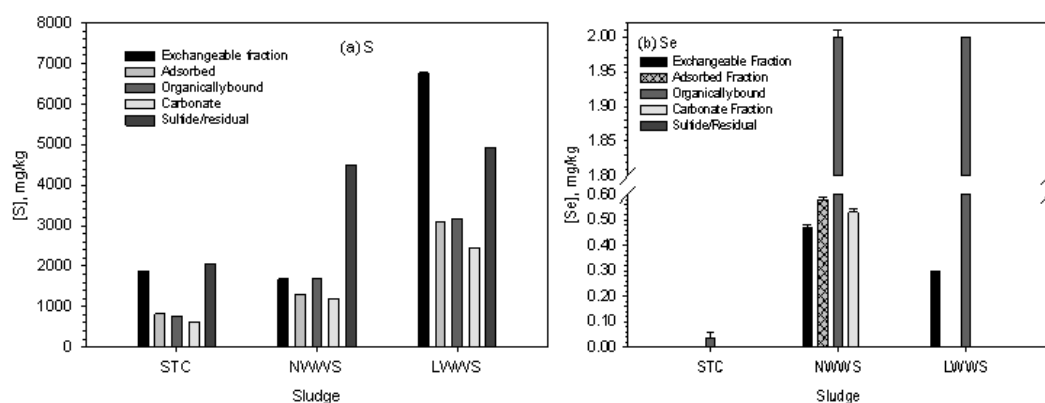
### 2.1. Collection of Samples and Instrumentation, and Quality Assurance

Sludge samples from three wastewater treatment plants, namely, NWWs, LWWS and NCF in East Texas (following References [1,11,12,13]) were investigated for their metal concentrations. The concentrations of metals in sludge samples were determined by using inductively coupled plasma optical emission spectroscopy or

inductively coupled plasma mass spectrometry (ICP-OES, Dual view, Thermo Scientific (USA) and ICP-MS) [14] were used for element concentration analyses. Triplicate or quadruplicate samples from each wastewater treatment plants were assessed. The raw data in this paper show actual absolute metal concentrations and their speciation into five different forms (Figure 1, Figure 2, Figure 3, Figure 4, Figure 5), and the approximate compositions. The data for metal concentrations and corresponding bar graphs, is presented herein in Figures 1, 2, 3, 4, and 5. Principal component analysis (PCA) was used to statistically find the relative and predominant forms prevalent in different fractions for each metal (Figure 6, Figure 7, Figure 8, Figure 9). Figures 6 - 9 depict sample Principal Component Analysis data (PCA) for the three samples showing concentrations partitioned into the respective fractions.



**Figure 3.** Sequential fractionation of Group 3A (panel I: (a) B and Al (b)), Group 4A (Pb) and Group 5A (Panel 3: P (a) and As (b)) in STC, NWWs, and LWWS. From Ref. # [9]. These figures are modified from Ref. [9] and represent absolute abundancies of elements



**Figure 4.** Sequential fractionation amounts of Group 6A elements S (a), and Se (b) in STC, NWWS, and LWWS biosolids. From Ref. # [9]. These figures are modified from Ref. [9] and represent absolute abundancies of elements

## 2.2. Quality Assurance and Quality Control

Previous reported data [14] showed the quality assurance and quality controls between the measured and expected concentrations. For analysis of total metals in sludge, 2.0000 g air-dried samples were digested using concentrated HCl/HNO<sub>3</sub> following USEPA method 3050B in a digestion block as stated in Refs. [1,11,12,13]. Triplicate samples were run as depicted in References [1,11,12,13]. Briefly, samples were digested in SCP digitubes in a digestion block ((SCP Science, www.scpscience.com, Granham, NY). After complete digestion, solutions were filtered and the filtrate analyzed using an ICP-OES (iCAP™ 7400, ICP-OES spectrometer, Dual view, Thermo Scientific (USA)). The metal concentrations in solution samples were then determined by using known standards (5 ppm, 25 ppm, 50 ppm) and plotting standard calibration curves, as described in Ref. [9].

## 3. Results & Discussion

### Principal Component Analyses

The statistical technique, Principal Component Analysis (PCA) was used to find components with largest possible variance in the data set. The PCA method was utilized to partition the available data into linearly uncorrelated variables in a way that concentrates the maximum variance in the group into the first few components. Interrelations amongst metal concentrations in the five fractions were investigated by PCA for each WWT sludge. In addition, biplots of the first two PCs was used to provide a visual assessment of the metals and the speciation fractions were separated in PC space. Principal Component Analysis (PCA) was performed using XLSTAT software (Version 2020.1) and R version 4.0.3 (2020-10-10, <https://www.R-project.org/>) with function: prcomp.

Two main component groups were observed by PCA for all fractions, contribution ratios of the first and second principal components were 54.85 and 37.94% (92.79% total) for NWWS, 58.65 and 35.84% (94.50% total) for LWWS samples, 59.80 and 18.95% (78.75% total) for NCF, respectively. Figures 6, 7, 8 and 9 show that the first two components F1 and F2 contribute (F1 (Component 1) = exchangeable, F2 = adsorbed, F3 = organically bound, F4 = carbonate, F5 = sulfide/residual) greatly to the

speciation of the metals in the three biosolids, in the range 35.84% - 58.65% and 37.84% - 54.85% for LWWS and NWWS, respectively. This shows that the metals are bioavailable to the environment on continuation application to soils; in agreement with published data [7,15]. Further it is noted that positive correlations are evident between the exchangeable and adsorbed, and organically bound/ carbonate /sulfide residual fractions for all biosolids (Figure 6, Figure 7, Figure 8). It is further noted that, with the exception of Group 1A metals, most metals in biosolids are speciated in higher concentrations in the sulfide/residual fractions. This is in agreement with studies by Tessier et al. [4] and Onchoke et al. [9].

## 4. Conclusions

Deciphering the bioavailability and speciation of metals - and in general, elements in environmental matrices, is critical to understanding mechanisms through which they are transported. Notably, the modified Tessier speciation protocol provides the absolute concentrations in biosolids generated from wastewater treatment plants in East Texas. Notably, most speciation of metals in the biosolids investigated provide similarities in metal concentrations. This indicates that the design of the WWTPs that generate biosolids are similar. Although, results show most of the regulated metals are below USEPA regulations, it is suggested that future assessments of other pollutants (such as emerging pollutant) be probed. In particular, the bioavailability of elements from the residual fractions for longer periods of study is necessary.

### Ethics Statement

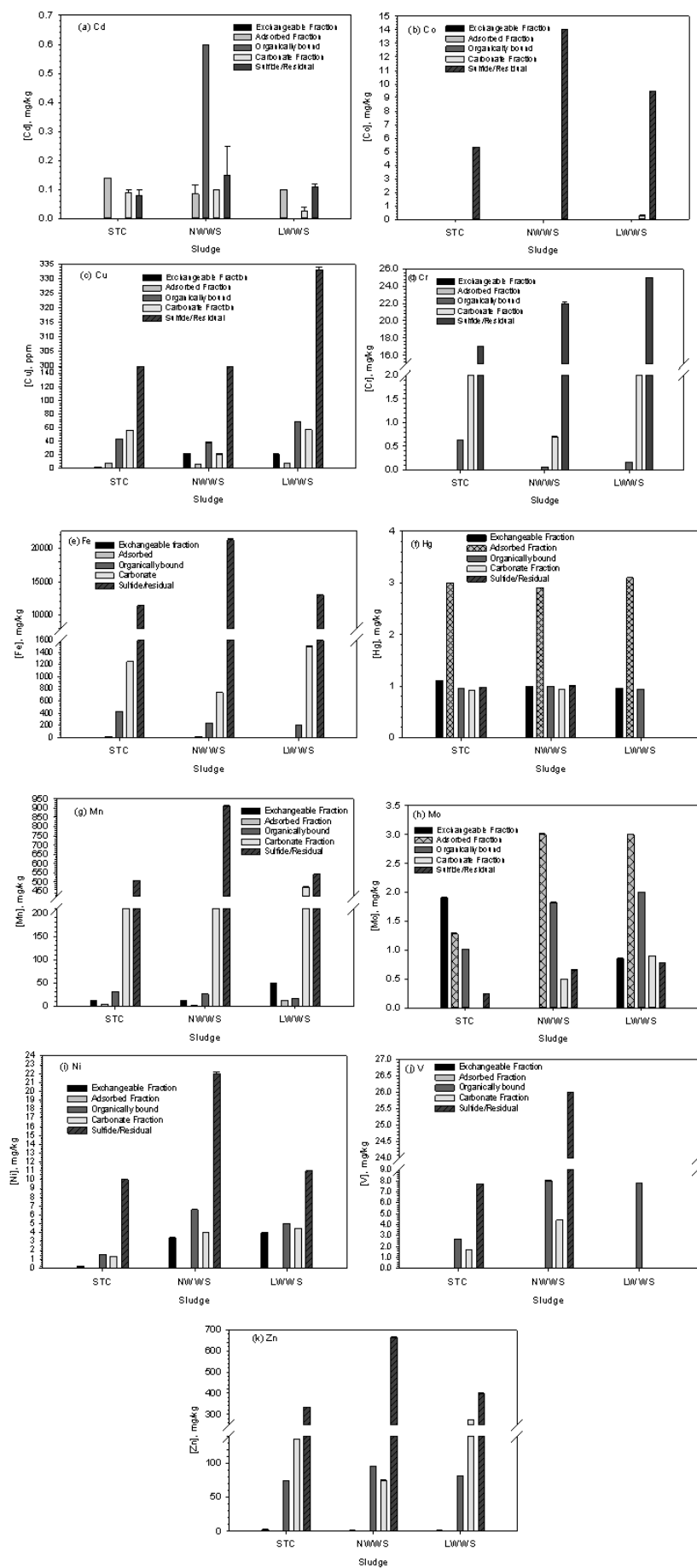
Not applicable.

### CRedit Author Statement

**Kefa K. Onchoke (KKO):** Project administration, Conceptualization, Resources, Methodology, Investigation, Data Curation, Formal Analysis, Validation, Writing - original draft, Writing- reviews and editing, Visualization. Supervision, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.



**Figure 5.** Sequential fractionation of transition metals (Groups Transition metals Groups 1B -8B). From Ref. # [9]. These figures are modified from Ref. [9] and represent absolute abundances of elements

## NWWS1

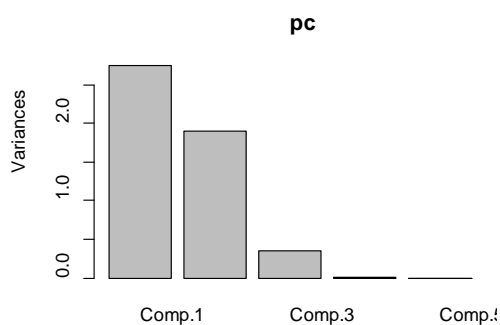
Importance of components:

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5
Standard deviation	1.6560	1.3773	0.5915	0.0871	0.056051
Proportion of Variance	0.5485	0.3794	0.0700	0.0015	0.00063
Cumulative Proportion	0.5485	0.9279	0.9979	0.9994	1.0000

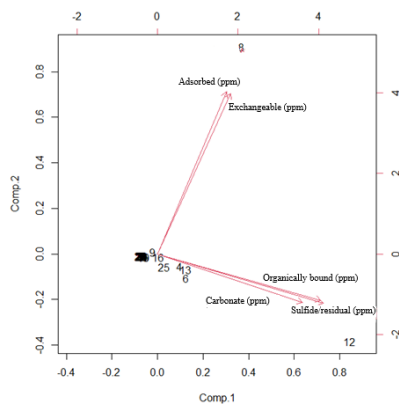
## LWWS1

Importance of components:

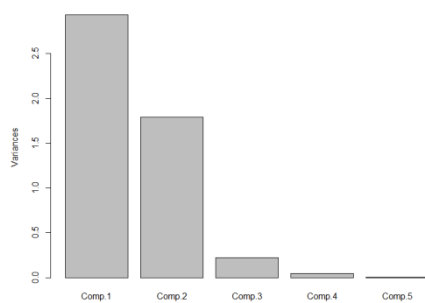
	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5
Standard deviation	1.7125	1.3387	0.4737	0.2120	0.0766
Proportion of Variance	0.5865	0.3584	0.0449	0.0090	0.00120
Cumulative Proportion	0.5865	0.9450	0.9000	0.9988	1.0000



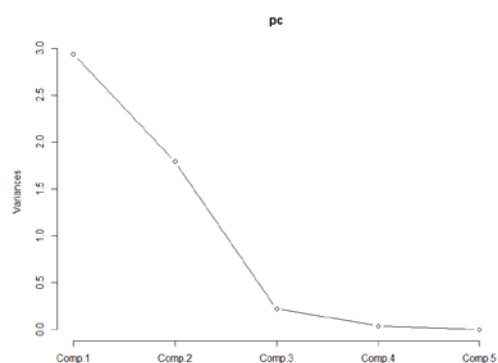
**Figure 6.** Principal component analysis (PCA) for fractionations of metals in NWWS Importance of the components (PC1 (F1) versus PC2 (F2) biplot exhibiting correlation among the different inductively coupled plasma reported elements in NWWS



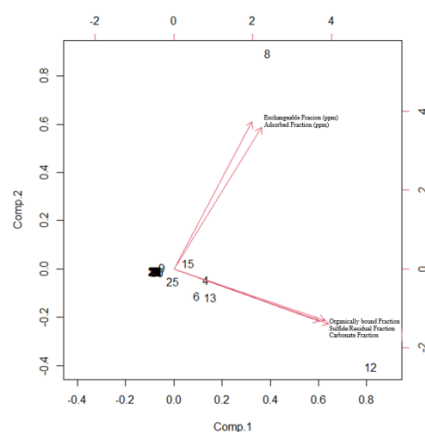
**Figure 7.** Importance of the components (PC1 (F1) versus PC2 (F2) biplot exhibiting correlation among the different inductively coupled plasma reported elements in NWWS (F1 (Component 1) = exchangeable, F2 = adsorbed, F3 = organically bound, F4 = carbonate, F5 = sulfide/residual)



**Figure 8a.** Principal component analysis (PCA) for fractionations of metals in LWWS (F1= exchangeable, F2 = adsorbed, F3 = organically bound, F4 = carbonate, F5 = sulfide/residual)



**Figure 8b.** Graphical presentation of Principal Component Analysis (PCA) for fractionations of metals in LWWS (F1= exchangeable, F2 = adsorbed, F3 = organically bound, F4 = carbonate, F5 = sulfide/residual)



**Figure 9.** PC1 (F1) versus PC2 (F2) biplot exhibiting correlation among the different inductively coupled plasma reported elements (F1= exchangeable, F2 = adsorbed, F3 = organically bound, F4 = carbonate, F5 = sulfide/residual)

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