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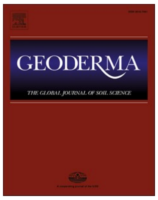

Soil colloidal particles in a subtropical savanna: Biogeochemical significance and influence of anthropogenic disturbances

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ABSTRACT

Soil colloids (diameter < 1000 nm) are comprised mainly of clay minerals and organic matter, and play major roles in determining ion exchange capacity and in regulating key biogeochemical processes. Consequently, it is important to understand how soil colloids and their functions are influenced by land cover and anthropogenic disturbances. In grasslands, savannas, and other dryland ecosystems across the globe, woody plants are encroaching due to livestock grazing, fire suppression, elevated CO_2 concentrations, and climate change. These major land cover changes could influence soil colloidal properties, with implications for soil C, N, and P cycles. We assessed how woody encroachment, livestock grazing, and fire interact to influence soil colloidal properties in a juniper-oak savanna. Surface soils (0–10 cm) from the southern Great Plains (Texas, USA) were collected from long-term treatments differing in grazing intensity (none, moderate, and heavy) and fire history. Within each treatment, soil samples were taken under grass, juniper, and oak canopies. Water dispersible soil colloids (WDC, d < 500 nm) were isolated and analyzed by asymmetric flow field-flow fractionation and their P species by liquid-state ^{31}P-nuclear magnetic resonance spectroscopy (^{31}P NMR). Soil beneath oak and juniper canopies had smaller WDC and elevated colloidal organic carbon (OC) and P concentrations, especially in nanocolloid (<30 nm) and fine colloid (30–160 nm) size fractions. Woody encroachment enriched Ca, Fe, Al, Si and Mg in WDC in the ungrazed control, but not in any of the other grazed or burned areas. Colloidal soil P mainly occurred as orthophosphate and orthophosphate diesters, and was present as OC-Ca-P complexes in fine and medium colloid fractions (30–500 nm), while P in the nanocolloid fraction (<30 nm) was in direct association with Ca. Moderate grazing did not affect the retention of colloidal P, while heavy grazing potentially increased the loss risk of colloidal P. Fire accelerated soil P loss from colloid fractions only in woody areas. Our findings highlight that woody encroachment strengthens the retention of OC and P by soil colloids, consequently increasing overall C and P pools in savanna soils.

1. Introduction

Natural colloidal particles (diameter < 1000 nm) are the smallest particulate phase in soils and consist of organic and inorganic components formed during litter decomposition and mineral weathering (Guggenberger and Haider, 2001; Yan et al., 2018). Some natural colloidal particles can enter the soil solution, potentially enhancing the mobile fraction in soil. The colloid fractions which tend to disperse in water from soil aggregates are referred to as water dispersible colloids (WDC), which can act as potential carriers of nutrients to groundwater (Seta and Karathanasis, 1996). Soil texture (Jiang et al., 2017; Moradi et al., 2020), pH (Sun et al., 2020; Wang et al., 2020; Zhang et al., 2021), organic matter and mineral composition (Krause et al., 2018; Sun et al., 2020), vegetation structure (Missong et al., 2018a), and anthropogenic disturbances (Lekfeldt et al., 2017; Li et al., 2019) all are known to influence soil colloid formation. For example, Jiang et al. (2017) found that nano-sized (1–20 nm) organic matter–Fe/Al–phosphorus (P) colloids were absent in soils with low redox potential (Cambisols) but

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present in soils with high redox potential (Stagnosol).

Natural colloidal particles are commonly regarded as a potential reservoir for soil P, driving P transformation from soil to soil solution where P is more bioavailable (Konrad et al., 2021; Menezes-Blackburn et al., 2021). In contrast to C and N, P limitation is pervasive in highly weathered soils of terrestrial ecosystems, including tropical forests and savannas (Rodrigues et al., 2016; Turner et al., 2018), due to limited source from bedrock weathering (Lang et al., 2016). In mesic temperate ecosystems such as forests and agroecosystems, P is often associated with colloidal organic matter as well as Fe/Al hydroxides (Henderson et al., 2012; Holzmann et al., 2016; Jiang et al., 2015; Li et al., 2021). However, in more arid and semiarid ecosystems, Ca seems to be the key element in colloidal P binding (Moradi et al., 2020; Turner et al., 2004). However, little is known regarding the soil colloidal responses to changes in land cover and use in savanna ecosystem.

Savanna ecosystems cover approximately 20 % of the earth's land surface (Lehmann et al., 2011) and store approximately 30 % of the total carbon (C) present in vegetation and soils globally (Houghton, 2014). Woody plant encroachment into savanna ecosystems is a geographically widespread phenomenon that appears to be driven by fire suppression, livestock grazing, climate change, and rising atmospheric CO_2 concentration (Archer et al., 2017; Boutton et al., 1998; Buitenwerf et al., 2012; Sankaran et al., 2005; Stevens et al., 2017). Woody encroachment generally increases soil organic C, nitrogen (N), and P storage in soils in arid/semi-arid regions (Blaser et al., 2014; Eldridge et al., 2011; Krull et al., 2005; Sitters et al., 2013), which likely increase the source of colloidal OC and P (Krause et al., 2020; Zhang et al., 2021). Furthermore, other soil properties may be altered following woody encroachment, such as porosity (Yu et al., 2018) and hydrologic characteristics (Holdo et al., 2020). Increased porosity, and high water holding capacity can retard soil colloid release (Lekfeldt et al., 2017; Mills et al., 2017). However, it remains unknown how woody encroachment will impact colloid formation and subsequently influence soil C, N, and P storage and dynamics in grasslands, savannas, and other arid and semiarid ecosystems.

Anthropogenic disturbances to savanna ecosystems, particularly grazing and the alteration of fire regimes, also have strong potential to influence nutrient storage in soils. In grasslands and savannas around the world, livestock grazing has been shown to drive changes in: (i) biodiversity of plant and microbial communities, (ii) rates of primary production, (iii) above- vs belowground biomass allocation patterns, (iv) soil chemical and physical properties, and (v) storage and turnover rates of soil C, N, and P (Eldridge et al., 2017; He et al., 2020; Liang et al., 2021; McSherry and Ritchie, 2013; Milchunas and Lauenroth, 1993; Pineiro et al., 2009). The direction and magnitude of these effects do vary with geography, climate, soil type, and grazing management practices (Byrnes et al., 2018; McSherry and Ritchie, 2013; Sanderson et al., 2020). Grazing directly decreases the organic matter input, probably resulting a decrease of colloidal organic matter, such as organic C and P (Li et al., 2021). Moreover, reduced organic matter input probably promotes the release of water dispersible colloids (Lekfeldt et al., 2017). Marquart et al. (2019) reported that a reduction in porosity caused by livestock trampling was counteracted by larger shrubs, and attributed this to the enhanced mass of litter and the increased density of soil surface macropores. At present, little is known in savanna ecosystems regarding the influence of grazing intensity on soil colloidal composition and function.

Similarly, fires in grasslands and savannas can also have significant impacts on C, N, and P storage in soils (Ansley et al., 2006; Holdo et al., 2012; Pellegrini et al., 2018; Pellegrini et al., 2015; Pellegrini et al., 2020). This is due to thermal mineralization, volatilization (Hatten and Zabowski, 2009; Zhao et al., 2012), as well as changes in vegetation structure (Coetsee et al., 2010; Holdo et al., 2012; Pellegrini et al., 2015). Therefore, fires may induce colloid disaggregation as a consequence of the organic matter destruction, or favor strong aggregation when minerals (like Fe/Al oxyhydroxides) recrystallize at high temperatures (Mataix-Solera et al., 2011). However, there is no information on colloid reaction to fire in the encroached savanna.

The purpose of this study was to identify how soil colloids react in a savanna ecosystem experiencing woody plant encroachment and subjected to different grazing intensities and fire regimes. We quantified concentrations of P and other elements in WDC < 500 nm and their size fractions in relation to vegetation cover type, livestock grazing, and prescribed fire by using asymmetric flow field-flow fractionation. The P species were characterized by ^{31}P NMR. We hypothesized that: (i) besides Fe/Al (hydr)oxides, Ca also can be a critical adhesive in colloidal P retention in savanna ecosystems; (ii) colloidal OC and P increase in line with total organic matter accrual in bulk soils during woody encroachment; and (iii) colloid formation and related P retention are hindered by grazing and fire.

2. Materials and methods

2.1. Site description

Field research was conducted at the Texas A&M AgriLife Sonora Research Station (30° 15′ 59″ N; 100° 33′ 57″ W) located in Texas, USA, on the western edge of the Edwards Plateau. The site has a dry-subhumid climate, with a mean annual temperature of 17.9° C, and mean annual precipitation of 586 mm. Surface soils are silty clays and clays of the Tarrant series (clayey-skeletal, smectitic, thermic Lithic Calciustolls) (USDA/NRCS, 2015). Bedrock is indurated limestone from the Lower Cretaceous. Soil properties (pH, texture, and concentrations of C, N, and P) for the study area are summarized in Table S1.

Vegetation in the study area consists of a grassland matrix dominated by the grasses *Hilaria belangeri*, *Bouteloua curtipendula*, *Nassella leucotricha*, and *Aristida* spp.; patches of woody plants dominated by *Quercus virginiana* (live oak) and *Juniperus ashei* are scattered throughout the grassy matrix (Smeins et al., 1976; Taylor et al., 2012). *Juniperus ashei* appears to have increased dramatically in the grasslands of the Edwards Plateau region during the past century (Fuhlendorf and Smeins, 1997; Jessup et al., 2003).

This region was heavily grazed by cattle, sheep, and goats beginning around 1880. In 1948, the Sonora Research Station implemented several long-term grazing treatments that have been maintained up to the present: (i) an 11 ha control where grazing was excluded, (ii) a 24 ha moderately grazed site, and (iii) a 7 ha heavily grazed site. Stocking rates for the moderately grazed area were 6–8 ha/animal unit/yr, while those for the heavily grazed site were 2–5 ha/animal unit/yr. The ratio of cattle:sheep:goats in the grazed areas has been approximately 60:20:20 since 1948 (Marshall, 1995). None of these grazing treatments have experienced fire since their establishment in 1948, and it is unlikely that they have burned since approximately 1880.

In addition to the grazing treatments, we sampled another experimental area (10 ha) where winter-spring fires were applied every other year from 1986 to the present. As with the grazing treatments, it is unlikely that this fire treatment site experienced any fires from 1880 to 1986. The ungrazed control treatment described in the previous paragraph also served as a control for the fire treatment since it had not experienced fire since about 1880, it was on the same soil type, and it was in close physical proximity (0.5 km) to the fire treatment.

2.2. Field sampling

In each of the grazing and fire treatments described above, soil samples were collected from three portions of the landscape: (i) open grasslands (n = 3), (ii) juniper woodlands (n = 3), and (iii) oak mottes (n = 3). Each sample was a composite mixture of bulk topsoil (0–10 cm) derived from three subsamples, each obtained from a 0.1 m^2 quadrat located within an area of approximately 4 m^2. Soils were stored frozen within 5 h of field collection.

2.3. Water dispersible colloids (WDC) extraction

The WDC extraction was based on the protocol of Séquaris and Lewandowski (2003). Soils were air dried and sieved to 2 mm to remove stones and large organic particles. Then, 50 g of soil were mixed with 100 mL Milli-Q water, horizontally shaken at 150 rpm for 6 h, and mixed with an additional 300 mL of water before sedimentation. Sedimentation time was calculated (27 h) for the desired particle size by Stoke's law (Section S1), based on the bottle size and water height (105 mm) in the bottle. Following sedimentation, the non-settling supernatant phase (including solutes and particles < 2 μm) was centrifuged (Biofuge, Heraeus, Hanau, Germany) for 10 min at 6000 g to obtain the desired colloids < 500 nm. The centrifugation time was calculated by Hathaway (1956) (Section S1). The 30 mL of final supernatant containing solutes and WDC ($d < 500$ nm) was the water extractable phase (WEP), and was refrigerated prior to field-flow fractionation. The remaining 300 mL supernatant was centrifuged again at 20,000 g for 4 h to separate the 30–500 nm colloid fraction from the "aqueous phase" fraction (including solutes and < 30 nm nanocolloids). Then both fractions were lyophilized for ^{31}P-Nuclear Magnetic Resonance spectroscopy (^{31}P NMR) measurement. Note that for each element, WEP concentration is the sum of water dispersible colloids-associated and the dissolved element concentration (Javidpour et al., 2009). The WDC concentration was determined from the WEP by using asymmetric flow field-flow fractionation.

2.4. Asymmetric flow field-flow fractionation

The nanocolloids and colloids were size separated using asymmetric flow field-flow fractionation (AF2000, Postnova Analytics, Landsberg, Germany). The field-flow fractionation was coupled online to a UV detector (Postnova Analytics, Landsberg, Germany), a dynamic light scattering detector (DLS; Malvern Instruments), an organic carbon detector (OCD; DOC laboratory Dr. Huber, Germany) and an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7500, Agilent Technologies, Santa Clara, California). The OC, P, Fe, Al, silicon (Si), Ca, and manganese (Mn) concentrations in the WDC fractions were determined by OCD and ICP-MS, respectively. The concentration of each element was converted from OCD or ICP-MS signals. Internal and external standards were added for the measurement and quantitative analysis. Further details of the field-flow fractionation technique and analytical element determination are described in Giddings (1993) and Schimpf et al. (2000). Details concerning the parameters of the separation method based on the previous experience (Missong et al., 2018a) are shown in Table S2.

2.5. ^{31}P-Nuclear magnetic resonance spectroscopy

In order to extract a wide range of organic P (P_o) and inorganic P (P_i) compounds, the procedure of Cade-Menun and Preston (1996) was used. In brief, 0.5 M NaOH and 0.1 M EDTA (Merck) were mixed in a volume ratio of 1:1. We extracted the 2 mm sieved soils, 30–500 nm lyophilized colloids as well as the lyophilized "aqueous phase" (containing solutes and nanocolloids < 30 nm) with the EDTA + NaOH reagent in a w:V ratio 1:10. The samples were shaken for 16 h on a horizontal shaker at 150 rotations min^{-1}, then centrifuged at 10,000 g for 30 min to extract the supernatant, which was lyophilized subsequently. Approximately 100 mg of each lyophilized material was dissolved in pH 13 matrix (0.1 mL 30 % NaOD mixed with 7.4 mL D_2O), and added with methylenediposphonic acid (MDPA, 0.84 mg/mL in pH 13 matrix) reference standard solution, then vortexed and centrifuged at 14,000 g for 30 min. The supernatant was transferred into an NMR tube for the ^{31}P NMR measurement. The ^{31}P NMR measurements were performed on a Varian 600 MHz spectrometer (Varian, Palo Alto, California USA) equipped with a 5 mm broadband probe tuned to the ^{31}P nucleus using methods described elsewhere (Wang et al., 2020). Briefly, the parameters were set as: 45° pulse calibrated at 6.0 μs, 0.4 s acquisition time, 5 s total relaxation delay, 15,800 scans, proton inverse gated decoupling, and a temperature of 293.15 K.

The ^{31}P NMR data analysis was conducted with the MestReNova Software (Mestrelab Research S.L., version 13). The phase and baseline correction as well as the signal assignment of phosphonate, orthophosphate, monoesters, diesters and pyrophosphate was based on previous work (Cade-Menun, 2015; Smernik et al., 2015), and their quantification analysis was conducted based on the ratios of their peak areas to the standard peak area (set as 17.5 ppm).

2.6. Data analyses

The original eluting time of field-flow fractionation was converted to colloid size by comparing the time in DLS fractogram, and the eluting time in field-flow fractionation fractogram. The raw data of the ICP-MS measurements were collected in counts per second with the ICP-MS MassHunter Workstation Software (Agilent Technologies, Santa Clara, California, USA). The raw data of OCD were collected in volts of the detector signal with the field-flow fractionation analytical software (Postnova, Landsberg, Germany). The raw data were exported to Excel® (Microsoft Corporation, Redmond, USA). The peak areas of the separated particle size fractions were integrated and converted to concentration in nmol by means of linear, multipoint calibration. Finally, the results were transformed into μg kg_{soil}^{-1} considering the water content of the samples and the extracted sample weight. One-way ANOVA tests for vegetation type and treatment, and two-way ANOVA tests for their interaction as well as Waller-Duncan T test ($p < 0.05$) were conducted to exam the statistical differences in SPSS (IBM, version 26, Armonk, New York, USA).

To identify the preferential binding partners among the distributed elements, hierarchical tree cluster analysis was applied for each particle size fraction across all sample sites (Gottselig et al., 2017). The distances are given as 1 – Pearson's coefficient, and the complete linkage rule applies for the distance analysis. Thus, the lower the distance, the bigger the occurrence of associations between the elements.

3. Results

3.1. Linkage between P and other elements in WDC size fractions

The particle size related peaks and trend in the OC fractogram of WDC matched those of P and Ca, but differentiated from Al, Si, Fe and Mg (Fig. 1 and S4). Clearly, OC (8–120 mg kg_{soil}^{-1}) dominated in all samples, following by Si, Ca and Al (0.4–12.0 mg kg_{soil}^{-1}), then Fe, Mg and P (0.1–3.8 mg kg_{soil}^{-1}) (Fig. 2a). The fractograms show that OC, P and Ca signals at the first peak of WDC were about 1.5–6 times higher in the oak soil samples compared to grassland (Fig. 1). Their signals in the juniper soil samples were generally intermediate between oak and grassland samples (Fig. S2). The WDC fractogram for OC was dominated by a single peak in the nanocolloids fraction, but with a large shoulder covering fine colloids and to a lesser extent the medium colloids fraction. For OC, P and Ca, the dominant peaks were always related to particle size (Figs. 1 and S4), and were independent of management (control, moderate and heavy grazing, fire) or vegetation type. Furthermore, the proportions of nanocolloidal OC, P and Ca were higher under oaks than under grasslands in every grazing treatment, but there was a decrease in medium colloids and no obvious change in fine colloids (Fig. 2b). Fire significantly reduced the OC and P concentrations in total WDC of oak encroached sites compared to control, especially P in nanocolloids (Figs. 1 and 2a). The interaction of vegetation type and treatment did not show an obvious effect on OC and Ca concentrations in total WDC (Fig. S3).

For Al, Si, Fe and Mg, the WDC fractogram started with a small but sharp peak in the nanocolloids fraction, through one or two wider peaks in fine colloids and finally reached a dominating peak in medium

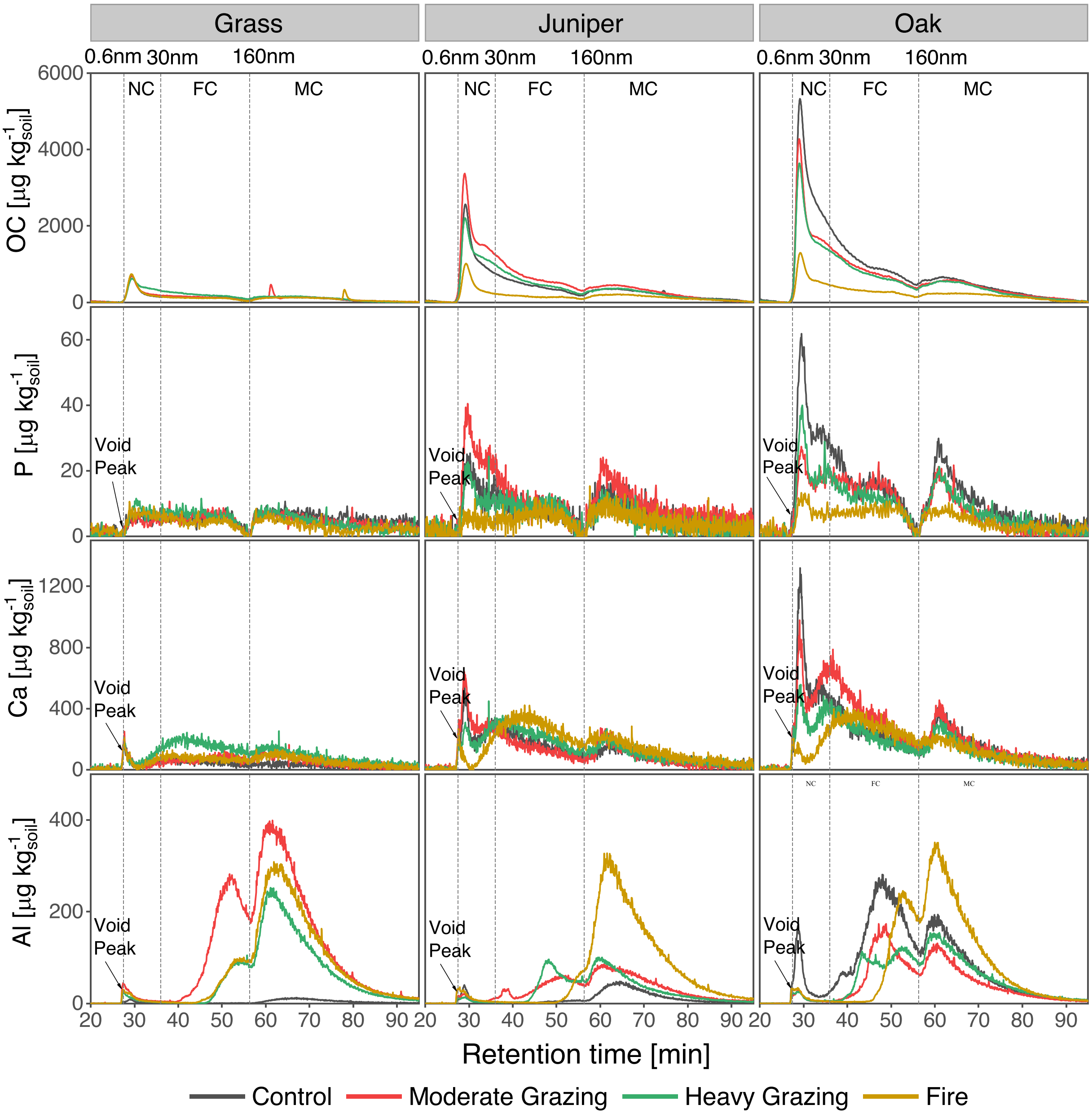

Fig. 1. Soil organic C, P, Ca, and Al concentration in water dispersible colloids (WDC) beneath grass, juniper, and oak with different treatments. Treatments included control, moderate grazing, heavy grazing and fire. The retention time in the x-axis indicated particle size. Nanocolloids (NC), 0.6–30 nm; Fine colloids (FC), 30–160 nm; Medium colloids (MC), >160 nm. One from every-three replicates was selected for the figures. All three replicates showed the same overall pattern in size fractions. Fractograms of other elements are showed in Fig. S2.

colloids fraction (Figs. 1 and S4). The differences in the colloidal size fraction peaks were apparent between vegetation types and land management. Sub-peaks emerged in fine colloids fraction when grassland was encroached by juniper and oak (Figs. 1 and S4), meanwhile the nano-, fine and medium colloidal Al, Si, Fe and Mg concentrations significantly increased (see control grass, juniper and oak sites in Figs. 2 and S5). Grazing and fire, compared to control, increased their values in grassland, but the differences were eliminated when juniper and oak encroached (Fig. S3). Furthermore, the proportions of Al, Si, Fe, and Mg in fine colloids fraction significantly ($p < 0.05$) increased, while that in medium colloids decreased when grasslands were encroached by juniper and oak, and the effects of vegetation type were independent of management methods (Fig. 2b). In grassland, grazing and fire increased the relative proportions of Si, Al, and Fe in fine colloids fraction. In soils beneath juniper, grazing elevated their proportions in fine colloids but reduced the values in medium colloids, while fire affected reversely. In oak encroached soil, heavy grazing and fire visually reduced their proportions in fine colloids fraction while moderate grazing did not affect the ratios.

The 1 - Pearson's coefficient (*r*) indicate that P clustered with Ca, Mg and Fe in the first fraction (<30 nm nanocolloids) (Fig. 3a), and with OC and Ca in the second (30–160 nm fine colloids) and third fractions (160–500 nm medium colloids) (Fig. 3b and c). Al, Si, Fe and Mg strongly associated with each other in fine and medium colloids fractions, with the 1 - Pearson's *r* distance diminishing from fine colloids fraction to medium colloids fraction (Fig. 3b and c).

3.2. *Phosphorus and organic carbon in water extractable phase and water dispersible colloids*

The P (Fig. 4a) and OC (Fig. 4c) concentrations in WDC and WEP were significantly ($p < 0.05$) lower in the grassland soils than those

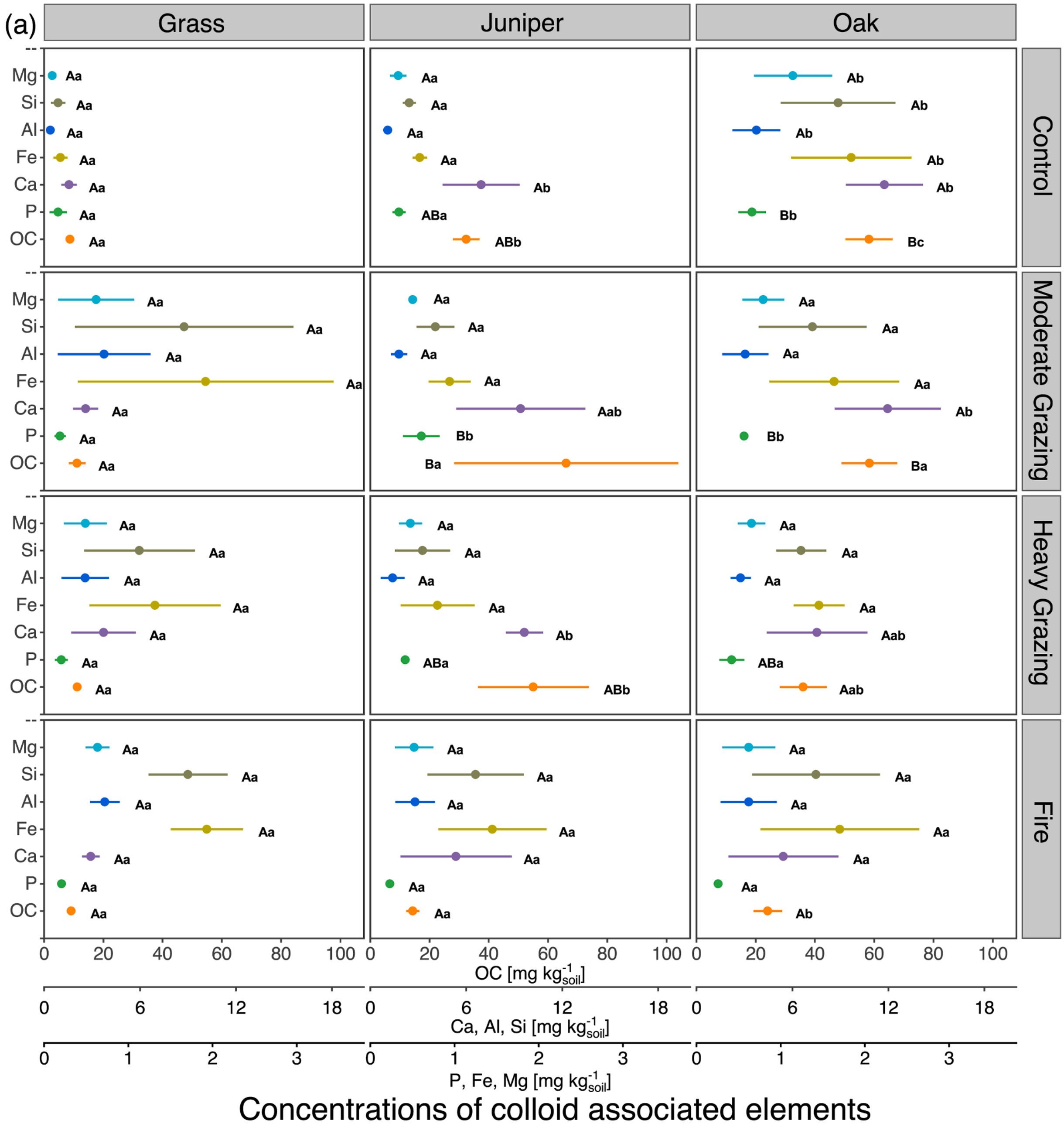

Fig. 2. Concentrations of the elements in WDC (a) and proportions of elements (b) distributed in different size colloids. Nanocolloids: 0.6–30 nm; Fine colloids: 30–160 nm; Medium colloids: 160 nm−500 nm. Values are means ± standard deviations (N = 3). Capital letters and lowercases represent difference between treatments and vegetation type, respectively ($p < 0.05$).

under woody plants. Regardless of vegetation cover, fire diminished ($p < 0.05$) both their WDC and WEP concentrations compared to other three treatments (Fig. 4b & d).

The WDC/WEP ratio was computed as an index of transportable elements. Higher WDC/WEP ratios indicate a lower relative contribution of dissolved elements. The WDC/WEP for P increased significantly ($p < 0.05$) from the oak sites to the grasslands (Fig. 4a). However, differences of WDC/WEP for P between management and their interaction with vegetation types were not significant (Fig. 4b). Moreover, WDC/WEP of P (0.30–1.08) exceeded that of OC (0.19–0.29).

3.3. Phosphorus speciation in bulk soil and water dispersible colloids

Higher total soil P concentrations did not necessarily lead to more colloidal P (P associated with 30–500 nm colloids) or "aqueous phase" P (including the P associated with < 30 nm colloids) (Fig. 5a). For instance, the most abundant soil total P (292 mg P kg$_{soil}^{-1}$) was in the moderately grazed juniper site, while the most colloidal P (0.86 mg P kg$_{soil}^{-1}$) was found in the control oak site, and the most "aqueous phase" P (1.18 mg P kg$_{soil}^{-1}$) in heavily grazed grassland. Moreover, control grassland contained the least colloidal P (0.14 mg P kg$_{soil}^{-1}$) and "aqueous phase" P (0.14 mg P kg$_{soil}^{-1}$) although it contained abundant soil total P (108 mg P kg$_{soil}^{-1}$).

Generally, a higher proportion of P_i (including orthophosphate and pyrophosphate) occurred in the 30–500 nm sized colloids (30–65 %) than in bulk soil (16–27 %) (Fig. 5b). For P_o, orthophosphate monoester dominated in bulk soil (59–73 %), but it was dramatically diminishing in colloids (6–14 %) and in some cases in the "aqueous phase" (2–64 %). In

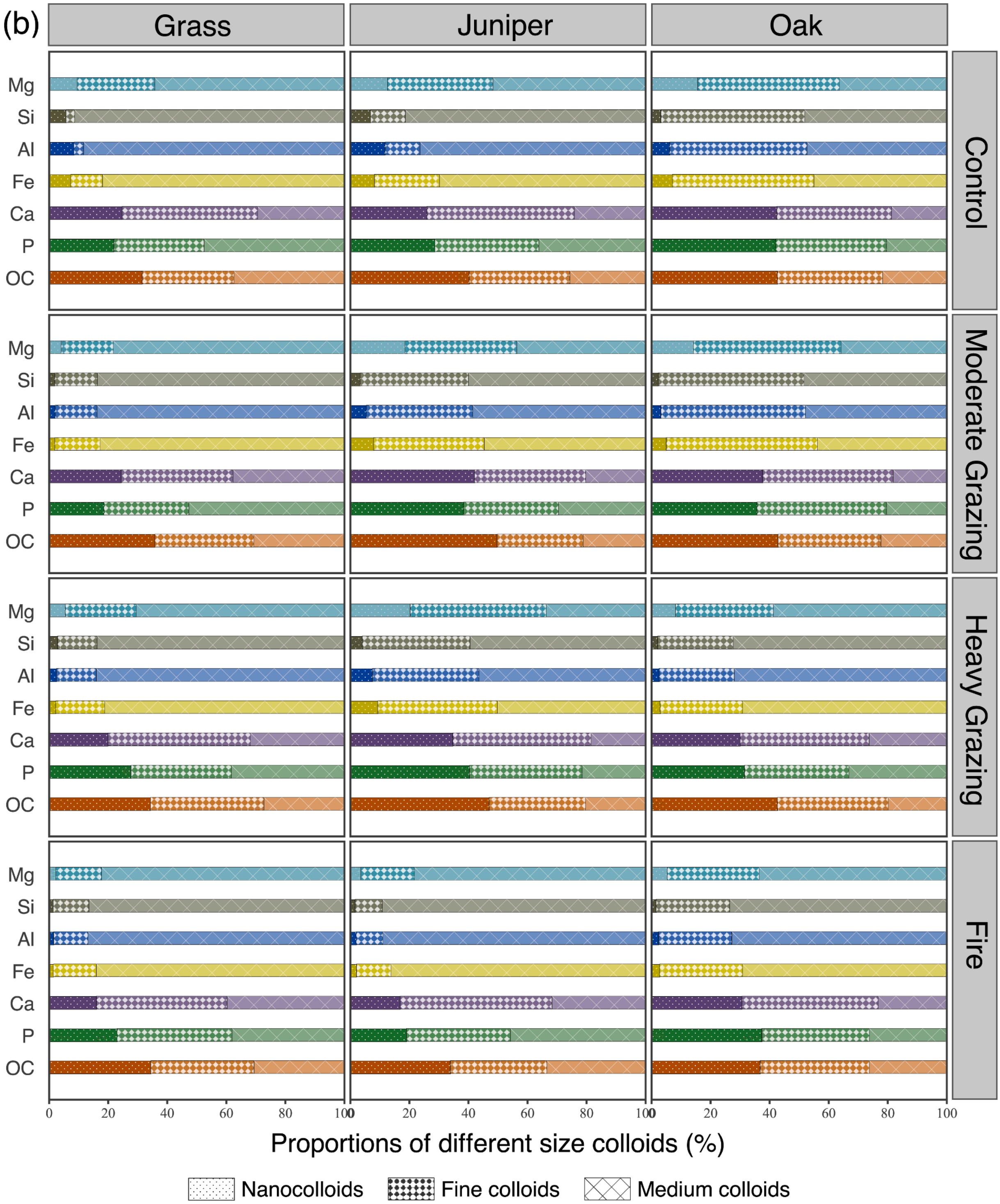

Fig. 2. (*continued*).

contrast, the relative proportion of orthophosphate diester increased sharply from bulk soil (8–17 %) to 30–500 nm colloid (28–55 %) and in some cases to "aqueous phase" (2–54 %). Furthermore, a higher proportion of phosphonate was present in 30–500 nm colloids and the "aqueous phase" compared to bulk soil (Fig. 5b). Orthophosphate proportion slightly increased between grass (14–20 %) to juniper (21–25 %) and oak (18–25 %) vegetation in the bulk soils, but decreased in 30–500 nm colloids (from 35 to 60 % in grassland to 22–37 % in oak site) and the "aqueous phase" (from 35 to 93 % in grassland to 0–35 % in oak site). From a management perspective, heavy grazing (18–93 %) and particularly fire (35–82 %) sharply increased orthophosphate proportions in the "aqueous phase". However, the differences of orthophosphate, orthophosphate diester and orthophosphate monoester proportions in 30–500 nm colloids between moderate vs heavy grazing treatments were not clear.

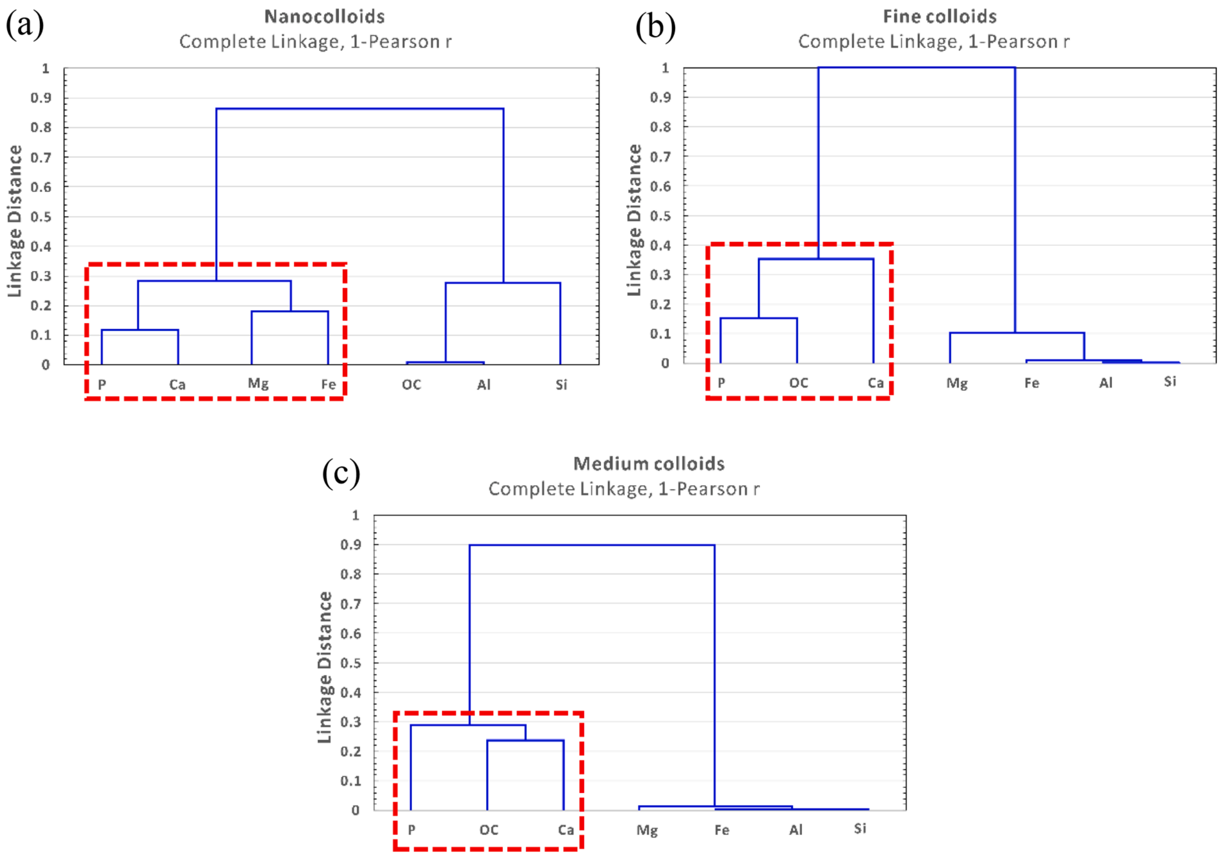

Fig. 3. Hierarchical tree clusters for preferential binding partners in nanocolloid fractions (a), fine colloid fractions (b) and medium colloid fractions (c) across all sample sites. The height of the boxes equals the 1 – Pearson's coefficient (r) distance. The complete linkage rule applies for the analysis. The lower the distance, the stronger the occurrence of associations between the elements. Nanocolloid fractions (NC): 0.6–30 nm; Fine colloid fractions (FC): 30–160 nm; Medium colloid fractions (MC): >160 nm.

4. Discussion

4.1. Water dispersible colloids constituents in soils

The clay minerals in the study areas are likely phyllosilicates with some Fe and/or Mg isomorphic substitutions, evidenced by the Si to Al ratios of 2:1 across all treatments in WDC and the clustered Fe and Mg (Fig. 3) (Tsiantos et al., 2018). SOC was more dominant in nanocolloids fraction than in fine and medium fractions (Fig. 1), suggesting the specific role of nanocolloids for SOC association (Missong et al., 2018a; Wang et al., 2020). In the nanocolloids fraction, SOC clustered strongly with Al, indicating the association of OC with Al species (Fig. 3a). The SOC dominance in nanocolloids was also reported by other studies (Krause et al., 2020; Missong et al., 2018a).

Due to the solubility of limestone and the alkaline environment, Ca^{2+} is particularly enriched in soil water of calcareous soils. Studies of grasslands occurring on limestone bedrock (Li et al., 2017; O'Brien et al., 2015) generally show a positive correlation between SOC and exchangeable Ca^{2+} concentration. The Ca^{2+} cation can act as bridge to connect SOC, negatively charged P species and minerals (Dlamini et al., 2019; Rowley et al., 2021; Rowley et al., 2018) in the WDC (Wang et al., 2020; Zhang et al., 2021). Furthermore, $CaCO_3$ colloids like calcite are positively charged below pH 8 (Somasundaran and Agar, 1967) and can bind SOC and P species. Phosphorus in nanocolloid fractions (Fig. 3a) was deemed reasonably to cluster with Ca, Mg and Fe via charge interactions. In the FC and medium colloids fractions of the studied WDC, P tightly clustered with OC and Ca (Fig. 3b and c), indicating that P can be present as organic P or as P species like orthophosphate attracted to organic substances via Ca^{2+} bridges (Wang et al., 2020). Therefore, our first hypothesis was confirmed namely, that Ca is the critical adhesive in colloidal P retention in our savanna soils.

The orthophosphate monoester fraction is derived from litter degradation, and accounted for most of soil total P in all bulk soils studied (Missong et al., 2016; Wang et al., 2020), followed by orthophosphate and orthophosphate diester. Compared to the dominance of orthophosphate monoester in bulk soil, the observed enrichment of orthophosphate and orthophosphate diester in 30–500 nm colloids revealed their tendency to be adsorbed or occluded by WDC. Orthophosphate, the dominant P_i form in the colloidal fraction, exists as an anion dissolved in "aqueous phase". It preferably binds to the negatively charged surface of soil colloids like clay minerals through cation bridging, or to the positively charged colloids such as iron oxides via electrostatic interaction (Jiang et al., 2015; Missong et al., 2018a; Pang et al., 2016).

4.2. Woody encroachment effect on WDC elements

In our study, colloidal OC and P concentrations were higher under oak compared to grassland (Fig. 2a) in the Edwards Plateau region. The mass percentages of WEP (Fig. S1) also increased following woody encroachment for the control area. It is therefore likely that SOC and P accumulate in bulk soil as a result of the higher SOC inputs and slower decomposition rates of woody plant litter in the encroached soil (Bendevis et al., 2010; Leitner et al., 2018; Liao et al., 2006).

In areas encroached by woody plants in the control plot, the nanocolloid fraction was more enriched in OC, P, Ca, and Mg than either fine or medium colloids. Following the decomposition of litter, the negatively charged P species and SOM are enriched in the nanocolloid fraction, and likely associate by cation bridges of Ca^{2+} and Mg^{2+} as well as the positively charged Fe/Al(hydr)oxide and $CaCO_3$ nanoparticles

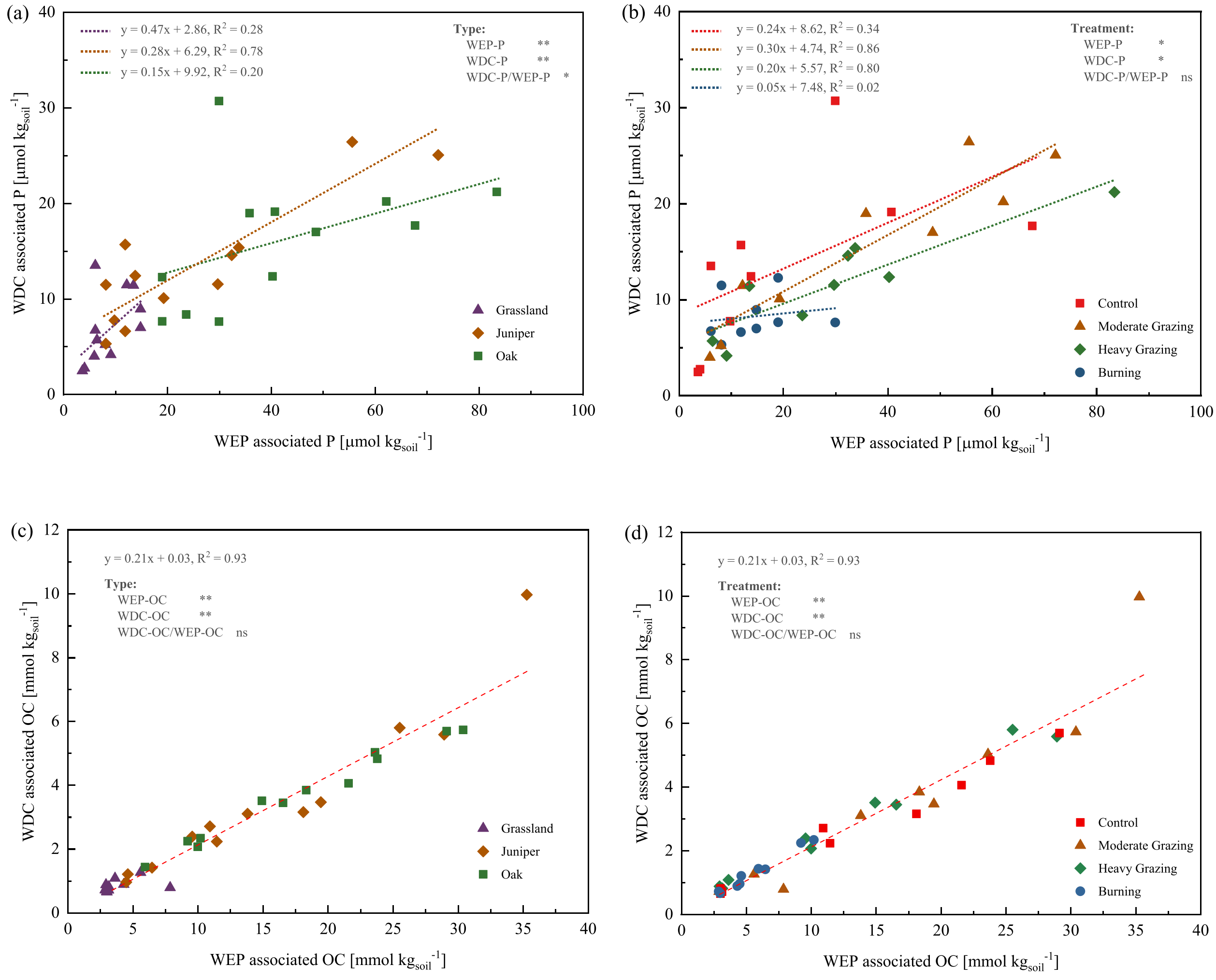

Fig. 4. Linear regression analyses between the water dispersible colloids-associated (WDC) concentration and the water extractable phase (WEP) concentration for phosphorus (a, b) and organic carbon (c, d) by different vegetation types and treatments. WEP content is the total amount of WDC content with dissolved phase content. One-way ANOVA (p-value) tests for vegetation type and treatment, and two-way ANOVA (p-value) tests for their interaction were conducted to examine the effects: * indicates $p < 0.05$; ** indicates $p < 0.01$; ns indicates no significant difference. Results of two-way ANOVAs (p-values) examining the interactions are: WEP-P ns, WDC-P ns, WDC-P/WEP-P ns; WEP-OC *, WDC-OC ns, WDC-OC/WEP-OC ns.

(Schwertmann and Fechter, 1982; Somasundaran and Agar, 1967; Wang et al., 2020). Similar findings in previous studies (Krause et al., 2020; Missong et al., 2018a; Zhang et al., 2021) suggest that higher SOM concentrations favor the formation of nano-colloids. This corroborated our second hypothesis that both colloidal OC and P increase in line with their general accumulation in bulk soils during woody encroachment. Noteworthy, the amount of colloids generally increased during woody encroachment. This finding can be attributed to the colloid stabilization by the negatively charged molecules deriving from lignin decomposition in the woody encroached soils.

The significant difference of the ratio WDC-P/WEP-P among vegetation types indicated that the adsorption effect of colloids on P was weakened with woody encroachment, but the dissolution of P from soil was favored, resulting in greater bioavailability of soil P for plants and microorganisms. This might be due to the fact that the increased organic matter concentrations in encroached areas is occupying the surface adsorption sites of clay particles, weakening their adsorption capacity for P (Li et al., 2021; Missong et al., 2018b; Siemens et al., 2008).

Both P_i and P_o concentrations increased in bulk soil and colloids following woody encroachment in the control area (Fig. 5a). This may be due to the increased SOM input (Rossatto and Rigobelo, 2016; Zhou et al., 2018) as well as the generally larger and more active soil microbial biomass compartment in soils beneath woody plants in savannas, as documented previously at this site (Marshall, 1995) and at other sites in the Great Plains and elsewhere around the world where woody plants are encroaching into grassland (Eldridge et al., 2011; Farella et al., 2020; George et al., 2018; Liao and Boutton, 2008; McCulley et al., 2004). As the main plant in the intermediate stages of encroachment, the effect of juniper laid generally intermediate between oak and grass. The proportion of P_i in the “aqueous phase” (which contained the nanocolloids < 30 nm) generally declined in encroached soils in the control (Fig. 5b). This can mainly be attributed to a relatively excessive consumption of soluble P_i during the growth of juniper and oak. Another reason could be the P_i sorption uptake of increased amounts of colloids, especially the fine or medium colloids fractions, which mainly consist of SOM and clay minerals. Additionally, larger mass of P_o input and P_i consumption by increased plant mass in oak encroached soils apparently promoted the presence of P_o in the “aqueous phase” and colloids as shown in Fig. 5.

4.3. Grazing effect on WDC elements

Consumption of vegetation by livestock and its conversion into excreta with high OC, N and P concentrations are the two additional pathways for element cycling in the grazed treatment areas compared to the ungrazed control (Sitters et al., 2020). Our study revealed that moderate grazing did not affect elemental concentrations in WDC

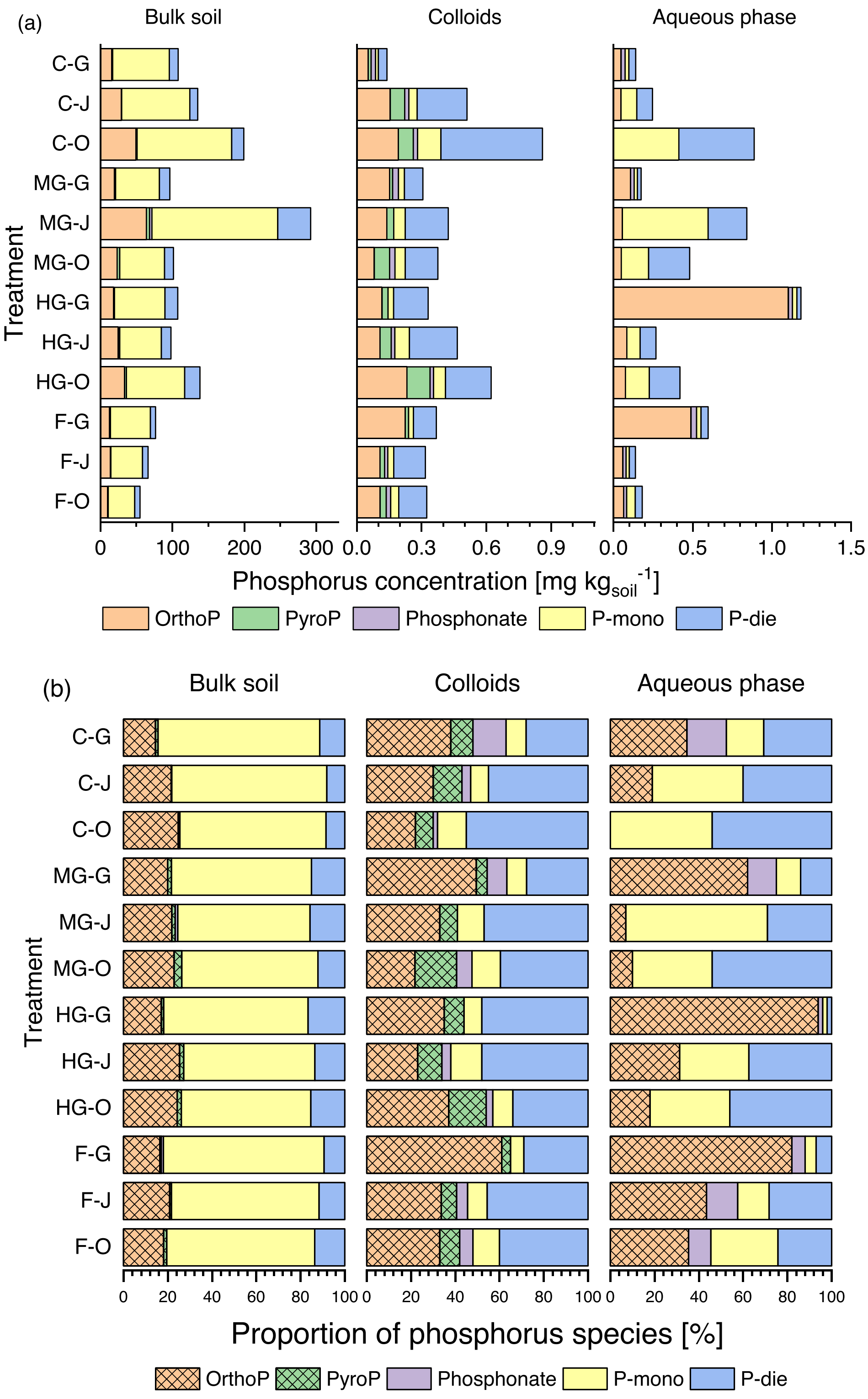

Fig. 5. Phosphorus composition and concentration (a) and percentages of each phosphorus species (b) in bulk soil (0–10 cm), 30–500 nm sized colloids and aqueous phase including nanocolloids < 30 nm. Treatments: C, Control; MG, Moderate Grazing; HG, Heavy Grazing; F, Fire. Vegetation types: G, Grassland; J, Juniper; O, Oak. It should be noted that the proportion of potential ribonucleic acid hydrolysis products was subtracted from the orthophosphate monoester (P-mono) proportion and was added to the orthophosphate diester (P-die) proportion.

(Fig. 2a), suggesting a balance between the output and input of elements like OC and P in this treatment, which differs from our third hypothesis that moderate grazing does stimulate colloid formation and related P retention. In contrast, heavy grazing significantly reduced WDC-OC in soils beneath oak (Fig. 2a). The potential excessive consumption of any grass under the heavy grazing beneath oak would reduce overall soil OC inputs and thus also decrease OC sequestration in WDC. Inputs from excreta may not offset the C removed by herbivore consumption in oak patches in the heavy grazing treatment since the animal excreta may be deposited on other portions of the landscape (Zhou et al., 2017), potentially facilitating the decrease of WDC-OC. Furthermore, the reduction in porosity caused by livestock trampling (Marquart et al., 2019) presumably impedes the vertical transport of mobile colloids and their interaction with soil, and may also induce OC and P loss through surface runoff (Chen and Arai, 2020). These results support our third hypothesis that colloid formation and related P retention are decreased by heavy grazing. Additional studies with increased sampling site density may help reveal in more detail how variations of different colloidal sized soil fractions relate to their OC and nutrient content at a more regional scale.

The two grazing intensities did not differ with respect to either the mineral element concentrations of WDC (Fig. 2a), or the relative proportions of SOM, Ca, Mg and P in their three size fractions (Fig. 2b). In the soil beneath grass and juniper, both moderate and heavy grazing strengthen the association of Si, Al and Fe in fine colloids over medium colloids, compared to control (Fig. 2b), potentially implying the stabilization of colloidal clay minerals and/or Fe/Al-(hydr)oxides by OC. But when oak encroached, heavy grazing and less OC rearranged mineral elements in three size fractions (Fig. 2a), and favored the occurrence of clay and Fe/Al-(hydr)oxides colloids, resulting in greater abundance of medium sized colloids. This suggests a crucial effect of OC on clay and oxides distribution in colloids. Overall, the SOM enrichment due to woody encroachment favored especially the formation of smaller soil colloids in this savanna landscape, suggesting that woody encroachment has a greater effect on colloid formation than either grazing intensity or fire occurrence.

On oak encroached sites, both moderate and heavy grazing reduced P_o concentration in bulk soils, colloids and aqueous phase (Fig. 5). This could be attributable to higher rates of plant consumption by herbivores compared to rates of excreta inputs, resulting in a loss of total P_o from the soil. Furthermore, the ratio of P_i to P_o did not vary in bulk soil and colloids, indicating the balance between P_i consumption rate, P_o input and mineralization rate under grazing. But the ratio notably increased in the aqueous phase of grassland soils, implying grassland seepage maybe more sensitive to grazing. Further studies are needed to investigate the specific mechanisms of colloidal P_i to P_o balances under grazing intensities in savanna ecosystem.

4.4. Fire effect on WDC-elements

The influence of frequent fires exhibited diverse effects on elemental concentrations in whole soils and in colloidal soil fractions. The WDC-OC and -P concentrations were not affected significantly by fire on grass dominated portions of the landscape (Fig. 2a), perhaps due to relatively low rates of annual above- and belowground organic matter compared to woody patches. In soils beneath oak patches with higher OC and P concentrations (Table S1), fire markedly reduced their WDC concentrations compared to the control (Fig. 2a), perhaps due to the combustion of aboveground biomass and the litter layer (Mataix-Solera et al., 2011), and the enhanced loss rate of WDC through increased preferential flow paths in the burnt soil (Bian et al., 2019; Moody et al., 2013). This in part supported our third hypothesis that fire would weaken the colloid formation and related P retention, but only in oak encroached soil. The P loss rate may have been amplified through the elevated proportions of P_i dissolved in the “aqueous phase” of frequently burned sites (Fig. 5b). Merino et al. (2019) and Santin et al. (2018) demonstrated the appreciable shift of the extractable P from organic P to inorganic P probably due to mineralization with burning, which could accelerate P loss from soil.

However, fire did not significantly affect WDC-Ca, -Si, -Al, -Fe or -Mg concentrations in soils beneath any of the three vegetation types (Fig. 2a). These mineral elements are usually derived from the soil matrix, and our results suggest that fire amplifies their association in the larger medium-sized colloid fractions (Fig. 2b). Al/Fe (hydr)oxides could suffer dehydroxylation and aggregation into robust particles with higher aggregate stability after fire (Ulery et al., 2017; Yusiharni and Gilkes, 2012). Ulery et al. (1996) reported the thermal destruction of soil organic matter and phyllosilicates. The thermally altered soil organic matter and phyllosilicates might form medium-sized colloid aggregates. Mataix-Solera et al. (2011) reported increased soil aggregate stability with fire severity in soils with high clay and $CaCO_3$ concentrations, where Fe and Al oxides functioned as cementing agents. Our results revealed that fire can diminish the impact of woody encroachment on the WDC formation of savanna soil via thermal destruction and aggregation. More work is required to evaluate the behavior of colloidal P, OC and other soil elements in fire affected regions.

5. Conclusion

Woody encroachment increased colloidal OC, P and Ca concentrations and elevated their proportions in nanocolloid fractions (<30 nm), highlighting its potential mechanism via enhanced bulk SOM on soil nanocolloid formation in savanna ecosystems. Moderate grazing did not modify colloidal concentrations, while heavy grazing significantly reduced WDC-OC in oak encroached soil. Fire reduced colloidal OC and P concentrations and amplified the association of medium sized (160–500 nm) colloid fractions with Ca, Si, Al, Fe and Mg in nano- (<30 nm) and fine colloid (30–160 nm) fractions. Phosphorus was associated with Ca, Mg and Fe in the nanocolloid fraction (<30 nm) and to OC via Ca^{2+} bridging in fine and medium colloid (>30 nm) fractions. While bulk soils were dominated by monoester-P, the colloidal and “aqueous phase” containing < 30 nm colloids had more diester-P and inorganic P. Vegetation type was more important than grazing or fire as a determinant of soil colloidal size distribution and nutrient content in this savanna ecosystem. Our novel results on the behavior of soil colloids in response to long-term grazing, fire history, and woody plant encroachment provide mechanistic insights that will enhance our understanding of the influence of land cover and land use changes on the biogeochemistry of grasslands, savannas, and other dryland ecosystems.

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.

Data availability

No data was used for the research described in the article.

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Note

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2022.116282.

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