Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20222

66 (2017) 346–357
March

Metal retention potential of sediment and water quality in the Mooi River, South Africa

Alusani Manyatshe[a], Elvis Fosso-Kankeu[a,*], Divan van der Berg[a], Nico Lemmer[a], Frans Waanders[a], Hlanganani Tutu[b]

[a] *School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, Potchefstroom, South Africa*
email: manyatshealusani@gmail.com (A. Manyatshe), kaelpfr@yahoo.fr (E. Fosso-Kankeu), divanvdberg1@gmail.com (D. van der Berg), nico.lemmer@nwu.ac.za (N. Lemmer), Frans.Waanders@nwu.ac.za, (F. Waanders)
[b] *Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, P. Bag X3, WITS 2050, South Africa,*
email: hlanganani.tutu@wits.ac.za (H. Tutu)

Received 8 April 2016; Accepted 9 September 2016

ABSTRACT

The potential metal retention by sediments along the Mooi River and connected streams in the vicinity of Potchefstroom, South Africa, was evaluated using the four-stage sequential extraction procedure. The sediments were characterized using XRD, XRF and FTIR techniques. The physico-chemical parameters and heavy metals content of water were also measured to evaluate their impact on water quality and fitness for human consumption. The highest percentages of Fe, total Cr and Mg (83.46, 27.43, and 88.83%, respectively) were predominantly associated with the residual fraction of the sediments. Elements such as Ca and Mn were mostly bound to the exchangeable fraction of the sediments. Association of Fe, total Cr and Mg with the residual fraction as predicted by speciation calculations suggests that these metals are strongly bound to the sediments and therefore less susceptible to cause pollution. The mobility order of the heavy metals in the sediments samples was Ca > Mn > Mg > Fe > Cr. For the first time the implication of organic matter in the sediments along the Mooi River on the retention of metals was investigated and it was found that organic matter occurring in various concentrations in these sediments, contained binding groups such as C–O, C–C=C, O–H and =C–H much likely to contribute to the retention of metals in the exchangeable fraction of the sediments. The amount of inorganic pollutants in water was found to basically decrease moving downstream, but the water quality remained unfit for human consumption at most of the sampling points.

Keywords: Bioavailability; Fractions; Metals; Mobility; Mooi River; Sediments; Sequential extraction

---

1. Introduction

The contamination of rivers by heavy metals is a worldwide problem [1]. Heavy metals are carried through the rivers and streams in different forms including dissolved species or as part of the suspended sediments [2] which contaminate the aquatic environment causing instability of the ecosystem due to their toxicity [3]. Some metals are essential to living organisms when available in small quantities, but they become toxic at higher concentrations [4] and thus leading to reduced quality of water, making it unfit for various uses [5]. The water quality is defined in terms of the chemical, physical and biological parameters that include the temperature, pH, rainfall, salinity, electrical conductivity, redox potential, dissolved oxygen and carbon dioxide [6]. The quality of water can also be reduced by the local geology; however, human practices have a much larger influence in the reduction of water quality [7]. For example, anthropogenic activities such as mining activities, industrial wastewater, domestic sewage, operation of wastewater treatment plant and agricultural practices are among the most vital sources of heavy metals found in the aquatic environment [8]. Heavy metals are among the major pollutants

---

*Corresponding author.

of the aquatic environment as they can be potentially detrimental to human health [9], and the situation is exacerbated because they are persistent and bio-accumulative in nature [10]. These heavy metals can be dispersed and accumulated in plants and animals [11], thus entering the food web [12]. The developing countries are affected the most by this metal pollution due to the poor management of their environment as well as incapacity to afford the operating costs of pollution treatments facilities [13]. When entering into the aquatic environment, metals are partitioned between the water column and sediments [14]. In the sediments, they are further partitioned into different phases including carbonates, oxides, hydroxides and sulphides [15].

The metal distribution, mobility and their availability in the environment do not necessarily depend on their total concentration but on the physical-chemical forms in which they are partitioned and this can be studied through sequential extraction and speciation techniques [16,17]. To determine the partitioning of heavy metals, various methods involving both the single and sequential extraction schemes have been employed for the past decades [8]. In this study, a four-stage sequential extraction procedure proposed by the European Communities Bureau of References (BCR) was employed. This method has been successfully used by other researchers [10,18].

The high concentration of heavy metals found in the Mooi River at Potchefstroom has been reported to be mainly influenced by the gold mining activities in the vicinity of the Wonderfonteinspruit [19,20]. However, the degradation of the water quality in the Mooi River as it flows through the city of Potchefstroom is also exacerbated by effluents from the municipality's waste water treatment works and some major industries [21]. Due to this concern, many studies have been conducted in the catchment of Wonderfonteinspruit (WFS) to determine the level of heavy metals in surface water and sediments [22–25]. However, to the best of our knowledge, no study has so far investigated the typical binding groups contributing to the retention of metals in the sediments along the Mooi River. The objectives of this study were: (i) to investigate the distributions of the selected metals in different fractions of the sediments collected from the Mooi River and connected streams using the BCR extraction procedure, (ii) to characterise the sediment samples using XRD, XRF and FTIR spectroscopy, (iii) to determine the organic groups in the sediment which are likely to bind to metals in solution, and (iv) to assess the quality of water.

1.1. Study area

The Mooi River originates from a large catchment area from the Bovenste Oog spring as well as the inflow of the Wonderfonteinspruit and the confluence with Loopspruit, south of Potchefstroom [18]. The study area is between the latitudes 26°22′ and 26°54′ and longitudes 27°5′ and 27°57′ (Table 1). The average temperature of the study area is 16.9°C, and the mean annual precipitation of 663.5 mm with a reported mean annual run-off into streams of 29.5 mm [26]. The Mooi River catchment includes several reservoirs, the largest of which are the Klerkskraal Dam (8 million m^3), Boskop Dam (21 million m^3) and Potchefstroom Dam (2 million m^3) [27]. The Klerkskraal, Boskop, and Potchefstroom Dams supply domestic and industrial water to Potchefstroom through the Mooi River State Water Scheme [18]. These dams are also used for irrigation purposes in Potchefstroom and the vicinity [28]. Geologically, the Mooi River is partly located on a dolomite rock system which covers almost 75% of the area [27].

Table 1
Sampling point description and coordinates

Sample number	Description	Location	
		S	E
1	Driefontein mine canal	26°22′30.71″	27°19′57.34″
2	Turffontein eye	26°24′51.04″	27°10′13.32″
3	Gerhardminebron eye	26°28′47.61″	27° 9′5.70″
4	Boskop Dam	26°33′56.0″	27°07′13.7″
5	Potchefstroom Dam	26°39′55.67″	27° 5′34.14″
6	Mooi River	26°40′55.6″	27°05′53.8″
7	Mooi River	26°42′04.1″	27°06′22.6″
8	Mooi River	26°42′34.1″	27°06′20.2′
9	Mooi River	26°52′49.8″	26°57′51.4″

2. Methodology

2.1. Sampling

A total of 9 sampling sites were selected along the Mooi River, karst spring and a mine canal to investigate the contamination of sediments and water by metals (Fig. 2). The coordinates of the sampling points are presented in Table 1. Sampling point 1 is the Driefontein mine canal connected to the Mooi River, sample 2 (connected to the karst spring) and 3 are streams forming part of the Mooi River systerm. Samples 4 and 5 are located within the Boskop and Potchefstroom Dams, respectively; both dams are situated along the Mooi River. Sampling points 6–9 are located along the Mooi River. These sampling points received effluents from anthropogenic sources such as mining activities (Fig. 1). The positions of the collection points were determined by personnel from the Department of Water and Sanitation located at Boskop Dam; these points are mapped for routine monitoring of pollution problems in the area.

The selected samples (collected once) were assessed for their metal retention potential. Sediment samples were collected inside of the Mooi River and connected streams (few metres away from the bank) and the depth varied from 0 to 5 cm using a grab sampler. A sub-sampling of the sediments was done by taking the upper 5 cm of the sample from the grab and then stored in clean plastic bags that was quickly tighten to avoid oxygen penetration (preserve biological or chemical equilibria). Sediment samples were then kept at 4ºC prior to the analysis. A large amount of sediment samples was collected (about 3 to 4 kg) at each site in order to have enough samples for experiments such as sequential extraction, mineralogical and chemical compositions, total organic carbon and identification of functional groups

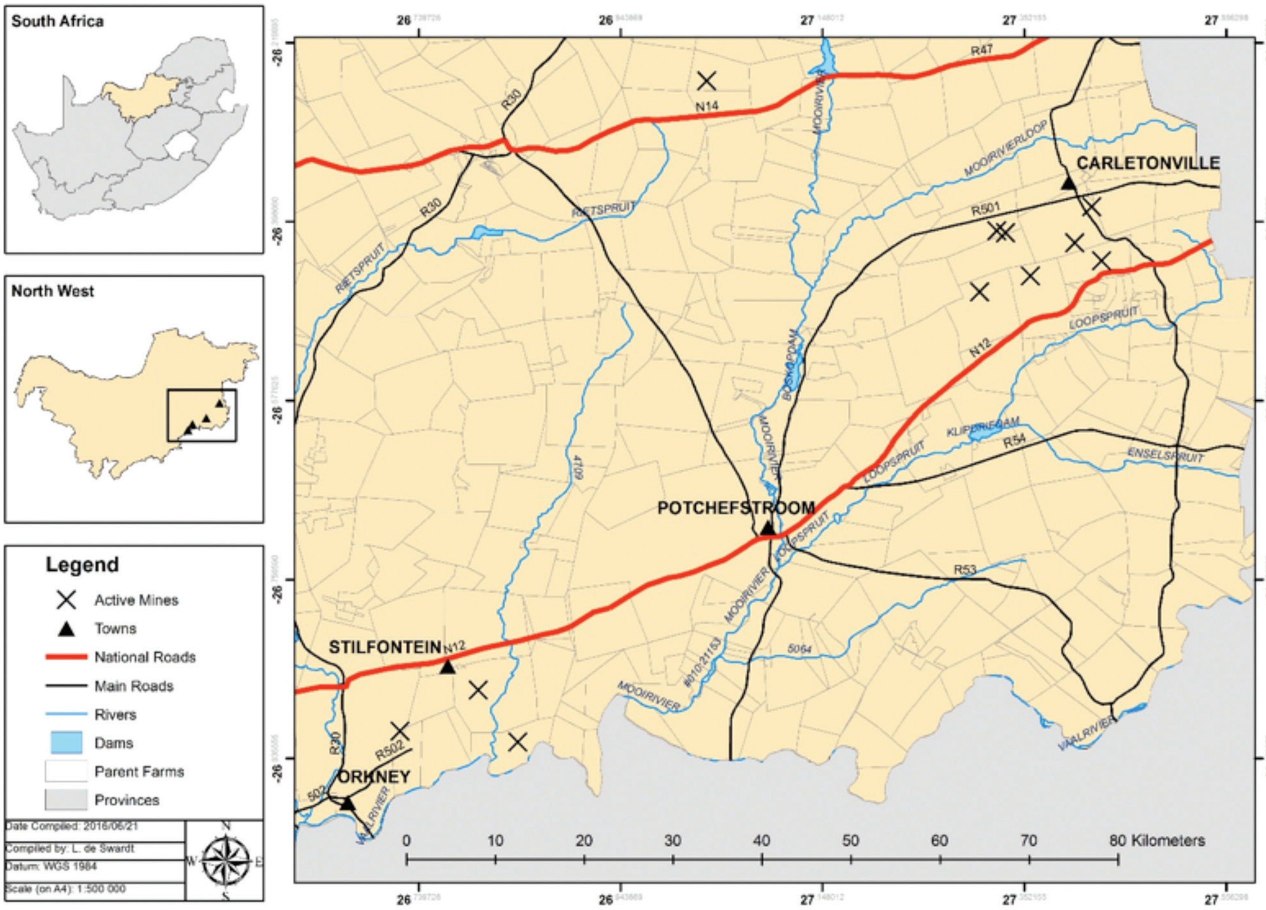

Fig. 1. The study area in the North West Province of South Africa (the Mooirivierloop is now known as the Wonderfonteinspruit).

using Fourier transform infrared spectroscopy (FTIR). Water samples were collected in 500 mL according to accepted methods [29]. Before use, the bottles were washed with deionised water and then rinsed with the water of the sampling site during sampling. The water samples were collected at the surface of the streams, using 500 mL polyethylene bottles that were rinsed with river water and then deep at the subsurface with the mouth of the bottle facing the direction of water flow. However, at the dams, samples were collected few metres from the Dam wall at the depth varied from ±1 to 2 m using a depth-sampler. Immediately after water sampling, the following physico-chemical parameters were measured using appropriate probes and meters (Hanna Instrument Inc, USA): temperature (°C), pH, electrical conductivity (mS/cm), dissolved oxygen (mg/L) and redox potential (mV). The pH meter was calibrated before analysis in the field, using reference buffer solutions. The samples were then stored in cooler boxes filled with ice to ensure proper preservation during transportation to the laboratory where further analyses were done.

2.2. Experimental protocol

Sediment samples were dried at 50ºC in an oven, ground using a mortar and pestle and sieved to particle sizes of <63 μm, which corresponds to the size fraction used in previous studies focusing on the analysis of heavy metals from sediments [30,31]. The sequential extraction of heavy metals was performed using the BCR sequential extraction method. The mineralogical composition and major components of metals were determined using XRD and XRF while the total organic carbon was determined by using the Wakley Balk titration method. The functional groups in the sediments were identified using FTIR spectroscopy (Thermo Scientific, France). The total analysis of heavy metals content in sediment samples was conducted using ICP-OES (Agilent Technologies, USA).

The alkalinity (as HCO_3^- and CO_3^{2-}) was measured through titration with 0.1 M H_2SO_4. The concentrations of SO_4^{2-}, NO_3^-, and CN^- in water samples were measured using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The concentration of Cl^- in water samples was measured through titration with a silver nitrate and potassium dichromate solution. The heavy metals concentrations (Fe, Ca, Mn, Mg, and total Cr) were measured using ICP-OES. Organic carbon content was determined according to the method reported by Avramidis et al. [32]. The BCR sequential extraction was conducted according to the procedure described in Fig. 3.

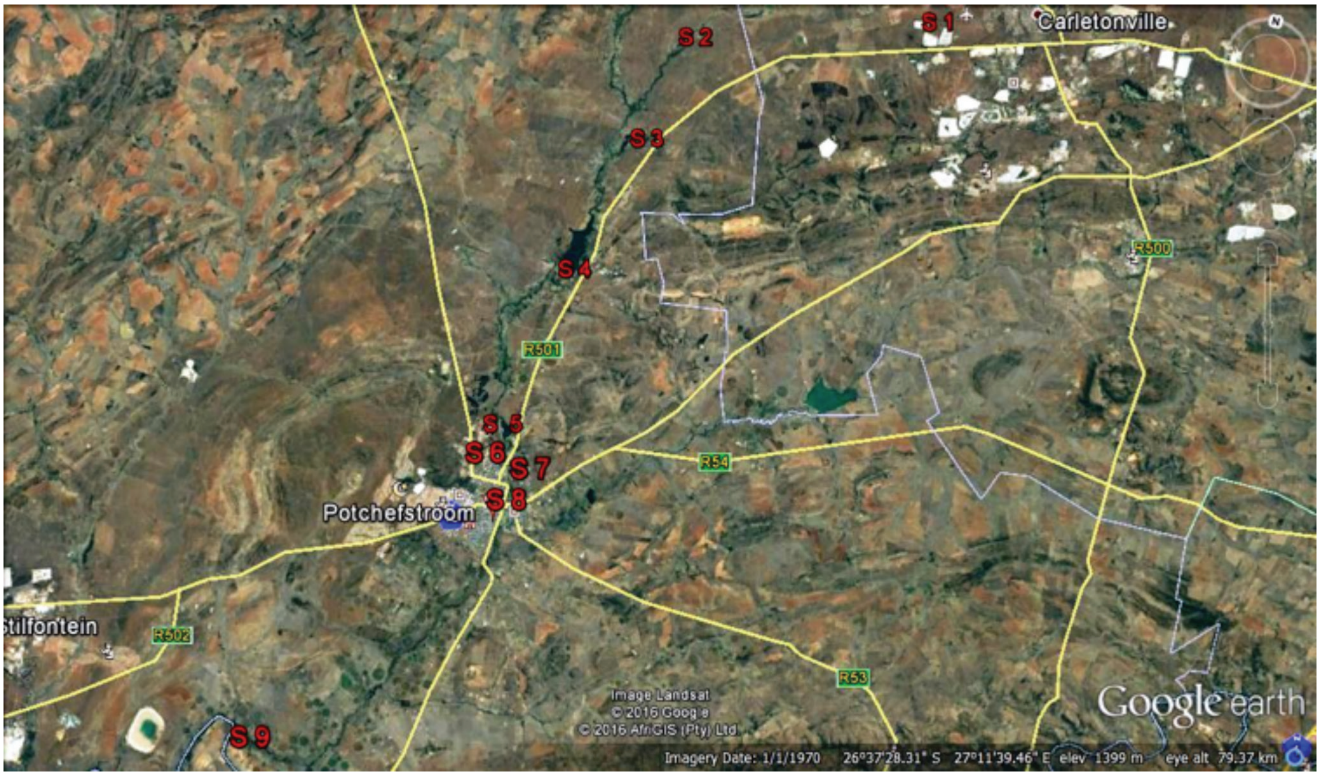

Fig. 2. Map of the study area showing sampling points (1–9).

2.3. Reagents

Sequential extraction: high quality reagents of analytical grade and deionised water, supplied by Oasis Water (Potchefstroom, South Africa), were used for all the preparations and analyses. Diluted standard solutions were prepared from the stock standard solutions. A working solution of 0.11 M acetic acid, 0.1 M $NH_2OH \cdot HCl$ (adjusted to pH 2 with 2 M nitric acid), 8.8 M hydrogen peroxide (pH of 2–3), 1.0 M ammonium acetate (adjusted to pH 2 by adding a concentrated HNO_3) and aqua regia (HNO_3 + 3HCl) were prepared using distilled water.

For the quantification of organic carbon, diluted standard solutions were also prepared from the stock standard solutions. Therefore, solutions of 1.0 M potassium dichromate (dried at 105°C), sulphuric acid 98%, 0.4 M ferrous sulphate and ferroin indicator were prepared using the deionised water.

To assess the quality of water, specific test kits were used to measure the level of sulphate, nitrate and cyanide in water. About 20 % nitric acid was used to dilute the water samples prior to the analysis of heavy metals by the ICP-OES instrument.

2.4. Fourier transform infrared spectroscopy (FTIR) method

The binding groups in the sediment samples collected from the Mooi River network and connected streams were identified using FTIR spectroscopy (Thermo Scientific Nicolet iS10 FTIR Spectrometer, France). The FTIR spectra were collected within the wavenumber range between 400 and 400 cm^{-1} using the potassium bromide (KBr) pellet technique.

2.5. Sequential extraction method

To evaluate the binding forms of heavy metals in the sediment samples, the BCR sequential extraction was applied. The details of the different steps and reagents used are shown in the following flowchart.

3. Results and discussion

3.1. XRD analysis of mineralogical composition

The mineralogical compositions of sediments are presented in Fig. 4. These results show that the most abundant mineral is quartz, within a range of 29–89% as determined in sediments samples collected from the Mooi River and its connected streams. The rest of the minerals such as clinoferrosilite, diopside, welinite, iron silicide, rutile, clinoenstalite, kyanite and calcium oxide iron were detected in one or more samples.

3.2. XRF analysis of major components

The results of the XRF analysis of the major components are illustrated in Fig. 5, presented as percentages

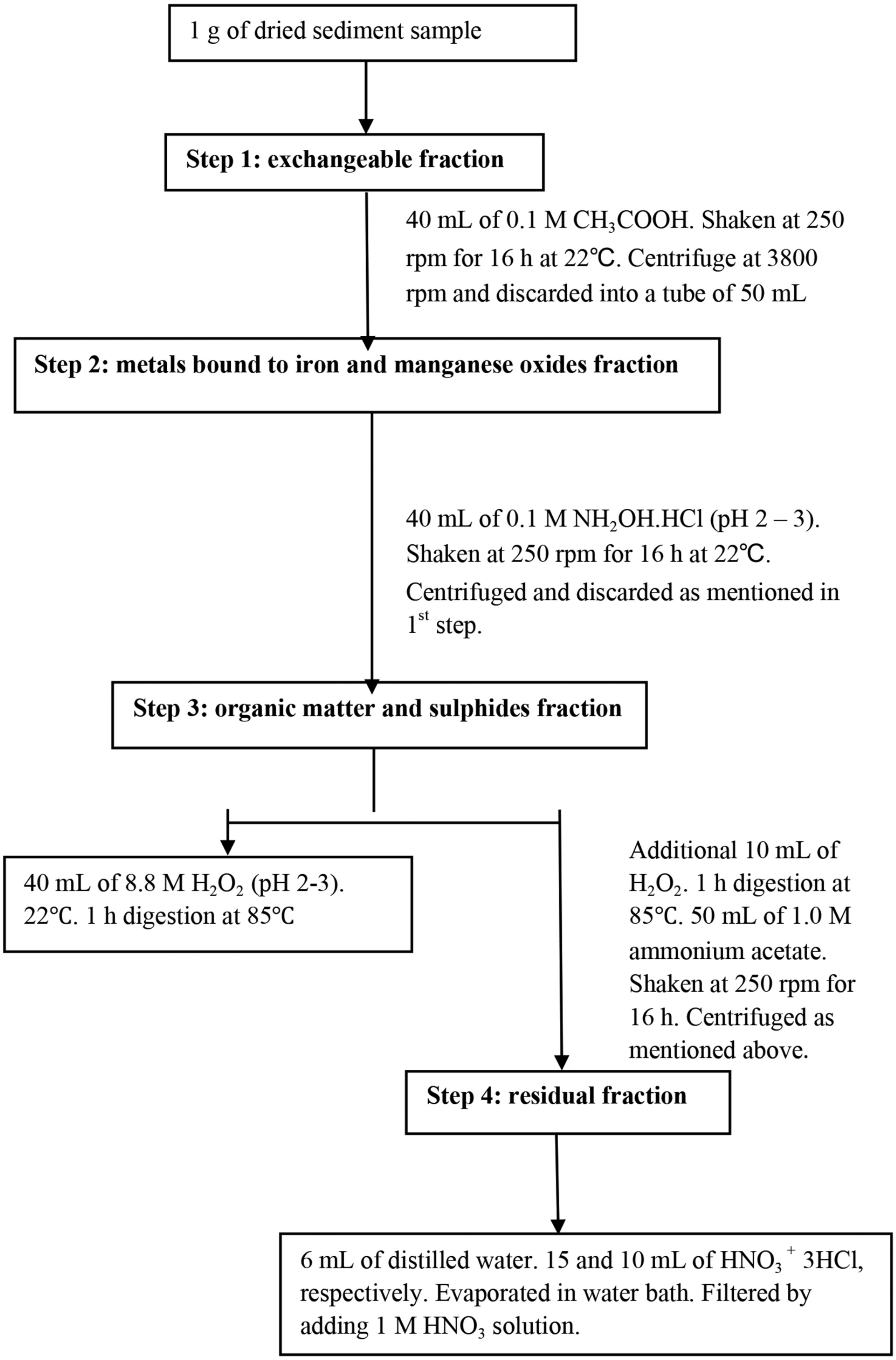

Fig. 3. Flowcharts for the BCR speciation scheme of sediments.

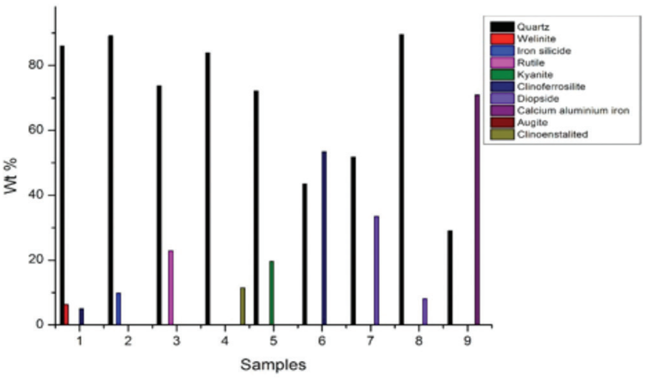

Fig. 4. Mineralogical composition of the sediments (fraction <63 μm) from the Mooi River.

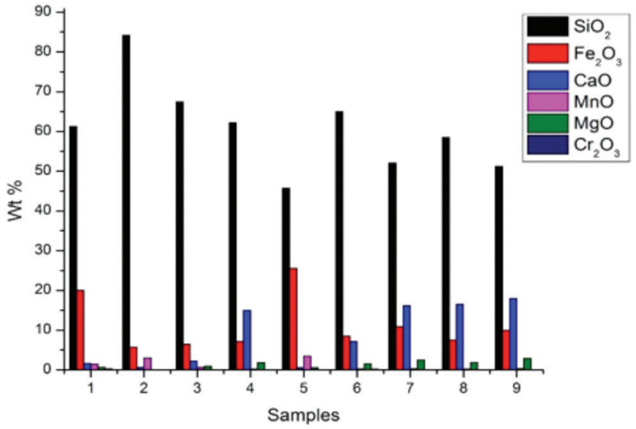

Fig. 5. Selected major and trace components of sediments (fraction < 63 μm).

of the corresponding oxides. The following oxides were observed to be dominant in all sampling sites studied: SiO_2 (45.72–84.13%), CaO (0.62–17.96%), Fe_2O_3 (5.73–25.51%), MgO (0–2.48%), MnO (0.16–3.45%) and Cr_2O_3 (0–0.25%). Most of these element oxides were mainly dominant in sample 1 to 8 (Mooi River and connected streams); however, higher concentrations of magnesium were found in sample 9 and 8 (Mooi River). The abundance of these elements is likely due to the type of rock, which covers most part of the study area. The dominant elements such as Si, Ca, Fe, Mg, Mn, and Cr can be potentially toxic to the aquatic environment. The nature of the sediments determined in this study is similar to that of the sediments from the four main rivers in Kolovo [30].

3.3. Metal speciation in sediment

The percentage concentrations of Fe, Ca, Mn, Mg and Cr extracted from sediments at each step are illustrated in Fig. 6. Elements such as Ca and Mn were mostly recovered in fraction 1 of the sediment samples collected from the Mooi River and connected streams. The rest of the metals were found to be strongly bound to the crystalline structure of sediments. Mobility and bioavailability of metals is related to the solubility; therefore, bioavailability decreases in order of exchangeable > reducible > oxidizable > residual. The mobility and bioavailability of metals extracted from the studied sediments samples, decreased in the following order: Ca > Mn > Mg > Fe > Cr. In this study, high concentration of Fe in sediments samples collected from the Mooi River and connected streams were associated with the residual fraction (83.46%) and a lesser extent to the exchangeable fraction (1.65%), reducible fraction (5.89%) and oxidizable fraction (7.25%). It therefore ensues that the mobility and bioavailability of Fe will be very low due to the smaller amounts bound to exchangeable fraction, and this implies that there will be a relatively lower risk of toxicity related to the presence of this element in the surface water. These results were in agreement with the studies performed by Yuan et al. [33] who found that more than 90% of the total Fe was bound to the residual fraction.

Ca and Mg were obtained in all four fractions of the BCR sequential extraction method. In sediments collected from the Mooi River and connected streams, high recovery percentages of Mg from the residual fraction were 88.83%. Its contribution to exchangeable, reducible and oxidizable were 21, 9.64 and 16.39%, respectively. Whereas, the distribution of Ca, as an exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction was as follows: 72.92, 83.29, 45.01 and 10.54%, respectively. High percentages of Mg and Ca associated with the exchangeable fraction, show that the mobility and bioavailability of these elements will be high, and this is prone to increase the hardness of water, which can result to the increase of pH in surface water. These high values of Mg and Ca extracted from sediments can be attributed to the underlying rocks constituted mainly of dolomite; however, in contrast to Ca, most of the Mg was bound to the residual fraction at sampling point 5, which indicates that only a small amount of Mg could be released into the water at this particular point.

Total Cr was mainly associated with the residual fraction suggesting relatively low mobility and availability of this metal, with the highest concentration of 27.43% extracted in the sediment samples. Its contribution to exchangeable, reducible and oxidizable fractions, was 1.27, 2.20 and 7.75%, respectively. It has been shown from other studies [31,34] that total Cr binds strongly to the crystalline structure of the sediments.

The distribution pattern of Mn in the sediments samples, showed that it was mainly bound to the oxidizable or organic matter and sulphides; with the highest percentage (64.19%) found in sediments from a stream connected to the Mooi River. The concentration of Mn in other fractions was 33.84% bound to exchangeable fraction (at Mooi River), 24.94% bound to Fe and Mn (at a stream connected to the Mooi River) and 43.82% bound to the residual fraction (at the Mooi River). Mn is released from the exchangeable and reducible fraction of these sediment samples and will be bioavailable, implying that it can be harmful to the biota. The distribution of Mn in sediment fractions, as observed in this study, is in agreement with previous studies carried out using the four-step (BCR) sequential extraction procedure in sediment samples from Tokat, Turkey, [35], which showed that Mn was mainly bound to the organic matter fraction.

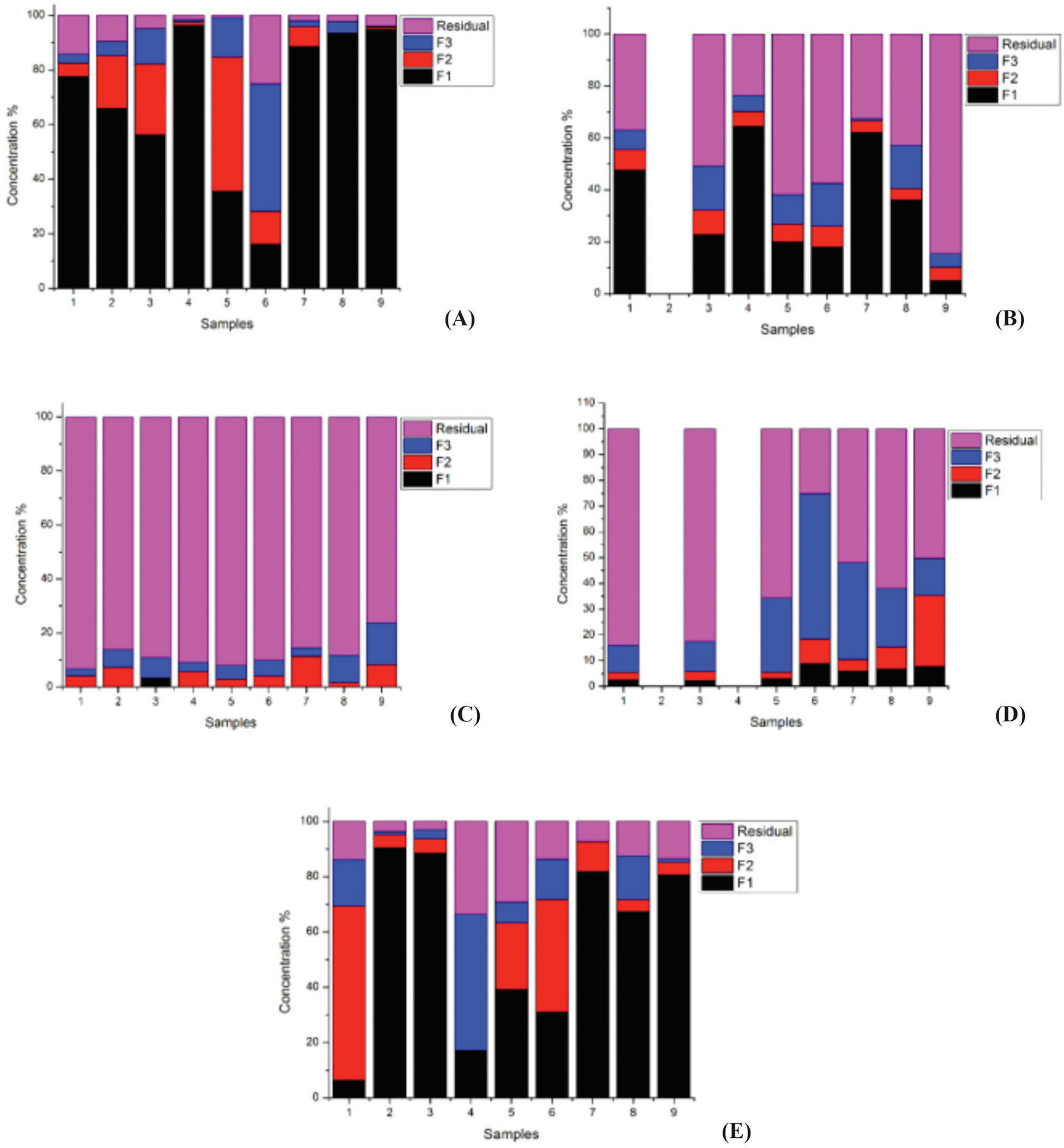

Fig. 6. Metal distribution among the different fractions: (A) Calcium, (B) Magnesium, (C) Iron, (D) Total Chromium and (E) Manganese).

3.4. Total organic carbon in sediments

It has been reported that the organic content is among the key factors influencing the bioavailability of metals in surface and ground water [36]. The values of total organic carbon (TOC) in the studied sediment samples are presented in Table 2. The variation of the organic carbon content among the different sediment samples was likely due to its origin in the aquatic environment. The values ranged between 0.37 and 2.88%, with the highest percentage recorded in sample 6 (Mooi River). The high content of organic carbon recorded in some of the sampling points indicates the decomposition of organic matter and thus likely to reduce trace metal bioavailability through complexation. It is therefore understandable that the impact of organic carbon content on the

Table 2
Total organic carbon of sediments samples from the Mooi River

Sample number	TOC %
1	0.45
2	1.15
3	1.21
4	2.02
5	0.37
6	2.88
7	1.65
8	2.82
9	1.41

distribution of elements bound to exchangeable, reducible and organic matter will varied per sampling site. Elements such as Ca and Mg which were predominantly found in the exchangeable and reducible fractions, are likely to be entrapped in the biological matters forming part of the sediments. The breakdown or degradation of these biological matters by microorganisms often contribute to resuspend (dissolve) the metals into the solution.

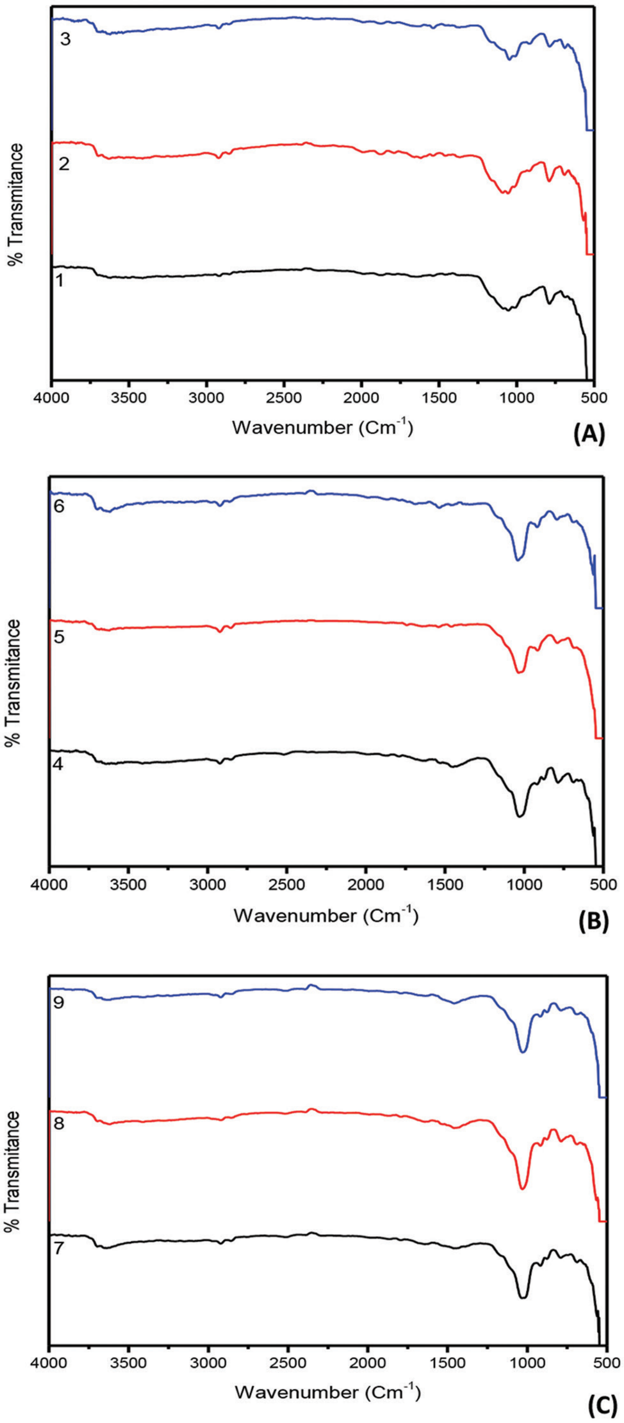

Fig. 7. FTIR spectra of samples: (A) Upstream, (B) Midway and (C) Downstream.

3.5. FTIR spectroscopy

It is suggested that the biological factors are poorly understood while they could strongly influence the bioaccumulation of metals and severely inhibit prediction of metal bioavailability [37]. It is therefore important to identify the binding groups which are likely to be involved in the bioaccumulation of metals on sediments. In this study, the FTIR analysis was conducted in order to confirm the presence of binding groups involved in the retention of metals in the sediments. The spectra of sediment samples collected along the Mooi Rivers and connected streams are shown in Fig. 7A–C, respectively. In general, the spectra of all the sampling points showed almost the same characteristics in their absorption bands.

Fig. 7A shows a band between 1300 and 1000 cm^{-1} which corresponds to the stretching vibrations of ester groups (C–O). The same trend of results was also observed in Fig. 7B and C, respectively. A slight twin peaks seen between 2918.29 and 3000 cm^{-1}, can be due to asymmetric and symmetric stretch of Alkanes H–C–H. A band between 1500 and 1450 seen in Fig. 7C can be assigned to asymmetric stretch of Aromatic Rings C–C=C group, however, this band was not seen in Fig. 7A and B. A wide band which can be seen between 3500 and 3000 cm^{-1} in all the figures is corresponding to the O–H stretch vibration, often found in organic compounds. A band between 1000 and 650 cm^{-1} can be ascribed to the strong alkenes =C–H group. A band between 690 and 515 cm^{-1} is corresponding to the medium stretching of alkyl halides C–Br group. These results are similar to those found in a study done by Reig et al. [38], these groups have high binding potential. The bands at 788.40, 690, 688.33, 629.56, and 629.25 cm^{-1} were found in all the sediment samples, and this is due to the inorganic materials, such as the clay and quartz minerals [39]. Hence, XRF results in this study show the dominance of SiO_2, CaO, MgO, Fe_2O_3, MnO and Cr_2O_3. This demonstrates that these inorganic metals were retained in the sediment, and the sequential leaching experiment shows that some of this metals such as Ca and Mg were mostly bound to the exchangeable fractions and this clearly indicate that their mobility will be high and thus prone to increase the hardness of the water, hence, the relatively high pH of the water samples. However, metals such as total Cr and Fe being associated with the exchangeable fractions even at low concentration they are prone to increase the toxicity in the aquatic environment, and their mobility will depend on the environmental changes overtime. On the other hand the results obtained are consistent with the presence of total organic carbon in sediment samples. According to a previous study [40] the organic peaks corresponding to organic compounds are those of aliphatic (3000–2800 cm^{-1}), aromatic and C=O groups (in the region 1700–1550 cm^{-1}) which are more pronounced in samples 9 than any other sample. According to Galle et al. [41], bands characteristics of the groups C=O, –OH and –NH, as well as aliphatic stretches in the 3500–2800 cm^{-1} region are reported to be the most prominent features of microbial spectra which have a significant correlation with the organic carbon content implicated in the biofilm growth. This clearly supports our findings; demonstrating the retention of metals in the exchangeable fraction mostly made of organic matters. Furthermore the presence of microorganisms is likely to result in the mobilization of the metals attached to that layer after degradation of the organic matter.

3.6. Water quality

Table 3a and 3b represent the results of the physico-chemical parameters and heavy metals measured in the surface water of the Mooi River and connected streams, respectively. The results show that there was a significant variation ($P < 0.05$) among the sampling sites. It is apparent from Table 3a and 3b that most of the parameters were within the recommended limit of SA drinking and irrigation water guidelines. However; for the parameters like the dissolved oxygen, redox potential and alkalinity, there is no specific limit set by the South African water guidelines [42]. The values of surface water temperature ranged from 10.10 to 19.50°C; these relatively low values can be attributed to the cold weather during a winter season. The mean and standard deviation for recorded concentrations of dissolved oxygen (DO) were 8.24 mg/L and 1.15 mg/L, respectively; with the highest concentrations measured at sampling point 5. High value of DO at this point can be correlated to the low value of temperature (12°C). According to Nezlin et al. [43]; the concentration of DO is an important water quality parameter because low DO concentration can be physiological stressful or lethal to aquatic organisms. The values of alkalinity varied between 160 and 312 mg/L, with a mean of 276.00 mg/L and standard deviation of 46.78 mg/L. The highest value of alkalinity recorded at sampling point 2 can be attributed to the underlying rock constituted mainly of dolomites. High alkalinity can result in physiological stress on aquatic organisms and that may lead to loss of biodiversity [6]. The values of pH ranged from 7.34 to 8.64, with the mean value of 8.18 and standard deviation of 0.52. It is apparent from Table 3a, that all the pH values were above neutral; these values were within the recommended limit of SA drinking water guideline, however, at some of the sampling sites these values were above the SA irrigation water guideline. According to the South African irrigation water guideline [44], high value of pH can cause a foliar damage which can result to the decrease of yield or damage to fruit or marketable product. High values of pH measured reflect the relatively high concentrations of Ca and Mg, as high percentages of Ca and Mg were associated with the exchangeable fraction in sediment samples. The value of EC varied between 0.70 and 1.52 mS/cm, with the mean value of 0.83 mS/cm and standard deviation of 0.17 mS/cm. The highest value of EC was recorded at sampling point 1 and such high value may result from contamination by the gold mine discharge, as sampling point 1 is situated within the mine canal. This is substantiated by elevated concentration of Ca, Mg, SO_4^{2-} and Cl^- at this point. The value of Eh ranged from 138.00 mV to 205.57 mV, with the mean of 158.30 mV and standard deviation of 25.68 mV. The highest value of Eh was recorded at sampling point 3 and this correlates with the lowest value of pH (7.24) recorded at this site. Therefore; the low value of Eh measured in the rest of the sampling point can be attributed to the relatively high values of pH which were above neutral.

The concentration of nitrate ranged from 0.00 to 11.20 mg/L, with the mean value of 2.43 mg/L and standard deviation of 3.46 mg/L. The highest concentration of nitrate was measured at sampling point 4 (11.20 mg/L). However, the decreasing trend was observed when moving downstream of the study area. The concentrations of nitrate were observed to be within class II limit of SA drinking water guideline. However, nitrate concentration at point 4 was above class I limit of drinking water guideline and the source of pollution at this point could be the effluent from the agricultural land surrounding the area; agricultural activities have been reported to contribute for more pollution of NH_4 and NO_3^- around the world [45]. In addition, high concentrations of nitrate at this point could also be attributed to contamination from the municipal and domestic sewage in the proximity of the Boskop Dam. The concentration of chloride ranged from 36.67 to 76.67 mg/L, with the mean and standard deviation of 48.52 and 13.96 mg/L, respectively. The highest concentration of chloride (76.67 mg/L) was observed at sample point 1 (Table 3a), and the source of pollution could be the effluent from the mines since this point is situated within a mine canal. However, the level of chloride was observed to be within the recommended limit of SA drinking and irrigation water guidelines. The value of cyanide ranged from 1.00 to 3.00 mg/L, with the mean and standard deviation of 1.56 and 0.73 mg/L, respectively. The relatively low value of SD indicates that there was no significant variation between the sampling points.

High concentrations of cyanide (Table 3b) were recorded at most of the sampling points and this could be ascribed to the contamination from the gold mine effluent, as it is known that some of the mines use cyanide for the extraction of gold from ore [46]. The concentration of CN^- was observed to be above the recommended limit of SA drinking water guideline. The level of sulphate varied between 110 and 420 mg/L, with the mean value of 153.89 mg/L. High value of standard deviation (104.04 mg/L) clearly shows that there was a significant variation between the sampling sites. The highest concentration was measured at sampling point 1 (420 mg/L), upstream of the study area. This elevated concentration of sulphate can be attributed to the effluent from the gold mines in the vicinity of Carleton-

Table 3a
Physico-chemical parameters and Major anions concentrations in water samples

	pH	T	Eh	EC	DO	Alkalinity	SO_4^{2-}	Cl^-
Sampling sites		°C	mV	mS/cm	mg/L	mg/L $CaCO_3$	mg/L	mg/L
1	8.50	18.30	135.57	1.21	8.80	160.00	420.00	76.67
2	7.34	19.50	196.57	0.79	7.00	312.00	120.00	40.00
3	7.24	16.30	205.57	0.82	5.90	296.00	120.00	50.00
4	8.55	12.00	142.00	0.71	9.10	304.00	110.00	36.67
5	8.45	12.00	144.00	0.74	9.20	296.00	90.00	36.67
6	8.64	10.80	138.00	0.70	9.00	268.00	110.00	36.67
7	8.45	10.10	147.00	1.00	7.60	272.00	195.00	53.33
8	8.3	11.70	153.00	0.74	8.60	268.00	110.00	43.33
9	8.12	12.00	163.00	0.84	9.00	308.00	110.00	63.33
Average ± SD	8.18 ± 0.52	13.63 ± 3.46	158.30 ± 25.68	0.83 ± 0.17	8.24 ± 1.15	276.00 ± 46.78	153.89 ± 104.04	48.52 ± 13.96
SA-DWG [a]								
Class I	5.00–9.50	–	–	< 1.50	–	–	< 400.00	< 200.00
Class II	4.00–10.00	–	–	1.50–3.70	–	–	400.00–600.00	200.00–600.00
SA-IWG [b]	6.50–8.40	–	–	–	–	–	–	–

Note: SD, Standard deviation; a, (South African-drinking water guideline, 2006); b, (South African-irrigation water guideline, 1999); Class I (recommended operational limit); Class II (max.allowable for limited duration).

Table 3b
Major anions and heavy metals concentration in the water samples

	NO_3^-	CN^-	Fe	Ca	Mg	Mn	Cr
Sampling sites	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	0.00	1.00	0.15	81.79	53.93	0.09	0.15
2	0.00	2.00	0.19	76.23	47.75	0.02	0.08
3	1.50	1.00	0.00	65.87	39.88	0.01	0.15
4	11.20	1.00	0.00	54.93	39.31	0.00	0.19
5	2.20	3.00	0.00	49.36	43.33	0.00	0.17
6	0.00	1.00	0.00	59.86	48.04	0.00	0.16
7	2.20	1.00	0.09	81.73	64.60	0.00	0.18
8	2.10	2.00	0.08	43.49	45.40	0.00	0.18
9	2.70	2.00	0.00	42.94	44.86	0.00	0.17
Average ± SD	2.43 ± 3.46	1.56 ± 0.73	0.51 ± 0.07	61.80 ± 15.49	47.46 ± 7.81	0.01 ± 0.03	0.16 ± 0.03
SA-DWG[a]							
Class I	< 10.00	< 0.05	< 0.20	< 150.00	< 70.00	< 0.10	< 0.10
Class II	10.00–20.00	0.05–0.07	0.20–2.00	150.00–300.00	70.00–100.00	0.10–1.00	0.10–0.50
SA-IWG[b]	–	–	5.00–20.00	–	–	0.02–10.0	0.10–1.00

Note: SD, Standard deviation; a, (South African- drinking water guideline, 2006); b, (South African- irrigation water guideline, 1999); Class I (recommended operational limit); Class II (max.allowable for limited duration).

ville, since this point is located along the mine canal joining the Mooi River. A decreasing trend was observed when moving downstream of the study area. These clearly show that effluents from the respective mine contribute to the pollution while the sediments may be naturally involved in the mitigation of pollutants dispersion.

The concentration of total Cr ranged from 0.08 to 0.18 mg/L, with the mean and standard deviation of 0.16 and 0.03 mg/L, respectively. Low value of SD clearly indicates that there was no significant variation between the sampling sites. The highest value of total Cr was recorded at sampling point 4 (0.19 mg/L). The concentrations of total Cr were observed to be within the recommended class II limit of SA drinking and irrigation water guidelines. However, all the sampling sites except point 2 showed concentrations above class II of drinking water guideline therefore degrading water quality. Total Cr is one of the toxic elements in the aquatic environment, for example Cr (VI) can cause cancer to human beings if high concentration is ingested in drinking water [47]. The source of total Cr can be the effluents from the respective gold mines in the vicinity of the study area. The concentration of Fe ranged from 0 to 0.19 mg/L, with the mean of 0.51 mg/L and standard deviation of 0.07 mg/L. Elevated concentration measured at sampling points 1 and 2 can be attributed to contamination by effluents from the gold mines (Fig. 1).

A decreasing trend of Fe concentration were observed when moving downstream of the study. This may be partly due to the retention on the sediments across the river. Nevertheless, high concentrations of Fe were recorded at sampling point 7 (0.09 mg/L) and point 8 (0.08 mg/L). However, the source of pollution at these points (Potchefstroom area) could not be ascertained. The concentrations of Fe were observed to be within the recommended limit of the SA drinking and irrigation water guidelines. The mean concentration of Mn was 0.01 mg/L, with the highest concentration measured at sampling point 1 (0.09 mg/L). Elevated concentration of Mn could be attributed to the effluent from gold mines in the vicinity of Carletonville area. However, a decreasing trend was observed when moving downstream of the study area and this may be partly due to the retention on the sediments. The concentration of Ca and Mg ranged from 42.94 to 81.79 mg/L and 39.31 to 64.60 mg/L, respectively. These concentrations of Ca and Mg can be ascribed to the nature of the underlying rock constituted mostly by dolomites and they are likely to increase the hardness of the water, hence a relatively high pH value was observed. However, Ca and Mg concentrations were within the required limit of SA drinking water guideline.

4. Conclusions

The sediments from the Mooi River and its connected streams are dominated by oxide minerals and contain mainly Fe, Cr, Mg, Mn and Ca. According to the modified BCR sequential extraction results, it is sound to say that the bioavailability tendency of most of the elements except Ca and Mn was on the lower side as they were predominantly bound to the residual fraction; implying that the major concern may be the continuous increase of water hardness due to high level of dissolved Ca. Elements such as Fe, Cr, and Mg, being strongly bound to the residual fraction, indicate that they are less likely to cause pollution of water. However, portion of Fe and Cr associated with the exchangeable and reducible fractions at some sampling points, may be progressively released at a speed that will vary depending on the environmental conditions and could therefore degrade the quality of water. The distribution of metals in the various fractions of the sediments informed of the attachment affinity further investigated by FTIR analysis. The FTIR results revealed the presence of binding groups on the organic compounds which could have been involved in the retention of metals in the sediments. The water quality was found unfit for drinking purpose due to high concentrations of SO_4^{2-}, CN^-, NO_3^- and total Cr above the recommended class I limit in some of the sampling points. The water was observed to be fit for irrigation purpose. It is however noticeable that the interaction of the observed pollutants with the sediments may have contributed to the mitigation of pollution, decreasing metal concentrations across the river.

Acknowledgements

The authors are grateful to the sponsor from the North-West University and the National Research Foundation (NRF) in South Africa. Any opinion, findings and conclusions or recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto. The authors appreciate the contribution of Mr E. Malenga and Ms N. Baloyi from the University of Johannesburg in South Africa; Mr G. Van-Rensburg, Mrs L. Swardt from the North-West University and the personnel from the Department of Water and Sanitation located at Boskop Dam.

References

[1] J.-F. Peng, Y.-H. Song, P. Yuan, X.-Y. Cui, G.-L. Qin, The remediation of heavy metals contaminated sedimen, J. Hazard. Mater., 161 (2009) 633–640.

[2] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu, Heavy metal pollution and human biotoxic effects, Int. J. Phys. Sci., 2(5) (2007) 112–118.

[3] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, Implication of plants and microbial metalloproteins in the bioremediation of polluted waters: A review, Phys. Chem. Earth, 67–69 (2013) 242–252.

[4] V. Deepti, G. Dessai, G.N. Nayak, Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, central west coast of India, Environ Monit Assess., 158 (2008) 117–137.

[5] S. Nazeer, M.Z. Hashmi, R.N. Malik, Heavy metals distribution, risk assessment and water qualitycharacterization by water quality index of the River Soan, Pakistan. Ecol. Indic., 43 (2014) 262–270.

[6] E.O. Lawson, Physico-chemical parameters and heavy metal contents of water from the mangrove swamps of Lagos Lagoon, Lagos, Nigeria, Adv. Biol. Res., 5(1) (2011) 8–21.

[7] T. Manickum, W. John, S. Terry, K. Hodgson, Preliminary study on the radiological and physicochemical quality of the Umgeni Water catchments and drinking water sources in KwaZulu-Natal, South Africa, J. Environ. Radioactiv., 137 (2014) 227–240.

[8] M. Esshaimi, N. Ouazzani, A. El Gharmali, F. Berrekhis, M. Valiente, L. Mandi, Speciation of Heavy Metals in the Soil and the Tailings, in the Zinc-Lead Sidi Bou Othmane Abandoned Mine, J. Environ. Earth Sci., 3(8) (2013) 2224–3216.

[9] A. Enuneku, L. Ezemonye, F. Adibeli, Heavy metal concentrations in surface water and bioaccumulation in fish (Clarias Gariepinus) of the river Owan, Edo state, Nigeria, Eur. Int. J. Sci. Tech., 2(7) (2013) 31–31.

[10] K. Nemati, N.K. Abu Bakar, M.R. Abas, E. Sobhanzadeh, Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia, J. Hazard. Mater., 192 (2011) 402–410.

[11] H.-T. Lim, J.-S. Lee, H.-T. Chon, M. Sager, Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea, J. Geochem. Explor., 96 (2007) 223–230.

[12] O.I. Davutluoglu, G. Seckin, C.B. Ersu, T. Yilmaz, B. Sari, Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey, J. Environ. Manage., 92 (2011) 2250–2259.

[13] Q. Wu, H. Zhou, N.F.Y. Tam, Y. Tian, Y. Tan, S. Zhou, Q. Li, Y. Chen, J.Y.S. Leung, Contamination, toxicity and speciation of heavy metals in an industrialized urban river: Implications for the dispersal of heavy metals, Mar. Pollut. Bull., (2016) 1–9.

[14] S.I. Korfali, B.E. Davies, Speciation of metals in sediment and water in a river underlain by limestone: role of carbonate species for purification capacity of rivers, Adv. Environ. Res., 8 (2003) 599–612.

[15] C. Boukhalfa, M. Chaguer, Characterisation of sediments polluted by acid mine drainage in the northeast of Algeria, Int. J. Sediment Res., 27 (2012) 402–407.

[16] C. Durand, V. Ruban, A. Amblès, Mobility of trace metals in retention pond sediments, Environ. Tech., 25 (2004) 881–888.

[17] G.A. Di Luca, M.A. Maine, M.M. Mufarrege, H.R. Hadad, G.C. Sánchez, C.A. Bonetto, Metal retention and distribution in the sediment of a constructed wetland for industrial wastewater treatment, Ecol. Eng., 37 (2011) 1267–1275.

[18] S. Tokalioglu, S. Kartal, G. Birol, Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway S oils, Turk J. Chem., 27 (2001) 333–346.

[19] F. Winde, L.A. Sandham, Uranium pollution of South African streams – An overview of the situation in gold mining areas of the Witwatersrand, GeoJournal, 61 (2004) 131–149.

[20] F. Winde, challenges for sustainable water use in dolomitic mining regions of South Africa—A case study of uranium pollution Part II: Spatial patterns, mechanisms, and dynamics, Phys. Geography, 27 (2006) 379–395.

[21] J.D. Malan, The impact of the gold mining industry on the water quality of the Kromdraai catchment. University of Johannesburg, (2002) https://ujdigispace.uj.ac.za Date of access 19 Oct. 2015.

[22] H. Coetzee. F. Winde, P.W. Wade, An assessment of sources, pathways, mechanisms and risks of current and future pollution of water and sediments in the Wonderfonteinspruit Catchment, WRC Report No 1214/1/06, (2006) https://www.researchgate.net/.../263067189 (Accessed on 28 Jun 2016).

[23] J.F. Durand, The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa, J. Afr. Earth Sci., 68 (2012) 24–43.

[24] T. Marara, L.G. Palamuleni, E.E. Ebenso, Access to Potable Drinking Water in the Wonderfonteinspruit Catchment, J. Soc. Sci., 29 (2011) 3–79.

[25] P.W. Wade, S. Woodbornel, W.M. Morris, P. Vos, N.V. Jarvis, Tier 1 Risk Assessment of Radionuclides in Selected Sediments of the Mooi River, WRC Report No: 1095/1/02, (2002) http://www.wrc.org.za/Knowledge%20Hub%20Documents/Research%20Reports/1095-1-02.pdf (Accessed 01 July 2016).

[26] I. Opperman, The remediation of surface water contamination: Wonderfonteinspruit. University of South Africa, (2008) http:// hdl.handle.net/10500/2123 (Accessed 30 Mar 2016).

[27] E. Annandale, E. Nealer, Exploring aspects of the water history of the Potchefstroom region and the local management of it. New Contree., 62 (2011) 111–124.

[28] S. Barnad, A. Venter, C.E. van Ginkel, Overview of the influences of mining-related pollution on the water quality of the Mooi River system's reservoirs, using basic statistical analyses and self organised mapping, Water SA, 39 (2013) 655–662.

[29] H.F. Hermond, E.J. Fechner-Levy, Chemical Fate and Transport in the Environment, Academic Press, San Diego, USA, 2000.

[30] F. Gashi, S. Franciskovic-Bilinski, H. Bilinski, Analysis of sediments of the four main rivers (Drini Bardhe, Morava E Binces, Lepenc and Sitnica) in Kosovo, Fresenius Bull., 18(8) (2009) 1462–1471.

[31] D.T, Cuong, J.P. Obbard, Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure, Appl. Biochem., 21 (2006) 1335–1346.

[32] P. Avramidis, K. Nikolaou, V. Bekiari, Total Organic Carbon and Total Nitrogen in Sediments and Soils: A Comparison of the Wet Oxidation – Titration Method with the Combustion-Infrared Method, 4 (2015) 425–430.

[33] C. Yuan, J. Shi, B. He, J. Liu, L. Liang, G. Jiang, Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction, Environ. Int., 30 (2011) 769–783.

[34] M.S. Dundar, H. Altundag, V. Eyupoglu, S.C. Keskin, C. Tutunoglu, Determination of heavy metals in lower Sakarya river sediments using a BCR-sequential extraction procedure. Environ. Monit. Assess., 184, (2011) 33–41.

[35] M. Tuzen, Determination of trace metals in the River Yes¸ilırmak sediments in Tokat, Turkey using sequential extraction procedure, Microchem. J., 74 (2002) 105–110.

[36] D.A. John, J.S. Leventhal, Bioavailability of metals. https://pubs.usgs.gov/of/1995/ofr-95–0831/CHAP2.pdf, Accessed 07/07/2016.

[37] S.N. Luoma, Can we determine the biological availability of sediment-bound trace elements? Hydrobiologia, 176/177 (1989) 379–396.

[38] F.B. Reig, J.V.G. Adelantado, M.C.M.M. Moreno, FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method. Application of geogical samples, Talanta, 58 (2002) 811–821.

[39] G. Haberhauer, B. Rafferty, F. Strebl M.H. Gerzabek, Comparison of the composition of forest soil litter derived from three different sites at various decompositional stages using FTIR spectroscopy, Geoderma, 83 (1997) 331–342.

[40] J. Poulenard, Y. Perrette, B. Fange, P. Quetin, D. Trevisan, J.M. Dorioz, Infrared spectroscopy tracing of sediment sources in a small rural watershed (French Alps). Sci. Total Environ., 407 (2009) 2808–2819.

[41] T. Galle, B. Van Lagen, A. Kurtenbach, R. Bierl, An FTIR-DRIFT Study on River sediment particle structure: implications for biofilm dynamics and pollutant binding, Environ. Technol., 38 (2004) 4496–4502.

[42] South African Bureau of Standard (SABS), Drinking water, SANS 241 (2005) 1–17.

[43] N.P. Nezlin, K. Kamer, E.D. Stein, Dissolved oxygen dynamics in a eutrophic estuary, Upper Newport Bay, California, Estuarine, Coastal and Shelf Science, 82 (2009) 139–151.

[44] Department of Water Affairs and Forestry, South African Water Quality Guidelines, Agricultural Water Use: Irrigation, 4 (1996) 1–199.

[45] M.S. Islam, M. Tanaka, Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach for management: a review and synthesis, Mar. Pollut. Bull., 48 (2003) 624–649.

[46] E.N. Bakatula, M.E. Cukrowska, L. Chimuka, H. Tutu, Characterization of cyanide in a natural stream impacted by gold mining activities in the Witwatersrand Basin, South Africa, Toxicol. Environ. Chem., 94 (2012) 7–19.

[47] A. Zhitkovich, Chromium in drinking water: sources, metabolism, and cancer risks, Chem. Res. Tech., 24 (2011) 1617–1629.