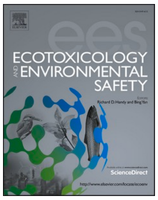
Ecotoxicology and Environmental Safety 207 (2021) 111468

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Research paper

Relationship of arsenic and chromium availability with carbon functional groups, aluminum and iron in Little Washita River Experimental Watershed Reservoirs, Oklahoma, USA

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ARTICLE INFO

Edited by Dr. Hyo-Bang Moon

Keywords:
Arsenic
Carbon
Chromium
Ecologic-risk
Extractable
Pollution
Reservoirs
Sediments
Sorption

ABSTRACT

Sediment from three reservoirs located in the Little Washita River Experimental Watershed (LWREW) in Oklahoma, USA with contrasting dominant land uses were analyzed for total and extractable concentrations of arsenic (As) and chromium (Cr), and the potential ecologic risk to benthic organisms. Extractable As ranged from 0.24 to 1.21 mg kg^{-1}, in the order grazing > cropland > forest and 0.13–0.58 mg kg^{-1} for extractable Cr, in the order of forest > grazing > cropland. However, only approximately < 1.5% of total As and < 4% of total Cr were extractable. Total As ranged from 16.2 to 141 mg kg^{-1} and total Cr ranged from 5.06 to 40.1 mg kg^{-1} both in the order of cropland > grazing > forest. The sediment exhibited an alkaline pH (8.0–8.7). As sorption exhibited a positive relationship with Al ($r = 0.9995$; $P = 0.0001$), Fe ($r = 0.9829$; $P = 0.0001$), and C ($r = 0.4090$; $P = 0.0017$) and Cr correlated positively with Al ($r = 0.9676$ $P = 0.0001$), Fe ($r = 0.9818$; $P = 0.0001$), and C ($r = 0.3368$; $P = 0.0111$). In addition, both As and Cr exhibited positive relationships with carbon (C) functional groups in the order of O-alkyl C > methoxyl C > alkyl C > aromatic C > carboxyl C > phenolic C. The sediment concentration analysis results illustrated that As in all reservoirs exceeded their respective Threshold Effect Level (TEL) and/or Probable Effect Level (PEL) indicating that existing concentrations of metals in these sediments were sufficiently high to cause adverse effects. However, Cr concentrations in all reservoirs evaluated was lower compared to the TEL and PEL.

1. Introduction

Reservoirs are man-made lakes that are used for recreational activities, flood control, rural and municipal water supplies, irrigation, wildlife habitat, and generation of hydroelectric power (Ali et al., 2019; Schleiss et al., 2016). In recent years, increasing levels of pollutants in water reservoirs have been reported, which may impact the environment, animals and human health (Tume et al., 2018). Arsenic (As) and chromium (Cr) are generally the most potentially toxic metals in the environment. While they are natural components of the earth's lithogenic inputs via weathering of parent materials, they also can enter in the environment through anthropogenic sources for example untreated industrial wastewater, sewage effluent, surface run-off, traffic emissions, chemical fertilizers and metal based pesticides (Ali et al., 2019). As the pollution of As and Cr in reservoirs are primarily associated with anthropogenic activities (Wu et al., 2014), contamination of those toxic metals in surface water bodies pose a long-term risk for human beings and aquatic systems due to their toxic nature, non-biodegradability and accumulative behaviors (Wang et al., 2018).

Arsenic and Cr when introduced into reservoirs could be deposited through the processes of precipitation and sedimentation and accumulate in the sediment (Rodriguez and Avila-Pérez, 1997). However, when environmental conditions in the sediments change, chemical and biological processes may allow the accumulated toxic metals to be released back into the water column, which can turn sediments into an internal pollution source (Hill et al., 2013). As a result, reservoir sediment can

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https://doi.org/10.1016/j.ecoenv.2020.111468
Received 9 June 2020; Received in revised form 2 October 2020; Accepted 6 October 2020

act both as a sink and potential secondary source for metals and sediment quality in a reservoir and can indicate the status of water pollution (Wu et al., 2014). Control of contaminant sources in the reservoirs is key because the toxic contaminants like As and Cr can mobilize and migrate into ground and surface water or through marine organisms that can uptake these chemical elements, that can eventually enter into the food chain (Finnegan and Chen, 2012).

Arsenic and Cr are carcinogenic metals, with concentrations in natural waters varying by several orders of magnitude depending on the source and local geochemical environment (Smedley and Kinniburgh, 2002; Fendorf et al., 2000). Arsenate (AsV) and arsenite (AsIII) are two common forms of inorganic As in the environment. In natural water, AsV dominates in oxic environments and can strongly sorb to soil particulates, rendering it less mobile and exists as $H_2AsO_4^-$ $HAsO_4^{2-}$ at pH 3–11. AsIII is present under anoxic conditions and exists as $H_3AsO_3^0$ at $pH < 9.2$ and $H_2AsO_3^-$ at $pH > 9.2$ (Lenoble et al., 2005). The common valences of Cr in soils include chromite (CrIII) and chromate (CrVI), however, they differ in toxicity. While CrVI is mobile and usually present as chromate (CrO_4^{-2}) or dichromate ($Cr_2O_7^{-2}$) in soils, CrIII is often present as oxides and is less mobile (Fendorf et al., 2000). Due to their toxicity, the guideline by World Health Organization for As and Cr in drinking water is 10 μg L^{-1} and 50 μg L^{-1}, respectively (WHO, 2017).

Several studies on heavy metals in sediments of reservoirs have focused on Asia including China (Zhu et al., 2019, 2017), India (Dhanakumar et al., 2015), and Vietnam (Van Thinh et al., 2018); South America including Brazil (Quadra et al., 2019); and Europe including Germany (Hahn et al., 2018), and Poland (Sojka et al., 2019). For example, Arfaeinia et al. (2019) investigated total metals contents in sediment from 41 areas with different land uses (industrial, urban, agricultural and natural fields) in the northern coasts along the Persian Gulf.

The release of As and Cr from soils and sediments into groundwater is governed by several geophysicochemical processes, of which, As and Cr sorption behavior is of principle significance (Wang and Mulligan, 2006). For example, As concentrations up to 12 mg L^{-1} have been reported in groundwater from a sandstone aquifer in the Fox River valley in eastern Wisconsin, USA (Schreiber et al., 2003). Therefore, As sorption mechanisms onto sediments are of paramount importance because this process regulates As sediment mobility, which further influences the As bioavailability and potential toxicity (Rahman et al., 2017).

Following the USA's Flood Control Act of 1944 (PL-534) and the Watershed Protection and Flood Prevention Act of 1954 (PL-566) (Hanson et al., 2007; Hunt et al., 2011) > 2000 water reservoirs were constructed in Oklahoma to control flooding. Forty-five of the structures were constructed in the headwaters of the Little Washita River Experimental Watershed (LWREW) between 1969 and 1982. However, over the years, sedimentation has reduced the water holding capacity of the reservoirs (Moriasi et al., 2018). Although these reservoirs were built primarily for flood control, they have also been used for recreation and livestock water supply; however, it remains unclear if potential pollutants are building up in the sediment.

Even though the LWREW reservoirs are widely studied (Moriasi et al., 2018; Steiner et al., 2014), there is still a gap regarding heavy metals contamination in the sediments, exposure and its risk to human health. Therefore, the objective of this study was to characterize sediments from three reservoirs in the LWREW to: (1) determine the concentration of total of As, Cr, Al, and Fe; (2) determine the concentration of extractable As and Cr in relation to EPA limit levels in water; (3) determine the relationship between As and Cr sorption with C functional groups, Al, and Fe; and (4) estimate the potential ecological risk associated with As and Cr toxicity.

2. Materials and methods

2.1. Study area

The study area is the 610 km^2 Little Washita River Experimental Watershed (LWREW) located in central Oklahoma and consists of mixed agricultural land use, including pasture and rangeland that covers 68% of the total area (Steiner et al., 2014). The specific reservoirs were located at approximately LW11 (grazing): 34°53′37″ N, 97°59′47″ W; LW20 (forest): 34°50′2″ N, 98°8′56″ and LW24 (cropland): 34°52′3″ N, 98°12′9″ W. The watershed includes parts of Caddo, Comanche, and Grady counties that is a tributary of the Washita River, which drains into the Red River on the Oklahoma-Texas border. The climate is sub humid, with average annual rainfall of 800 mm. The topography is rolling with a maximum relief of 180 m with sandy to loamy soils. Three of the 45-flood control reservoirs were selected for this study (Fig. S1) with different predominant land cover types (grassland, cropland and forest). The characteristics of the three selected reservoirs, obtained from Moriasi et al. (2018), are presented in Table S3.

2.2. Sample collection

The sampling and field surveys took place in February, 2018. Four transects were ran across each reservoir, along each transect four samples were collected, sectioned according to depths and composited. The samples were collected using VibraCore device manufactured by Specialty Devices Inc. with 7.62 cm diameter coring tube. In the cropland watershed, the reservoir sediments, cores were 100 cm deep while in grazing and forest watersheds, they were 75 cm deep. The difference in depth sampled between cropland versus grazing and forest watershed reservoirs was because after the construction, sedimentation of the reservoirs has been occurring over decades at varying sedimentation rates depending on the land use and soil types. The cores were sectioned into 0–25, 25–50, 50–75 and 75–100 cm. Under each land use category 16 soil cores were collected and sectioned every 25 cm up to 100 cm depth for cropland watershed and 25 cm depth up to 75 cm in both grazing and forest watersheds. Under each core sectioning category, four sections of similar depth were composited to make four composite replicates. The samples were stored in acid cleaned plastic container and carried within zip-mouthed PVC packages.

2.3. Sample digestion and analysis for total and extractable arsenic and chromium

All glassware was soaked in 10% HNO_3 and HCl bath for at least 24 h and then rinsed three times with deionized water prior to use. All chemicals were of analytical grade or better. Perchloric acid (trace metal grade), and hydrochloric acid were obtained from Fisher Scientific (Waltham, MA). All reagents including HNO_3, HCl and H_2O_2 were of analytical reagent grade (Merck).

2.3.1. Total and extractable arsenic, chromium, iron and aluminum determination

Sediment sub samples were dried at 75 °C for 3 days, homogenized with a pestle and ground into fine powder to obtain a representative sample (Hendożko et al., 2010). About 0.5 g of the sample was digested with HNO_3/H_2O_2 using USEPA Method 3050B on a hot block (Environmental Express, Ventura, CA). Arsenic, Cr, Al, and Fe from the digested samples were analyzed by inductively coupled plasma mass spectrometry (ICPMS; Perkin-Elmer Corp., Norwalk, CT).

Extractable concentrations of As and Cr in the sediments were digested with Mehlich 3 solution (Mehlich, 1984), with $HClO_4$ and HCl on a hot block (Environmental Express, Ventura, CA) at 80 °C. The digests were left to cool at room temperature and diluted with 10 N HCl. Elemental contents were analyzed by inductively coupled plasma (ICP; Perkin-Elmer Corp., Norwalk, CT). Multi-element standard solution

(Perkin-Elmer, Inc. USA) was used after appropriate dilution for calibration and quality assurance and quality control protocol. Standard solution and sample blanks were analyzed after every 20 samples to monitor the stability of the ICP. In this study it was assumed that the difference between total As/Cr and extractable As/Cr was sorbed As/Cr.

2.4. Determination of biogeochemical parameters

Sediment pH was determined using wet soil at a 1:1 ratio (soil: deionized water) (McLean, 1983), using Fisher Scientific pH meter (Fisher Scientific accumet AAE150 pH benchtop meter). Sediment subsamples were oven dried at 75 °C for 3 days (Hendożko et al., 2010) before ball milling using a Mixer Mill MM 400 (Retsch, Newton, PA, USA) at 25 Hz for 10 min. Total C and $\delta^{13}C$ were determined with a Thermo Electron DeltaV Advantage isotope ratio mass spectrometer coupled with a ConFlo II interface linked to a Carlo Erba NA 1500 CNHS Elemental Analyzer. Samples were loaded into tin capsules and placed in a 50-position automated Zero Blank sample carrousel on a Carlo Erba NA1500 CNS elemental analyzer. After combustion in a quartz column at 1020 °C in an oxygen-rich atmosphere, the sample gas was transported in a He carrier stream and passed through a hot reduction column (650 °C) consisting of elemental copper to remove oxygen. The effluent stream then passed through a chemical (magnesium perchlorate) trap to remove water followed by a 0.7-m GC column at 120 °C to separate N_2 from CO_2. The sample gas next passed into a ConFlo II preparation system and into the inlet of a Thermo Electron Delta V Advantage isotope ratio mass spectrometer operating in continuous flow mode where the sample gas was measured relative to laboratory reference N_2 and CO_2 gases.

2.5. ^{13}C solid state nuclear magnetic resonance (ssNMR)

Samples were air dried until soil samples had a constant weight before, they were ground into fine particles using Mixer Mill MM 400 (Retsch, Newton, PA, USA) at 25 Hz for 10 min. Ground samples were analyzed by magic angle spinning (MAS) ^{13}Css NMR. MAS ^{13}Css NMR experiments were carried out on a Bruker 300 MHz DRX NMR spectrometer equipped with a Bruker 4.0 mm double resonance MAS NMR probe. Samples were packed into 4.0 mm zirconia rotors with Kel-F drive caps and spun to 9.5 kHz at RT using a Bruker pneumatic MAS unit. All ^{13}C signals were enhanced by Cross Polarization: a 4.0 μs 1H $\pi/2$ pulse followed by a 1H spin-lock field of 45 kHz for 1.5 ms contact time, during which the ^{13}C RF field will be ramped from 35 to 50 kHz. All ^{13}C signals was recorded under the irradiation of the SPINAL64 decoupling sequence (Fung et al., 2000) with 1H RF amplitude of 62.5 kHz. The number of scans used to accumulate the signals varied between 10,000 and 50,000, depending on the samples, with a recycle delay of 3 s. The MAS ^{13}C ssNMR spectral regions were integrated to determine the contribution of each C functional group in the sample based on assignments from Knicker (2011): alkyl (0–45 ppm), methoxyl (45–60 ppm), O-alkyl (60–110 ppm), aromatic (110–140 ppm), phenolic (140–160 ppm), and carboxyl (160–220 ppm). Total C concentration was used to estimate the concentration of each C composition.

2.6. Quality control

QA/QC protocols in this study included digestion blanks, four replicates analyses, sample matrix certified reference materials (CRMs) and the use of standard and spiked solutions every 10 samples. Certified reference material was analyzed as samples with each batch. The results Al $= 568 \pm 11$; As $= 0.110 \pm 0.003$; $\pm$ 0.005; Cr $= 2.05 \pm 0.110$ and Fe $= 361.9 \pm 5.4$ mg kg^{-1}) were in agreement with the certified values Al $= 598 \pm 12$; As $= 0.112 \pm 0.004$; Cr $= 1.99 \pm 0.06$ and Fe $= 367.5 \pm 4.3$ mg kg^{-1}, respectively). The agreement between the analytical results for the certified reference material was satisfactory; i.e. the recovery and the standard deviation were $> 98\%$ and $< 10\%$, respectively. The mean recovery of standard solutions was 96 ± 1.5%, while the spike recovery was 94 ± 3.6%. The performance of the ICP was checked by running an intermediate calibration standard every 10 samples. All calibration standard checks were within the acceptable range (80–120%).

2.7. Data analysis

Elemental concentrations were calculated on a dry weight basis following Hendożko et al. (2010) and expressed as means of four replicates with standard error of mean. Correlation analysis was used to elucidate the interrelationship among the sediment indices. Significant differences in the means between reservoirs were compared using Tukey tests at $P < 0.05$. All statistical analyses were performed using JMP®Pro 13.0 statistical software (SAS Institute, Inc., Cary, NC, USA).

3. Results and discussion

3.1. Physico-chemical properties of sediments

The basic physico-chemical properties of the sediments are presented in Table S3 and Table 1. Based on grain composition, sediment material from the LWREW reservoirs was classified sandy loam and silt loam. Sandy loam soils were predominant in grazing and forest sites and silt loam in the cropland site (Table S3), as reported by Steiner et al. (2008).

The pH is an important determinant of metal bioavailability in sediment (Ali et al., 2019). High pH values ($>$ 6.5–7.0) can limit their solubility and bioavailability via promoting adsorption and precipitation (Equeenuddin et al., 2013). Low pH will reduce the negative surface charge of clay particles, including organic matter and Fe/Mn/Al (hydro) oxides, and increase the activity of cations such as H^+, Fe^{3+}, and Al^{3+} that will compete with As and Cr (Guan et al., 2018). In this study the sediments displayed an alkaline pH which ranged from 8.0 to 8.7 (Table 1).

3.2. Total arsenic and total chromium concentrations

Total concentration of both As and Cr varied between land use and sediment depth. Generally, total As concentration ranged from 16.2 to 141.7 mg kg^{-1} (Fig. 1a), which is higher than the 8.2 mg kg^{-1} mean value for total As reported by the US National Oceanic and Atmospheric Administration (NOAA) (NOAA, 1999) and the 5.9 mg kg^{-1} mean value from the Canadian sediment quality guidelines (Canadian Council of Ministers of the Environment, 2002). Total As in the reservoirs were in the order of cropland $>$ grazing $>$ forest (Fig. 1a and Table 1). Total As concentration in the cropland site presented the highest value variation within the four layers evaluated, with mean concentrations increasing from the top sediment to the deepest layers as follow: $106.4 < 119.74 < 132.4$ mg kg^{-1} for the layers 0–25, 25–50 and 50–75 cm, respectively (Table 1). This was much higher compared to 12.2 mg kg^{-1} reported by Schaefer et al. (2017) at 1.5 m depth in central Yangtze River Basin that is surrounded by agricultural land. On the other hand, for the grazing and forest sites, the greatest concentrations of total As was generally found in surface or sub-surface sediments (Table 1), the concentrations decreasing with sediment depth. The top 0–25 cm depth contained 38% and 20% more As compared to 50–75 cm depth for grazing and forest land uses, respectively. Elevated concentrations of As in LWREW sediment pose an environmental risk because of the carcinogenic properties of As and the potential for its migration to deep aquifers that could serve as a future drinking water source (Kabata-Pendias and Pendias, 2010). The mean total As in the full sediment column for cropland was 118.5 mg kg^{-1} followed by grazing at 64.4 mg kg^{-1}, both were much higher than the Threshold Effect Level (5.9 mg kg^{-1}) (Canadian Council of Ministers of the Environment, 2002).

Total Cr concentrations ranged from 5.06 to 40.1 mg kg^{-1}, (Fig. 1b) and were lower compared to the ranges reported by Richards et al.

Table 1
Total C, As, Cr and extractable concentrations of As and Cr in the Little Washita River Experimental Watershed Reservoir (LWREW). The data indicate mean - ± standard error of mean, determined using Tukey tests at $P < 0.05$. Different letters in super script indicate significant difference.

Reservoir ID/ land use	Depth (cm)	pH	Total C (g kg^{-1})	Total As	Total Cr	Extractable As	Extractable Cr (mg kg^{-1})
LW11/Grazing	0–25	8.07 ± 0.12^{a}	33.3 ± 8.93^{a}	85.1 ± 7.11^{a}	25.5 ± 2.47^{a}	1.06 ± 0.09^{a}	0.25 ± 0.02^{a}
	25–50	8.22 ± 0.16^{a}	16.6 ± 8.21^{a}	54.7 ± 22.7^{a}	21.2 ± 6.51^{a}	0.66 ± 0.12^{b}	0.30 ± 0.03^{a}
	50–75	8.30 ± 0.15^{a}	11.4 ± 5.92^{a}	53.4 ± 27.1^{a}	21.5 ± 9.60^{a}	0.66 ± 0.11^{b}	0.26 ± 0.02^{a}
	P-value	0.56	0.17	0.50	0.53	0.04	0.38
LW20/Forest	0–25	8.06 ± 0.20^{a}	23.9 ± 13.7^{a}	48.1 ± 21.5^{a}	11.6 ± 4.23^{a}	0.53 ± 0.10^{a}	0.27 ± 0.03^{a}
	25–50	8.69 ± 0.17^{a}	6.10 ± 4.05^{a}	32.0 ± 8.05^{a}	9.02 ± 1.60^{a}	0.31 ± 0.02^{a}	0.34 ± 0.08^{a}
	50–75	8.56 ± 0.23^{a}	4.53 ± 3.29^{a}	38.3 ± 9.65^{a}	10.0 ± 2.05^{a}	0.38 ± 0.07^{a}	0.22 ± 0.03^{a}
	P-value	0.12	0.25	0.73	0.80	0.13	0.35
LW24/Cropland	0–25	8.07 ± 0.04^{ab}	36.9 ± 8.06^{a}	106 ± 6.23^{b}	26.0 ± 1.77^{b}	0.47 ± 0.05^{a}	0.23 ± 0.04^{a}
	25–50	8.01 ± 0.06^{b}	33.7 ± 6.49^{a}	119 ± 3.36^{ab}	29.2 ± 1.00^{ab}	0.66 ± 0.12^{a}	0.23 ± 0.01^{a}
	50–75	8.22 ± 0.03^{a}	21.5 ± 1.98^{a}	132 ± 3.76^{a}	32.5 ± 0.99^{a}	0.66 ± 0.06^{a}	0.22 ± 0.01^{a}
	75–100	8.15 ± 0.06^{ab}	34.3 ± 11.1^{a}	115 ± 5.01^{b}	25.9 ± 1.30^{b}	0.70 ± 0.15^{a}	0.24 ± 0.03^{a}
	P-value	0.05	0.51	0.01	0.01	0.43	0.94

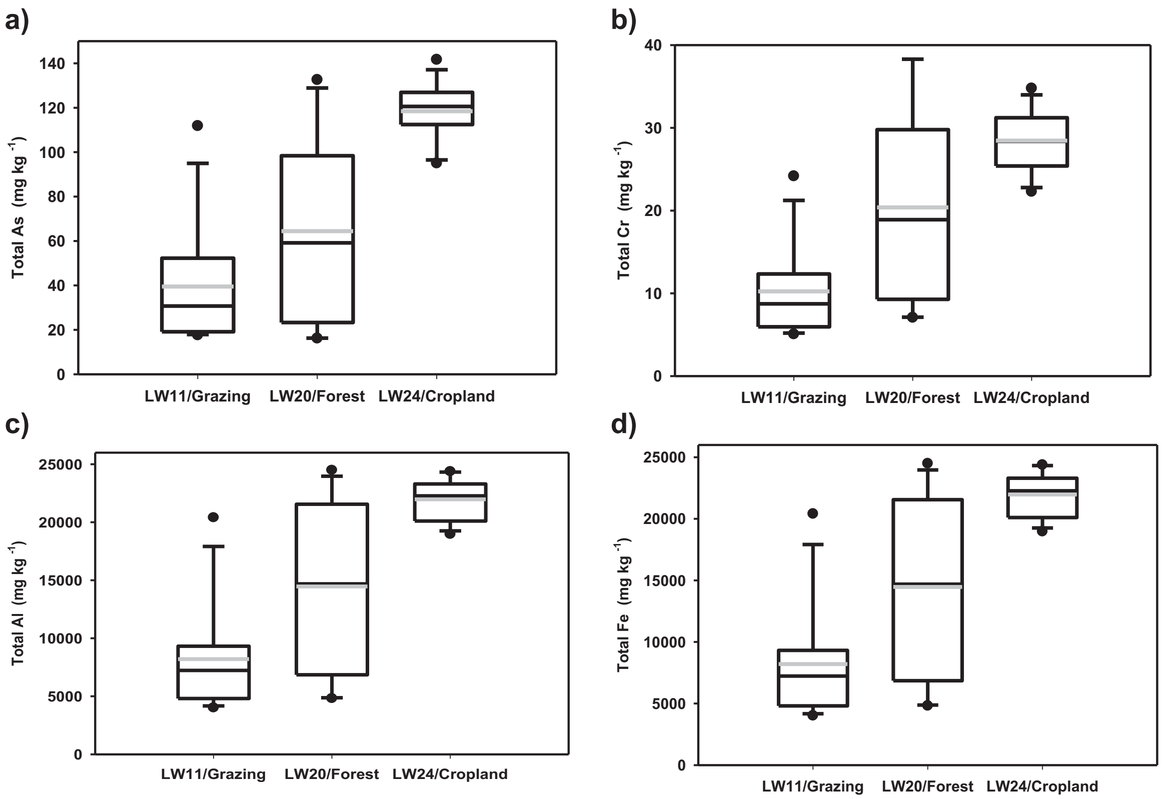

Fig. 1. Total As (a), Cr (b) Al (c), and (Fe) concentrations in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs. • = *maximal/minimal concentration; median values are indicated by a blue line inside the boxes.* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(2012) for Oklahoma soils (4.30–69.7 mg kg^{-1}). The values were also lower than the 81 mg kg^{-1} mean value for total Cr reported by the US National Oceanic and Atmospheric Administration (NOAA) (NOAA, 1999), but the range exceeded the value reported by Canadian sediment quality guidelines (37.3 mg kg^{-1}) (Canadian Council of Ministers of the Environment, 2002). The total Cr concentration in the reservoirs is in the order of cropland > grazing > forest (Fig. 1b and Table 1). The cropland use exhibited the different total Cr concentration between depths with 50–75 cm depth (35.5 mg kg^{-1}) containing significant higher total Cr concentration than the surface sediment (26.4 mg kg^{-1}) ($P = 0.0111$). However, in both grazing and forest land use there was no significant difference between depths (Table 1).

3.3. *Extractable arsenic and chromium concentrations*

The toxicity of heavy metals in sediments often cannot be ascertained from only total metal concentrations, especially when background values are unavailable. Available/extractable concentrations of the metals in sediments provides more information on metals associations and availability to biota (Fernandes et al., 2008). So, it is necessary to estimate the possible bioavailable fraction or extractable fraction, which is defined as the amount of metal that can be released to the water or exchanged with aquatic organism and incorporated into their tissues (Hendożko et al., 2010). All samples contained detectable extractable concentrations of As and Cr.

The extractable As ranged from 0.31 to 1.06 mg kg^{-1} (averaging 0.62 mg kg^{-1}) (Fig. 2a), accounting for 1.37% of total As concentration. When considering all three reservoirs, extractable As concentration was

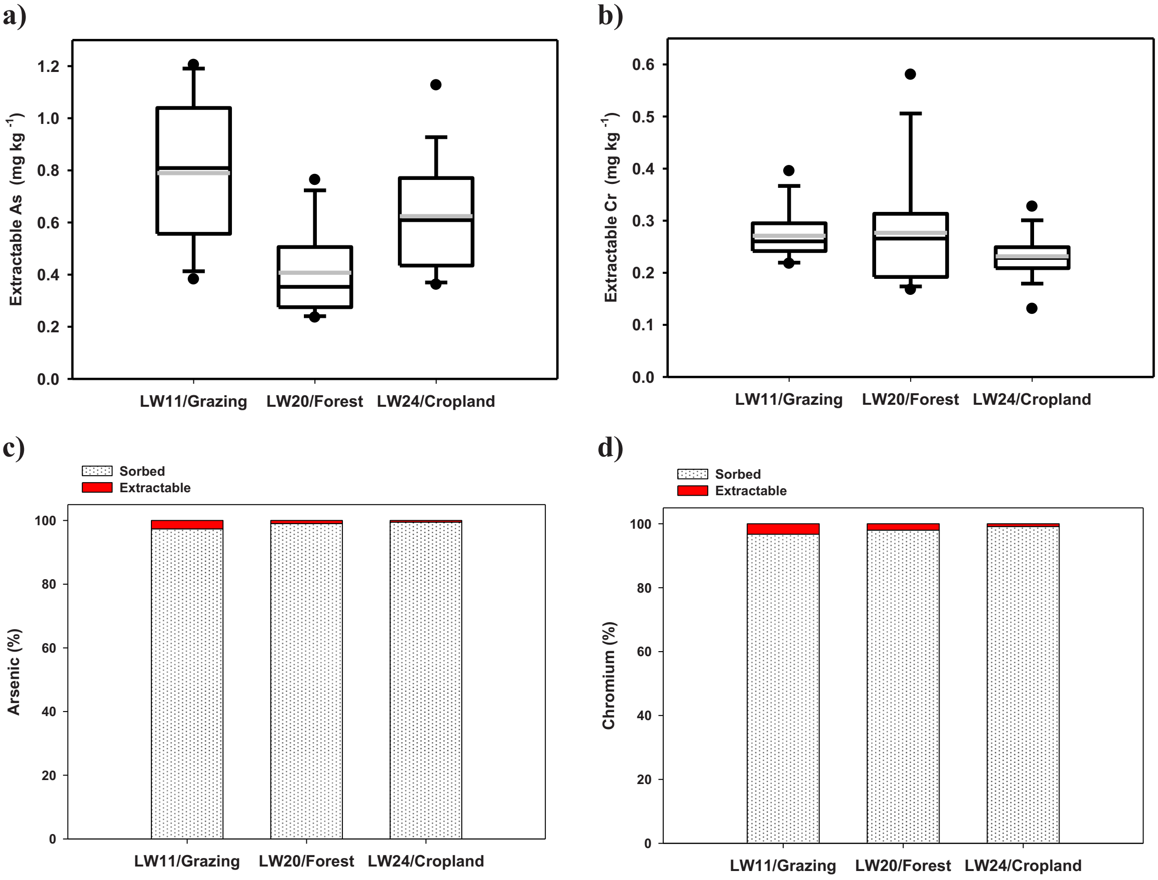

Fig. 2. Extractable and sorbed As (a, c) and Cr (b, d) concentrations in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs.● = *maximal/minimal concentration; median values are indicated by a line inside the boxes.*

in the order of grazing > cropland > forest (Fig. 2a). The metal contents varied with the depth (Table 1). The highest As concentration was in grazing site at 0–25 cm depth (1.06 mg kg^{-1}) and followed by cropland at 75–100 cm depth (0.70 mg kg^{-1}) compared to other depths. The proportion of extractable As for cropland, grazing and forest was 0.53%, 2.65% and 0.95% (Fig. 2c), respectively, which demonstrate that more than 97% of As in the sediment is unextractable. However, As is not permanently bound to sediments, and may be released into the water column when the environmental conditions and soil chemistry change (Goldberg, 2002; Wu et al., 2014) potentially worsening As toxicity. This is because sediments serve both as a sink and source of heavy metals, releasing them into the water column which could lead to contamination of groundwater. The adsorption, desorption, and subsequent concentrations of heavy metals in sediments are affected by many physico-chemical factors such as temperature, hydrodynamic conditions, redox state, content of organic matter and microbes, salinity, and particle size (Zhao et al., 2014). An important determinant of metal bioavailability in sediments is pH. A lowering in pH increases the competition between metal ions and H$^+$ for binding sites in sediments and may result in dissolution of metal complexes, thereby releasing free metal ions into the water column (Nowrouzi et al., 2014).

The extractable Cr ranged from 0.18 to 0.34 mg kg^{-1} (averaging 0.25 mg kg^{-1}) (Fig. 2b), accounting for approximately 1.46% of the total Cr. Extractable Cr concentration was higher than the WHO level in water (50 μg L^{-1}) (WHO, 2017), for all sites and depths (Fig. 2b and Table 1). The mean extractable concentrations of Cr in all reservoirs (cropland, grazing and forest) were 0.23 and 0.27 and 0.28 mg kg^{-1} (Fig. 2b), respectively. While cropland had the lowest mean Cr at depth 50–75 cm (0.11 mg kg^{-1}) forest at 25–50 cm had the highest concentration (0.34 mg kg^{-1}) (Table 1). Although Cr exhibited a high concentration level in the reservoir sediment, most of it was not extractable and potential adsorbed or complexed with oxides/hydroxides of Al and Fe, that influence the distribution of Cr in the sediment (Zhang et al., 2018). Less than 0.94% of Cr was observed in the extractable fraction, suggesting that most of the Cr was sorbed to the sediment (Fig. 2d) (Lilly et al., 2015). Chromium has been proven to be a carcinogenic substance, which is toxic to aquatic organisms even at low concentrations (Ali et al., 2019).

Arsenic and Cr were present in all the sediment samples collected from the LWREW during this study (Table 1 and Fig. 2). This observation suggests these metals are ubiquitous contaminants of the sediments in these systems. This could be from multiple sources associated with geogenic processes as well as anthropogenic activities. Anthropogenic sources such as the input of fertilizers, pesticides and other soil amendments such as biosolids, animal manures and drilling mud may increase heavy metals levels in soils and sediments (Zhang and Schroder, 2014). For example, lead arsenate was used on cotton fields and orchards as a pesticide in the 1940s (Adriano, 2001). Richards et al. (2012) determined background levels of As and Cr in Oklahoma benchmark soils from various locations representing major land resource areas across the state and found the mean background level of As and Cr in Oklahoma soils were 6.25 and 26.2 mg kg^{-1}, respectively. Richards et al. (2012) argued that the relatively high level of As in these soils is probably due to naturally occurrence of As in geologic parent materials. However, it is generally believed that aquatic ecosystems could be polluted with heavy metals enriched by various anthropogenic sources (Wei et al., 2019; Qu et al., 2018). Birch and Apostolatos (2013) demonstrated that anthropogenic metals have higher mobility and bioavailability than metals from geogenic origin. Potential pollution of the associated reservoirs by As and Cr is probable, and it is important to continuously monitor the sediment and water quality to prevent further deterioration of water resources. While heavy metals in the reservoirs are generally bound to the sediments, (Zhang et al., 2016), they may be released into the water column via sediment resuspension, due to changing chemical and hydrological conditions and could accumulate in plants and animals (Zhang and Schroder, 2014).

3.4. Influence of carbon functional groups on As and Cr availability

Total C concentration ranged from 4.53 to 36.9 g kg^{-1} (Table 1). This wide range in total C improves the ability to determine the relationship between C and As and between C and Cr. Total C differed significantly between land-use and depths, highest concentration was found in the cropland at 0–25 cm depth (36.9 g kg^{-1}) followed by grazing (33.3 g kg^{-1}) and lowest in the forest (4.53 g kg^{-1}) at 50–75 depth cm (Table 1). Cropland reservoir had the highest C probably as a result of agricultural activities that disturb the soil which can lead to erosion and runoff which deposits sediments in the reservoir (Olson et al., 2016). The high concentration of C in the sediment of grazing reservoir may have been as a result of animal fecal matter as well as trampling that enhances soil erosion and deposition of sediment in the reservoir (Giguet-Covex et al., 2014). The forest site had lower disturbance and greater soil cover, which potentially minimize translocation of sediment to the reservoirs (Lawrence et al., 2016).

In this research, correlation analysis was used to evaluate the relationship of total C content with the accumulation of As and Cr. Correlation analysis showed that As and/or Cr and total carbon were related to each other and were layer-dependent (Fig. S2). It was clear that C had a significant positive relationship with both As ($r = 0.4090$; $P = 0.0017$) (Fig. S2a) and Cr ($r = 0.3368$; $P = 0.0111$) sorption (Fig. S2b). These findings were consistent with previous findings that reported the presence of organic matter might increase the adsorption of As, thus reducing As mobility (Xu et al., 1991). On the other hand, organic acids could also reduce As mobility by serving as a binding agent and/or by forming insoluble complexes, especially when saturated with metal cations (Wang and Mulligan, 2006).

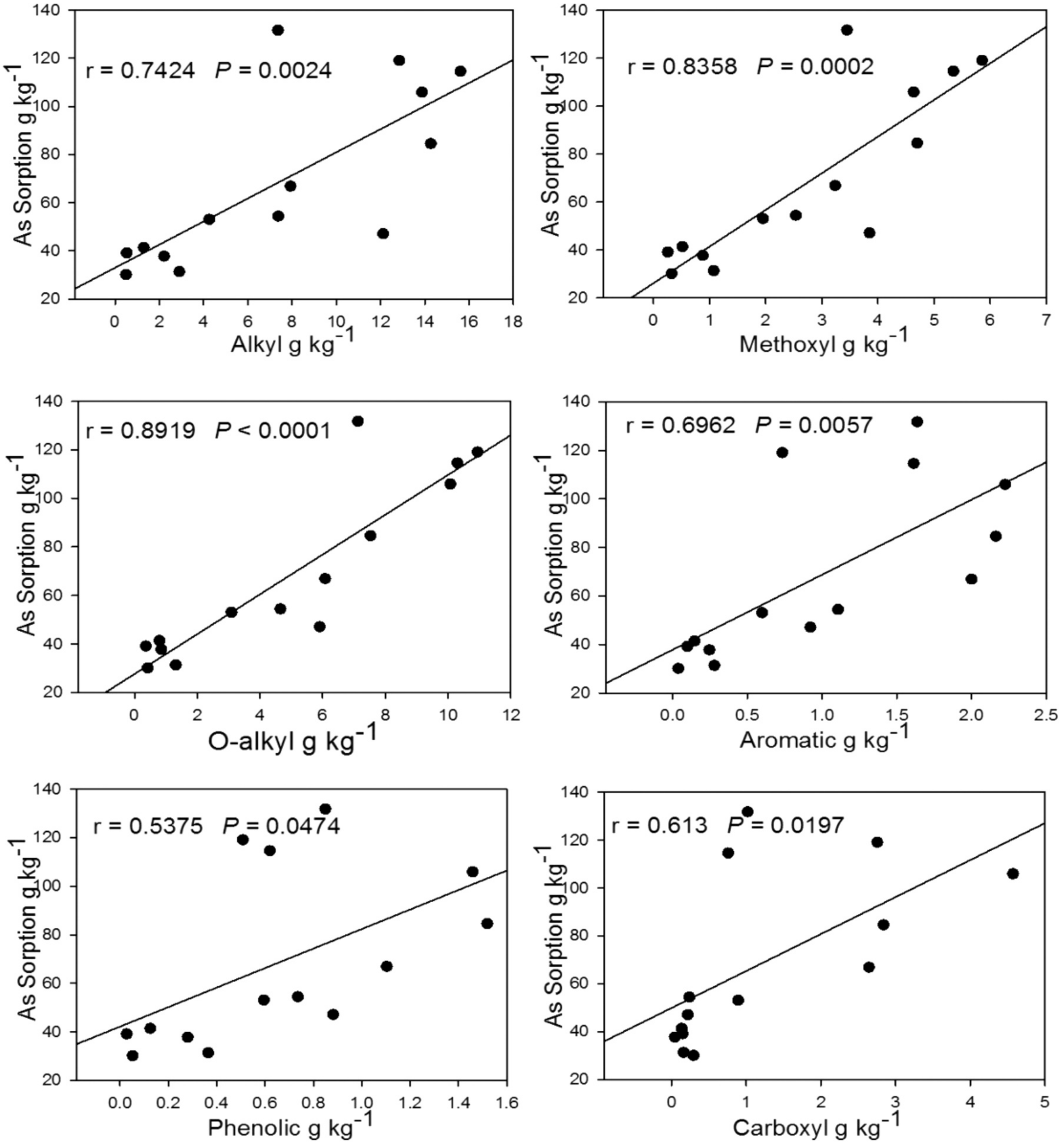

Fig. 3. Arsenic sorption and C functional groups relationship in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs.

To reveal the influencing mechanism of total carbon on As and Cr adsorption, ^{13}C nuclear magnetic resonance (NMR) spectroscopy was employed to characterize the sediment samples. Therefore, this study further identified how specific C functional groups influenced the As and Cr sorption. The As relationship with total C functional groups was in the order of O-alkyl C ($r = 0.8919$; $P < 0.0001$) $>$ methoxyl C ($r = 0.8358$; $P = 0.0002$) $>$ alkyl C ($r = 0.7424$; $P = 0.0024$) $>$ aromatic C ($r = 0.6962$; $P = 0.0057$) $>$ carboxyl C ($r = 0.6130$; $P = 0.0197$) $>$ phenolic C ($r = 0.5375$; $P = 0.0474$) (Fig. 3). Similarly, Cr relationship with C functional groups followed the same order but different levels of significance; O-alkyl C ($r = 0.8675$; $P < 0.0001$) $>$ methoxyl C ($r = 0.8251$; $P = 0.0003$) $>$ alkyl C ($r = 0.7336$; $P = 0.0028$) $>$ aromatic C ($r = 0.7193$; $P = 0.0037$) $>$ carboxyl C ($r = 0.6321$; $P = 0.0153$) $>$ phenolic C ($r = 0.6031$; $P = 0.0224$) (Fig. 4). It was evident that the C functional groups decreased with increasing depth in all sites (Table 2). The carbon functional groups in all sites were in the order of alkyl C $>$ O-alkyl C $>$ methoxyl $>$ carboxyl $>$ aromatic $>$ phenolic C. However, O-alkyl had the strongest relationship with both As and Cr sorption (Figs. 3 and 4). This contrasted previous studies, which indicated that C functional groups involved in Cr retention and inhibition of its mobility include aromatic (Zhang et al., 2017), carboxyl (Chen et al., 2011; Huang et al., 2012) and phenolic C (Hsu et al., 2009; Zhao et al., 2016). O-alkyl C is a labile form of C that contain high content of polysaccharides found in fresh plant and microbial biomass, as the labile O-alkyl C is decomposed this results in accumulation of more chemically stable alkyl C (Baldock and Skjemstad, 2000; Hamdan et al., 2012). This suggests that the stronger relationship between O-alkyl C and As and Cr sorption could be as a result of dominance of As and Cr from less

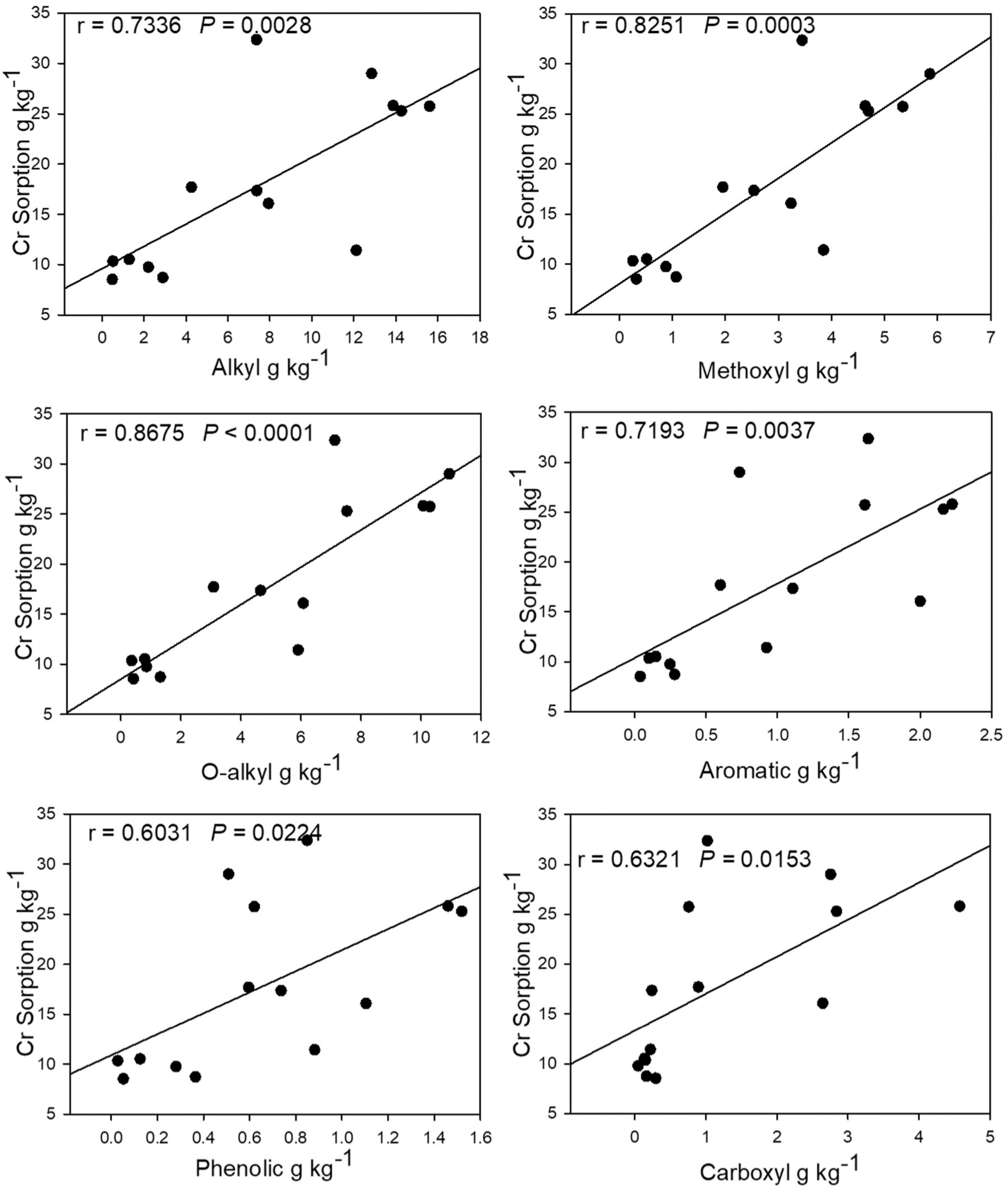

Fig. 4. Chromium sorption and C functional groups relationship in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs.

Table 2
Total C functional groups concentrations (g kg^{-1}) in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs.

	Depth (cm)	Alkyl	Methoxyl	O-alkyl	Aromatic	Phenolic	Carboxyl
		(g kg^{-1})					
FW11/Grazing	0–25	14.27	4.70	7.53	2.16	1.52	2.84
	25–50	7.37	2.54	4.66	1.11	0.74	0.24
	50–75	4.26	1.96	3.09	0.60	0.60	0.89
FW20/Forest	0–25	12.1	3.85	5.91	0.92	0.88	0.22
	25–50	2.90	1.07	1.32	0.28	0.36	0.16
	50–75	2.22	0.88	0.86	0.25	0.28	0.
FW24/Cropland	0–25	13.9	4.60	10.1	2.23	1.46	4.57
	25–50	12.8	5.90	10.9	0.73	0.51	2.76
	50–75	7.36	3.45	7.13	1.64	0.85	1.02
	75–100	15.6	5.30	10.3	1.60	0.60	0.80

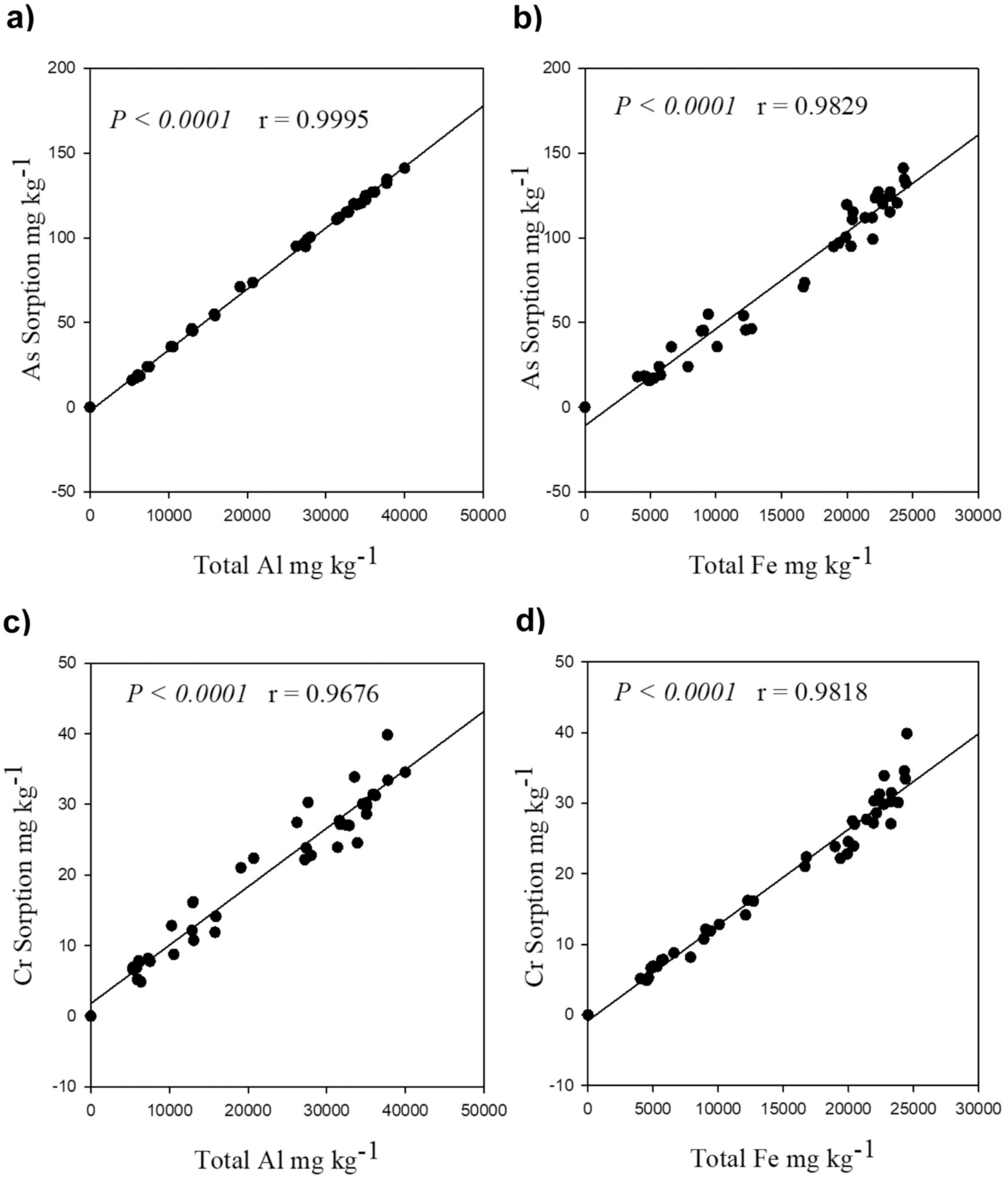

Fig. 5. Arsenic and Cr relationship with Al (a and c) and Fe (b and d) in sediment samples of the Little Washita River Experimental Watershed (LWREW) reservoirs.

decomposed organic material from the surrounding area. This could be as a result of plant uptake of As and Cr from the surrounding area, and the labile organic matter from plants in the surrounding area is translocated to the reservoir (Houel et al., 2006). This result is further supported by the relatively higher content of O-alkyl C in the 0–25 cm depth compared to subsequent depths, suggesting accumulation of lesser decomposed organic matter from relatively recently deposited sediments. If the strong relationship between As and Cr with O-alkyl is as a result of plant uptake of the As and Cr, considering that O-alkyl is labile form of C that is easily degraded, it suggests that if the O-alkyl C is degraded the As and Cr are likely to be released to the water (Bauer and Blodau, 2006). However, the anaerobic conditions in the reservoir are likely to result to low organic matter decomposition rates (Steinmuller et al., 2019), preserving the O-alkyl C and consequently retaining most of the As and Cr in unavailable form.

3.5. Influence of Al and Fe on As and Cr availability

It is well established that As sorb rapidly and extensively onto a variety of metal (e.g., Fe, Al) (hydro)oxides, carbonates, organic matter, and clay minerals (Goldberg and Johnston, 2001), which are the main pH-dependent charged surfaces in soil and sediments. Concentrations of total Al and Fe ranged from 5336 to 40,011 and 4025 to 24,496 mg kg^{-1} (Fig. 1c, d), respectively, with Al being the most abundant metal in sediments. These wide ranges in sediment chemical properties are conducive to the identification their relationship with heavy metals concentrations in the sediments.

This study observed positive relationship between sorbed As and Cr with Al and Fe fractions in the sediment reservoir (Fig. 5). Arsenic sorption correlated positively with total Al ($r = 0.9995$; $P = 0.0001$) (Fig. 5a), and total Fe ($r = 0.9829$; $P = 0.0001$) (Fig. 5b), suggesting that Al-As and Fe-As were also critical in regulating As availability and transformation in sediments which explain the exhibited very low available of As in the sediment (1.37%) (Fig. 2a) suggesting that these constituents play an important role in the As sorption capacity of sediments. The finding agreed with Girouard and Zagury (2009) that sediments rich in Fe and Al oxides and oxy-hydroxides have been shown to rapidly sorb As. In addition, the findings were consistent with previous studies indicating positive correlations between As adsorption and extractable Al and Fe content of sediments (Wauchope and Mc Dowell, 1984). Cai et al. (2002) examined As in soils from South Florida golf courses and found that As contents were correlated with the distribution of Al ($r = 0.5459$), Fe ($r = 0.4827$) and Mn ($r = 0.7674$). These previous studies concluded that oxides and hydroxides of Fe, Mn and Al control the distribution of As in these soils. The retention and bioavailability of As may largely depend on the content and composition of organic materials and the Al, Fe, and Mn content in the sediments. Arsenic is primarily bound to the residual fraction demonstrating that the majority of As in the sediments are likely to be incorporated with aluminosilicate minerals, displaying relatively limited mobility and bioavailability (Guan et al., 2018).

Similarly, Cr sorption had a positive relationship with total Al ($r = 0.9676$; $P = 0.0001$) (Fig. 5c), and Fe ($r = 0.9818$; $P = 0.0001$) (Fig. 5d). Positive correlation ($P < 0.001$) between As, Cr, Al, and Fe in surface sediments for all three reservoirs suggested that variation in the total concentration of the metals were influenced by sediments chemical properties. Likewise, Cr and As can be adsorbed by Al, Fe-Mn oxides (Alloway, 1990). These results suggest that the observed high unavailability of As and Cr was also influenced by both Al and Fe concentrations in the sediments.

3.6. Ecological risk assessment

The accumulation of toxic metals in the sediment poses a long-term threat to the aquatic environment. Consequently, there is a need for sediment quality indicators to assess the risks of contamination posed by heavy metals in aquatic environment. The potential toxicological effects of sediment As and Cr content were assessed in this section. We used the Threshold Effect Level (TEL) and Probable Effect Level (PEL) in the Canadian Quality Criteria (Canadian Council of Ministers of the Environment, 2002) and US National Oceanic and Atmospheric Administration – (NOAA, 1999) of heavy metals in freshwater sediments to evaluate contamination level of total As and total Cr in the sediments of the LWREW. Threshold Effect Level (TEL) is the concentrations below which adverse biological effects rarely occur. The TELs are considered to provide a high level of protection for aquatic organisms. The PEL is the concentrations above which adverse biological effects frequently occur. So, the PELs are considered to provide a lower level of protection for aquatic organisms.

It indicates that a sediment has been severely contaminated with serious toxicity to organisms when the concentration of a heavy metal in the sediments is greater than the PEL. In contrast, it suggests that the sediment has been lightly polluted or unpolluted when the concentration of the heavy metal is lower than the TEL, which has light or no biological toxicity effects. It shows that the sediment has a moderate pollution when the concentration lies between TEL and PEL, and there is an equal probability of this heavy metal producing toxicity and non-toxicity (Song et al., 2015). Arsenic concentrations in all sediment samples for the three sites in all depths exceeded the TEL (5.9 mg kg^{-1}) and the PEL (17 mg kg^{-1}) (Table S4). The mean concentrations of As for cropland (118.5 mg kg^{-1}), grazing (64.4 mg kg^{-1}) and forest (39.5 mg kg^{-1}) land-use were approximately twenty, eleven and seven times greater than the TEL and seven, four and two times greater than the PEL, respectively (Table S4). These results suggest that any organisms that lived in these sediments would likely be adversely affected, and toxic effects from long-term exposure to As would be predicted to occur. For example, As bioaccumulation in fish liver and kidney could result in depletion of enzymatic activities, immune system dysfunction and hyperglycemia (Kumari et al., 2017). On the other hand, total Cr concentrations in all reservoirs evaluated was found lower when compared to the TEL (37.3 mg kg^{-1}) and PEL (90 mg kg^{-1}). The highest Cr concentration (28.5 mg kg^{-1}) was found on the cropland use.

4. Conclusion

This study focused on the total and extractable As and Cr distribution in reservoirs sediments and examined how Al, Fe, total, C content and its functional groups affected the As and Cr availability. The results indicate that both total and extractable metal concentrations were highly variable and were affected by dominant land use in the watershed. The cropland site had the highest As and Cr concentrations followed by the grazing site. The study confirmed previous results (Pouschat and Zagury, 2006) and suggest that Al, Fe, total C concentrations and C forms are factors that significantly influence As and Cr unavailability in the sediments from the three reservoirs in the LWREW. O-alkyl C related strongly with As and Cr, however, O-alkyl lability is of concern in terms of retention of As and Cr in unavailable form in the long term, unless the anaerobic condition could favor low organic matter decomposition rates. Considering that the sediment in the study were dominantly alkaline and more than 95% of As and Cr were unavailable, suggesting that alteration of sediment pH to more acidic levels could potentially enhance availability of As and Cr. Therefore, further investigation is required to determine how changes in sediment pH, especially more acidic pH would affect As and Cr availability. The assessment of sediment quality was achieved by using sediment quality guidelines (NOAA and Canadian guidelines). The sediment concentration analysis results illustrated that As at all reservoirs exceeded their respective either TEL or PEL values, indicating that the existing concentrations of metals in these sediments were sufficiently high to cause adverse effects. However, Cr concentrations in all reservoirs evaluated was found lower when compared to the TEL and PEL. Our study raises the need to complement the information about the background levels of As and Cr in sediments from LWREW as well more research is needed on the concentration of As and Cr in the water.

CRediT authorship contribution statement

The following authors were involved with the indicated activities that led to the successful completion of this paper. **Ngatia L.W.** Study conceptualization, sampling design, data interpretation, writing. **De Oliveira L.M.** samples processing and analysis, data analysis and interpretation, writing. **Betiku O.C.** samples processing, data analysis and writing. **Fu R.** 13C NMR samples analysis, spectra processing, data interpretation and writing. **Moriasi D.N.** site identification, sampling design, data interpretation and writing. **Steiner J.L.** site identification, sampling design, data interpretation and writing. **Verser J.A.** sampling design, samples collection, sample processing and writing. **Taylor R.W.** data processing and interpretation, writing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Many thanks to Olumide Arigbede for all the statistical analysis. This work was funded by USDA Agricultural Research Service Cooperative Agreement Grant Number 58-3070-7-009. All NMR measurements were performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1644779 and the State of Florida.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2020.111468.

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