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Mineralogia de sedimentos ricos em fósforo e cobre

Maurício Sonda Tonello

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Maurício Sonda Tonello

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Edson Campanhola Bortoluzzi

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Dr. Edson Campanhola Bortoluzzi
Presidente da Comissão Examinadora
Orientador
Coordenador do PPGAgro

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UFRGS

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Dr. Eraldo Lourenso Zanella
Diretor da Faculdade de Agronomia e Medicina Veterinária,
Universidade de Passo Fundo

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RESUMO

Tonello, Maurício Sonda. Mineralogia de sedimentos ricos em fósforo e cobre. [151] f. Tese (Doutorado em Agronomia) – Universidade de Passo Fundo, Passo Fundo, 2019.

Os sedimentos produzidos pela agricultura podem estar carregados de íons e são facilmente transferidos para os recursos hídricos. A composição mineralógica desses sedimentos pode alterar sua capacidade de transporte e adsorção/dessorção dos íons nos ambientes onde o sedimento é depositado. Neste sentido, o objetivo da tese foi estudar sedimentos de diferentes locais (Brasil e EUA), com diferentes íons associados (Cu e P), para compreender o efeito da composição mineralógica sobre o comportamento do sedimento quanto ser fonte ou dreno de poluentes. O experimento foi dividido em 2 partes: i) estudo de campo sobre sedimentos carregados com Cu de uma paisagem de videira centenária acima de um riacho (sul Brasil), ii) e um estudo de um banco de sedimentos carregados com P presentes no Lago Superior - EUA. O objetivo do primeiro estudo foi o de avaliar a composição mineralógica dos sedimentos e as formas de cobre presentes na água e sua relação com a mineralogia dos sedimentos. Os sedimentos coletados no exutório da bacia hidrográfica com videiras apresentaram alto teor de Cu e uma mineralogia composta de: mica, caulinita, ilita, rutilo, hematita, quartzo, calcita, magnesita, albita e anortita, e minerais de cobre. Os sedimentos em suspensão coletados em vários pontos da bacia hidrográfica apresentaram ainda altas concentrações de cobre total (9,16 mg L^{-1}), trocável (2,81 mg L^{-1}) e solúvel (1,82 mg L^{-1}). Para o segundo estudo, os sedimentos provenientes do Lago Superior – EUA foram caracterizados e a labilidade de P foi avaliada. Esse estudo comportou um conjunto de amostras coletadas do fundo do rio, faixa de erosão, e do fundo do lago. Os sedimentos foram compostos por minerais de baixa reatividade e alta reatividade em relação a P, tais como os óxidos e argilominerais. A concentração de fósforo total nos sedimentos do rio, faixa de erosão e fundo do lago foram muito altas. Entretanto, o fósforo labil era menos de 10% do total. Mais de 80% do fósforo estava associado aos compostos de matéria orgânica e aos minerais carbonatados, com baixa biodisponibildiade. Isso é devido a presença de minerais de alta reatividade com potencial de adsorver fortemente o P. Nesse sentido, os resultados dos estudos sugerem que os sedimentos agem como: i) estoque de cobre para o ambiente, podendo se tornar fonte de cobre para o ambiente quando forem depositados; ii) sequestrante de fósforo de longa duração (P do lago superior). Ambos os comportamentos geoquímicos dos sedimentos foram fortemente influenciados pela sua composição mineralógica. A composição mineralógica dos sedimentos ricos em P e Cu é fator determinante na capacidade de sorção dos íons associados aos sedimentos, sendo a informação gerada pelas análises mineralógicas e geoquímicas fundamental nos estudos de comportamentos dos sedimentos contaminados.

Palavras-chave: 1. Sedimentos suspensos. 2. Óxidos. 3. Argilo minerais. 4. Sorção ions. 5. Geoquímica.

ABSTRACT

Tonello, Maurício Sonda. The mineralogy of sediments enriched by cooper and phosporus. [151] f. Thesis (Doctor in Agronomy) – University of Passo Fundo, Passo Fundo, 2019.

The agriculture sediments usually are enrich in contaminants, and are easily transferred to water bodies. The mineralogical composition of these sediments affect the transport capacity and adsorption/desorption behavior of this contaminants in the environment. In this sense, we will study sediments from different locations (Brazil and USA), with different associated ions (Cu and P), to understand the effect of the mineralogical composition on the sediments behavior in two different environments (stream channel and a lake). The study was divided in two parts: i) field study on copper sediments from a century-old vineyard (southern Brazil), ii) field study on P sediments present in Lake Superior - USA. Vineyard received large amounts of copper, so we estimate a copper rich sediment production. The aim of this study was to evaluate the mineralogical composition of the sediments and to relationship with the copper forms present in the sediment and stream channel water. A rich mineralogical mixture was present at the vineyard and also in the exutory, which was composed of: mica, kaolinite, illite, rutile, hematite, quartz, calcite, magnesite, albite and anortite, and copper minerals. The suspended sediments present in the vineyard area showed high concentrations of total copper (9.16 mg L^{-1}), exchangeable (2.81 mg L^{-1}) and soluble (1.82 mg L^{-1}). However, in the exutory the suspended sediments were rich only in total copper. The second study, presented the P lability of the sediments from Lake Superior. The relationship of P forms with the sediment mineralogy, and the geochemical characterization of these sediments remains poorly understood. The aim of this study is to provide information on the P lability of Lake Superior sediments, and to associate this information with the mineralogical composition and geochemical characterization of these sediments. Samples were collected from the input load (river bed), shoreline erosion, and Lake Bottom. The sediments were composed of minerals of low reactivity and minerals of high reactivity with P, such as oxides and clay minerals. The concentration of total phosphorus in the sediments of the input load, shoreline erosion and Lake Bottom were very high. However, labil phosphorus was less than 10% of the total. More than 80% of the phosphorus was associated with organic matter compounds and carbonate minerals, with low availability to biota. The sediments have a low concentration of bioavailable phosphorus to biota due to the presence of highly reactive minerals with the potential to adsorb P. The results suggest that the sediments act as: i) long-term phosphorus sink (P from Lake Superior), ii) sediments act as a copper stock for the environment, and can become a source of copper for the environment. Both sediment behaviors were strongly influenced by their mineralogical composition, in addition to their geochemical aspects. The mineralogical composition of the sediments rich in P and Cu is a determining factor in the sorption capacity of the ions associated with the sediments, and the information generated by the mineralogical and geochemical analyzes is fundamental in the studies of contaminated sediment behavior.

Key words: 1. Suspended sediments. 2. Oxides. 3. Clay minerals. 4. Ion sorption. 5. Geochemical.

SUMÁRIO

1 INTRODUÇÃO

A agricultura é uma atividade que ocasiona grande produção de sedimentos. O aumento da produtividade dos cultivos é alavancado principalmente pelo aumento dos volumes de fertilizantes aportados ao solo e pelo uso crescente de defensivos agrícolas (fungicidas, inseticidas e herbicidas) sobre os cultivos. Os compostos químicos contidos nesses produtos acabam enriquecendo as partículas do solo e iniciando um processo de contaminação. Ainda, as partículas carregadas com os compostos químicos podem ser transferidas das lavouras para os recursos hídricos, tornando esses sedimentos importantes fontes de contaminação.

Sedimentos são partículas sólidas que se transferem de um ambiente para outro e podem carrear consigo outras moléculas e gerar impactos no novo ambiente onde são depositadas. Os compostos químicos carreados com os sedimentos podem ter diversas naturezas, sendo comuns a presença de elementos (N, P, K, Ca,) ou metais (Zn, Cu, Pb, Fe, Cd), agentes biológicos (fungos, bactérias), agrotóxicos (fungicidas, herbicidas e inseticidas), medicamentos humanos e animais (antibióticos, reguladores hormonais, etc) entre outras substâncias.

Como forma de reduzir o impacto ambiental das atividades agrícolas, muitos estudos são conduzidos para identificar as características das partículas que carregam tais contaminantes. Identificar as características mineralógicas intrínsecas dos sedimentos é imprescindível para estimar seu potencial de dano e também construir as ações efetivas que podem evitar a contaminação ou pelo menos mitigar seus efeitos.

O objetivo do trabalho é o de estudar sedimentos oriundos de locais distintos, com composições mineralógicas variáveis, depositados em ambientes distintos e carregados com diferentes contaminantes, para compreender a relação entre a composição mineralógica dos sedimentos e seu comportamento ora como fonte e ora como dreno nos ambientes. Tal estratégia de estudo é importante para inferir sobre o potencial de impacto dos sedimentos nos ambientes.

A tese constitui-se de quatro capítulos, sendo que o primeiro é uma revisão sobre as formas de cobre no solo, água e nos sedimentos. O segundo capítulo traz o trabalho de campo realizado com sedimentos oriundos de uma videira centenária, onde o solo encontra-se com altíssimos teores de cobre. O terceiro capítulo, é uma revisão sobre os sedimentos carregados de cobre, pelo qual se discute as principais técnicas utilizadas para estudos de sedimentos ricos em fósforo. O quarto capítulo é o trabalho de campo sobre os sedimentos carregados de fósforo presentes no lago superior dos EUA e suas relações com a sua composição mineralógica.

2 REVISÃO DA LITERATURA

A utilização intensiva de fertilizantes e defensivos na agricultura tem contaminado os solos, produzindo sedimentos carregados de íons e moléculas orgâncias. O termo solo contaminado é utilizado quando os teores de íons encontrados são superiores aos que ocorrem em locais naturais, sem ação antrópica.

A contaminação por cobre e fósforo em solos agrícolas ocorre nas camadas superficiais do solo. Essa camada superficial é a mais reativa, podendo os íons reagirem com as partículas de distintas formas: complexação, precipitação/dissolução, sorção/dessorção e oxirredução, reagindo com os mais distintos constituintes orgânicos e inorgânicos do solo (SPOSITO, 1989). Sedimentos enriquecidos com fósforo e cobre podem gerar graves impactos no meio ambiente aquático. As águas contaminadas por P tem suas relações biológicas alteradas (STERNER et al., 2004). Esse desequilíbrio pode resultar no processo de eutrofização, e afetar toda a biodiversidade do ambiente. A utilização em excesso de cobre na forma de dejetos de animais ou como defensivos (fungicidas em determinadas culturas) são os responsáveis pelos processos de contaminação do solo, e consequentemente via seus sedimentos, a contaminação das águas.

A capacidade de uma partícula do solo em acumular determinado íon na sua interface sólido/solução é denominada de adsorção de íons (SPOSITO, 1989). Essa adsorção é regida por diferentes mecanismos: adsorção não específica (esfera externa), adsorção específica (esfera interna), troca iônica ou complexação pela matéria orgânica do solo (CAMARGO; ALLEONI; CASAGRANDE, 2001). Dentro das frações minerais do solo envolvidos nos fenômenos de adsorção encontram-se os filossilicatos, óxidos e hidróxidos, carbonatos, fosfatos (SPARKS, 2005). A identificação da partícula carreadora é fundamental para entendermos o seu comportamento no novo ambiente.

Simplificadamente, um sedimento pode assumir três comportamentos: i) agir como uma fonte de contaminantes, liberando a substância no ambiente (processo chamado de dessorção), ii) agir como um dreno, sequestrando uma nova substância do novo ambiente (processo chamado de adsorção), ou iii) ter ambos comportamentos (variáveis de acordo com as condições ambientais).

Os sedimentos presentes nas águas podem assumir simplificadamente dois comportamentos: fonte de íons (dessorção) ou dreno (adsorção), quando depositado em ambiente aquático (JIANG et al., 2006). A variação do ambiente pode mudar o comportamento de fonte para dreno ou contrário, em um mesmo sedimento. Termodinamicamente, todo o fósforo adsorvido pode ser dessorvido (BARROW, 1983), ou da mesma forma outros íons. Alterações no pH podem dissociar grupos funcionais da matéria orgânica ou da fração mineral liberando íons para o ambiente (CASALI et al., 2008).

O fenômeno de dessorção ocorre quando íons são liberados para a solução do solo, ou quando um sedimento depositado no ambiente aquático libera íons na água. Os fatores que afetam a adsorção, também afetam a dessorção de íons. O teor do elemento na solução, o pH do solo, a temperatura, a quantidade do elemento adsorvido e o tempo que o solo e a solução ficam em contato são importantes fatores controladores do processo de dessorção. O pH é o principal fator determinante na sorção de íons em partículas orgânicos e inorgânicos (UREN, 1992). Em ambientes ácidos, a maior dessorção ocorre devido a concentração de H^+ nos sítios de troca (GAO et al., 2003; MCBRIDE, 1989).

O meio urbano também é considerado um grande produtor de sedimentos contaminados. Com o crescimento das grandes cidades, o aumento populacional proporciona aumento da produção de sedimentos (HOROWITZ et al., 2012b). O ambiente urbanizado é produtor de sedimentos concentrado em Zn, Cu, Ni, Pb, P, C, N, associados aos sedimentos (ANDRADE et al., 2018b).

Diversas características dos sedimentos governam o seu potencial poluidor. Dentre elas, o tamanho da partícula é uma das principais características que afeta seu potencial poluidor, em ambientes urbanos (POLETO et al., 2009), e agrícolas. As partículas mais finas (argilas e siltes), de maneira geral, possuem maior capacidade de carregamento de poluentes associados (HOROWITZ, 1991; BORTOLUZZI et al., 2013).

Nas áreas agrícolas a contaminação por cobre ocorre pelo uso frequente de fungicidas cúpricos, utilizados na vitivinicultura. Desde os primórdios da agricultura no cultivo de videiras, o cobre vem sendo utilizado para controle das principais doenças nos parreirais. Várias regiões vitivinícolas no mundo vêm utilizando cobre por várias gerações, acumulando esse elemento no solo, chegando a teores considerados contaminantes.

No Brasil, a maior região produtora de vinhos é a Serra Gaúcha, localizada no sul do Brasil. Essa região montanhosa, colonizada por italianos vem cultivando videiras nas encostas dos morros desde os anos de 1850. Os fungicidas mais utilizados nessa região são a calda bordalesa e o oxicloreto de cobre (TIECHER et al., 2017b). Anualmente são adicionados sobre os vinhedos quantidades que variam de 20 até 80 kg ha^{-1} de cobre via fungicidas cúpricos (CASALI et al., 2008; NACHTIGALL et al., 2007; MIRLEAN; ROISENBERG; CHIES, 2007).

Quanto maior o acumulo de cobre no solo, menor a produção de matéria seca das culturas de cobertura, e mais exposto o solo fica a erosão (GIROTTO et al., 2016; MIOTTO et al., 2014). Nos solos o cobre é preferencialmente adsorvido pela matéria orgânica, a qual se concentra na superfície (FERNÁNDEZ-CALVIÑO et al., 2008c; ARIAS-ESTÉVEZ et al., 2007). Assim as partículas mais carregadas de cobre, são também as que estão mais sujeitas a erosão (PROSDOCIMI; CERDÀ; TAROLLI, 2016).

Entretanto, é possível que o cobre esteja associado em maior quantidade as frações minerais, comparativamente a fração orgânica, principalmente em áreas com ação antrópica intensa (BRUNETTO et al., 2014; CASALI et al., 2008). A associação entre menor matéria seca das plantas de cobertura, relevo montanhoso e precipitações intensas características da região, o processo de erosão é potencialmente aumentado, transferindo partículas para os riachos localizados no fundo dessas microbacias, que podem transportar esses sedimentos contaminados para os rios secundários, e estes rios desaguam no lago Guaíba que abastece milhões de pessoas na capital do estado do Rio Grande do Sul. Esse é o cenário geral da Serra Gaúcha, a qual possui mais de 25.000 ha de vinhedos (muitos centenários), em meio a um relevo montanhoso sob um clima subtropical bastante chuvoso (1.850 mm de chuva por ano).

É escassa a informação sobre os minerais que compõe os sedimentos carregados de cobre que são transferidos dos parreirais centenários para os ambientes aquáticos nessa região. Assim, o estudo da composição mineralógica de sedimentos carregados de cobre produzidos nesse ambiente contribuirá significativamente para o entendimento do efeito dos sedimentos e os teores de cobre encontrados nas águas.

O comportamento dos íons P e Cu nos ambientes é fortemente influenciado pelo pH do solo, capacidade de troca de cátions, mineralogia (conteúdo de óxidos e hidróxidos de Fe, Al e Mn, carbonatos) e o conteúdo e composição da matéria orgânica (BRADL, 2004; NOGUEIROL et al., 2010, TIECHER et al., 2017b). Os argilominerais, óxidos e a matéria orgânica influenciam fortemente o comportamento do P associado as partículas do solo (FINK et al., 2016; BORTOLUZZI et al., 2015). Os argilominerais podem possuir capacidade de sorção de P similar aos óxidos de Fe a Al, variando em função de sua superfície específica (GÉRARD, 2016).

O outro cenário discutido aqui nesta tese está localizado no norte dos Estados Unidos, fazendo referência ao elemento fósforo, um nutriente amplamente utilizado na agricultura. O fósforo é um nutriente que os agricultores fazem aplicações anuais para melhorar a desempenho das culturas, incrementando produtividade e qualidade aos seus produtos. O fósforo no solo é um dos nutrientes mais reativos, tendo grandes interações com as frações argila e silte (as frações mais reativas do solo).

O Lago Superior localizado na divisa dos Estados Unidos com o Canadá é o maior lago de água doce do mundo (em extensão), e está situado em uma área pouco habitada, porém com significativa atividade rural no seu entorno. O lago é a principal fonte de água para milhões de americanos, e isso o torna um cenário especial, onde muitos estudos sobre sedimentos são conduzidos. Este é o cenário escolhido para nosso estudo de sedimentos carregados com fósforo.

Apesar de ser alimentado por diversos rios e afluentes que percorrem centenas de quilômetros de regiões agrícolas, os teores de P encontrados nesse lago são considerados baixos, o que instiga muitos pesquisadores a aprofundar-se na reatividade desses sedimentos do lago. Esse baixo P poderia ser reflexo da ação dos sedimentos? Os sedimentos podem sequestrar e fixar o P, reduzindo sua atividade? Neste sentido, as partículas que compõe o sedimento atuariam como sequestrantes dos íons, reduzindo a biodisponibilidade dele no ambiente. Poucos trabalhos de mineralogia de sedimentos foram realizados nesse ambiente. A investigação a cerca dos minerais que compõe os sedimentos do Lago Superior, podem contribuir significativamente para o entendimento do efeito dos sedimentos e os teores de P encontrados no lago.

O comportamento de adsorção (dreno) e o comportamento de dessorção (fonte) são fortemente influenciados pela mineralogia dos sedimentos. Assim, a mineralogia é uma técnica fundamental e de grande potencial nos estudos para sedimentos de distintos contextos. Essa tese visa: i) revisar os aspectos importantes relacionados aos sedimentos carregados de Cu e P, ii) identificar os minerais que compõe os sedimentos de uma região vitivinícola centenária do sul do Brasil, e iii) identificar os minerais presentes nos sedimentos do maior lago de água doce do mundo localizado nos Estados Unidos. Entender o comportamento dos minerais e seus íons associados nos permite inferir sobre o potencial de poluição, bem como determinar as ações mitigadoras no solo que propiciam redução dos impactos causados pelos sedimentos nos ambientes aquáticos.

3 CAPÍTULO I

Copper transfer from terrestrial to aquatic systems: a review of Cu-forms in soil, water and sediments

3.1 Abstract

The frequent use of copper-based fungicides (Cu) is the main cause of soil contamination in the vineyards. The erosion that occurs in these soils allows the displacement of Cu-charged particles to water bodies. The determination of total Cu levels in soils or sediments, and the soluble Cu form in water does not correlate with the real bioavailability of Cu in the environment. We summarize here the main techniques and their results applied to Cu enriched sediments. Understanding the Cu forms in the soil, sediment and water is the first step towards the reduction of the environmental impact caused by the Cu application into rural areas.

Key-words: 1. Water contaminated. 2. Ions. 3. Soil contaminated.

3.2 Introduction

Copper is an element of multiple functions in agriculture, being used as a nutrient (essential to all plants) or as a defensive agent (broad-spectrum fungicide) in many crops. Also, there are several enzymes and proteins that contain copper and act in different systems: detoxification of superoxides, cytochrome oxidase, plastocyanin and electron transfer (EPSTEIN; BLOOM, 2006).

In agriculture, the excessive use of copper in the form of animal waste (organic fertilizers) and as fungicides has been responsible for the main processes of soil and water contamination. In urban environmenties, the production of contaminated sediments also occurs and it is proportional to the demographic density (HOROWITZ et al., 2012ab). The contamination occurs mainly by surface runoff after heavy rains or by the accumulated load in the sediments and deposited in the waters (FERNÁNDEZ-CALVIÑO et al., 2008c).

In south Brazil is concentrated more than 60% of the national wine cultivated area (IBGE, 2016). The climate - hot and humid (subtropical) - favors the development of several diseases that promote serious damage in vineyards. For this reason, this region has applied for many years, dozens kilograms of copper fungicides. The main copper fungicides used are Bordeaux ($Ca(OH)_2$ + $CuSO_4$) and copper oxychloride (TIECHER et al., 2017b). The Bordeaux mixture is the main fungicide applied to vineyards. The wine growers add to soils from 20 to 80 kg of copper per hectare per year with Bordeaux mixture (CASALI et al., 2008; NACHTIGALL et al., 2007; MIRLEAN et al., 2007).

The continuous use of cupric fungicides during many years in grapevines (more than 120 years) caused a copper accumulation around 1,300 mg kg $^{-1}$ in the soil, extracted by Mehlich 1 (KORCHAGIN et al., 2013). In this region, there is the highest Cu content in contaminated soils found in the literature, reaching 3,215 mg Cu per kg^{-1} of soil (MIRLEAN et al., 2007).

The concentration of copper at toxic levels in the soil reduces crop dry matter production, reducing nutrient cycling, soil cover and increasing erosion of contaminated particles (GIROTTO et al., 2016; MIOTTO et al., 2014). High soil copper concentrations has a direct effect on microbiology, reducing fungi and bacteria activities, besides reduce the activities of several important enzymes in biological processes in soils (MACKIE et al., 2013). This reduction in biological activity, reflect in less soil coverage, which can increase the potential of soil erosion, being the erosion rate in soils is higher when the lower is the soil organic matter (PROSDOCIMI; CERDÀ; TAROLLI, 2016).

In soils, the copper is preferential associated with the soil organic matter (SOM), being concentrated in soil surface, thus make it particles cupper loaded potentially more eroded. The organic matter (dominant in copper connections), the soil texture and the management practices are important aspects that define the availability of copper to the environment (DUPLAY et al., 2014). Consequently, those Cu-charged particles eroded are deposit in waters, generating contamination to fauna (FERNÁNDEZ-CALVIÑO et al., 2008c; ARIAS-ESTÉVEZ et al., 2007). Areas with undulating relief and without conservationist soil management sediment production increases, greatly increasing the potential for damage to all fauna (LONDERO et al., 2018).

This review aims to summarizing the forms that copper can be found in soil, water and sediments published in most recent studies around world.

3.3 Copper form in water

For a chemical element to be considered as pollutant it must be bioavailable to the fauna and flora. Ionic speciation in the solution of soil or aquatic environments is a set of techniques that aims determining in which chemical form the element is, allowing one to infer about its bioavailability. In complex systems such as soil solution or in water bodies, the chemical species in which the contaminating element is and its binding agent are determinant factors that influence it bioavailability in the environment.

The speciation of copper in water differs greatly from other metals. In solution, copper is present in two ionic forms: cuprous form (Cu^{+}) or cupric form (Cu^{+2}). Cuprous copper is oxidized to cupric form. The cuprous form is present only in complexes (EPSTEIN; BLOOM, 2006). Modeling the geochemical speciation of copper forms dissolved in a river in Poland, the authors determined that more than 96% of Cu is in the form of $Cu(OH)_2$. The $Cu(OH)_2$ form plus the $Cu^{+2,}$ ionic form was the main components of the samples, the other forms are insignificant in the study of copper contamination in fluvial waters (WOJTKOWSKA; BOGACKI; WITESKA, 2016).

The use of soil correctives to reduce the bioavailability of copper (limestone, calcium silicate, zeolites and vermicompost) caused changes in the soil solution, having an increase of at least two units in the pH solution. For all treatments there was a change in the Cu species in the solution, with reduction in ionic copper (Cu^{+2}) and increase of the copper in the form of hydroxide ($CuOH^{+}$). The highest reduction occurred in vermicompost where most of the copper was associated with dissolved organic matter (FERREIRA et al., 2018a).

Copper-contaminated soils (with grapevine production) have received high doses of zinc-based fungicides instead of cupric fungicides. In a competitive system with high doses of Zn (270 mg kg^{-1}) added to a soil contaminated with copper, there was only a twofold increase in the copper activity in solution, compared to the soil that did not receive Zn application. This behavior is due to a large fraction of the copper being bound to organic matter (45%), and approximately 30% in its free form (Cu^{+2}) (TIECHER et al., 2016b).

The bioavailability of copper is dependent on pH, cation exchange capacity and organic matter. When we have soils with high pH, high CTC and high levels of organic matter we have less bioavailability of copper in the systems, being less toxic to plants and microorganisms (MACKIE; MÜLLER; KANDELER, 2012). The amount of negative chargers and the strength of the bond between the funccional groups and the copper, diminuished it availability to the environment.

3.4 Copper form in Soil and Sediments: sequential fractionation

The determination of the total content of an element associated with a particle is not a relevant indicator of its toxicity (PASSOS et al., 2011). The sequential fractionation method is a commonly technich used to better explain the toxicity potential of particles. Sequential fractionation is a technique that use several extractors organized chronologically, so each extraction only extract the volume of the metal associated with a given binder. Each copper form has a specific biding energy, which is representative by one copper form. This set of techniques is fundamental as an indicator criterion of the pollutant potential of particles. This technique separates the different forms in which the copper is associated, inferring about its binding force, and consequently its bioavailability to the environment. The copper sequential fractionation is determinant in the environmental studies with contamination risk. Determinate how much copper is in available forms and other forms recalcitrant is the aim of the studies.

The sequential chemical fractionation of Cu applied to soils or sediments indicates the amount of copper associated with weaker ligands (greater bioavailability) through several fractions until they reach stronger ligands, which represents lower bioavailability to the environment (TESSIER et al., 1979).

Factors such as soil pH, cation exchange capacity, mineralogy (content of oxides and hydroxides of Fe, Al and Mn, carbonates) and the content and composition of organic matter are main factors that control the behavior of elements in the environments (BRADL, 2004; NOGUEIROL et al., 2010; TIECHER et al., 2017b). The strong association of copper with organic material reduces its bioavailability to the environment. However, changes in soil pH may increase its availability associated with mineral fraction and organic matter, dissociating some functional groups and releasing Cu to the environment (CASALI et al., 2008).

The mineralogy of the particles strongly interferes with the energy and type of bonds made with the metals. The speciation indicated that overestimation of Cu binding with the organic matter may be occurring, and underestimation of its binding with expansive clay minerals, which have very high bond strength. With this bound with clay minerals, there are indications of percolation of these minerals with copper in suspended depth in the infiltrating water (DAMO et al., 2006).

The Table 1 provides a brief overview of the main extractors used in sequential and non-sequential chemical fractionation from diverse authors.

Table 1 – Resume of copper and metals chemical fractionation extractors applied to soils and sediments. Passo Fundo, 2019

Fractions	Extractors	Source
Exchangeable / Soluble	- MgCl with pH 7 ou NaOAc with pH 8.2.	Tessier et al. (1979)
	- Ammonium acetate pH 7	Gupta and Chen (1975)
	- EDTA	Lakanen and Erviö (1971)
	- EDDS	Komárek et al. (2008)
	- DTPA	Lindsay and Norvell (1978)
	- Mehlich I (0.05 M HCl +0.125 M H_2SO_4) e II	Tedesco et al. (1995)
	- NH_4Ac (pH7)	Fernández-Calviño et al. (2008c)
Associated carbonate / Reduced	- NaOAc adjusted to pH 5 with HOAc.	Tessier et al. (1979)
	- Hydroxylammonium chloride with pH 1.5 adjusted with nitric acid.	Ure and Davidson (2002)
Associated Hydroxides/Oxides (Fe, Mn and Al)	- NH_2OH-HCl em 25% (v/v) com HOAc.	Tessier et al. (1979)
	- $Na_2S_2O_4$+ Na-citrate + H-citrate	Anderson and Jenne (1970)
Associated with organic matter / Oxidable	- HNO_3 and 30% H_2O_2 adjusted to pH 2 with HNO3> 30%.	Tessier et al. (1975).
	- H_2O_2 (pH 2 with HNO_3)> NH40Ac in 20% (v / v).	Gupta and Chen (1975)
	- H_2O_2	Ure and Davidson (2002)
	- Na-pyrophosphate	Fernández-Calviño et al. (2008c)
Residual (total)	- HF-$HClO_4$	Tessier et al. (1979)
	- HNO_3, HCl and HF	Ure and Davidson (2002)
	- HCl, HNO_3, H_2O_2	Kingston (1988)

Source: Author data.

The most common sequential fractionation method is the one suggested by Tessier et al. (1979), in which five fractions are determined (exchangeable, bound to carbonates, bound to Fe and Mn oxide, bound to organic and residual), developed for sediments, yet widely used in soils. The first three fractions have a higher pollution potential (greater bioavailability), since the energy and the type of bond between the compounds and the metals are more easily broken, making the metal available to the environment (TESSIER et al., 1979).

The European Union recommends the use of chemical fractionation suggested by Ure and Davidson (2002), approved by the Standarts Measurements and Testing Program, known as BCR method. Three fractions are determined (soluble/exchangeable, reducible, oxidizable) and an isolated residual extraction is usually add (PASSOS et al., 2011). It is common in the literature that methods such as BCR are use in soils and sediments from various locations outside the European Union.

In many articles adaptations are made, modifying the fractions in order to reach a better adjusts to different situations in which they are applied. Working with acidic soils from southern Brazil, the authors added a soluble fraction (deionized water) and excluded the fraction bounded to the carbonate, in the model proposed by Tessier et al. (1979). The bioavailable copper was concentrated on the surface, being bound to the mineral fraction of the soil, with saturation of the functional groups of the organic matter. The bioavailability of copper was higher in the more sandy soils, and lower in the more clayey soils (GIROTTO et al., 2014).

The use of combinations from different fractions is also usual. Duplay et al. (2014) used sequential chemical fractionation with 5 fractions: exchangeable, carbonates, Fe and Mn oxides, organic matter and sulfites, and residual, adapted from several authors (MCKEAGUE; DAY, 1966; RAURET et al., 2000; TESSIER et al., 1979; SEMHI; ABRI; KHANBASHI, 2013) in soils contaminated with copper.

Comparative works between extractors are frequently found in the literature. Studies such as the one of Komárek et al. (2008), where chemical fractionation demonstrated higher concentrations of copper in the reducible and oxidizable fractions, and the use of $CaCl_2$ in alkaline soils did not represent well the bioavailability of Cu compared to EDTA and EDDS. Working with different extractors of the available forms (EDTA and Acetic Acid) compared to BCR in soils with high Cu (133 to 306 mg kg^{-1}), the exchangeable fraction that extracted the most copper was EDTA. The content extracted by acetic acid was higher than that extracted in sequential extraction, but not more than 10%. The affinity relation of Cu to the chelates is reaffirmed in the use of EDTA (VÁZQUEZ; CID; SEGADE, 2016). Exchangeable copper undergoes greater influence of pH in water than total copper content. On the other hand, the copper that is potentially available (EDTA and DTPA) had a high correlation with total copper (FERNANDÉZ-CALVIÑO et al., 2013). The EDTA extractor had more acid pH (4.65) and was used in higher concentration, thus obtaining a higher copper extraction. For Feng et al. (2005), EDTA is the most suitable extractor for use in acid soils.

The residual fraction of copper in a fractionation is characterized by being the least polluting. Most copper was distributed in the residual fraction, characterized by low mobility, but the more superficial layers in the older vineyards had a higher amount of Cu associated with organic matter (BRUNETTO et al., 2018).

The bioavailability of heavy metals (Cu, Zn, Pb and Cd) in bottom sediments of the Ultrata river in Poland was tested by the fractionation of Tessier et al. (1979). More than 80% of the copper is bound to fractions 4 and 5 (organic matter and residual). However, in all the fractions there is an expressive amount of the studied metals, demonstrating that the potential of damage is high to the environment when these metals are found in sediments. The concentration of copper in the bottom sediment is a better indicator of pollution potential than its dissolved concentration in water (WOJTKOWSKA; BOGACKI; WITESKA, 2016).

In suspended sediments of a river in the north of Brazil, it was found 41% of copper of its content in the residual fraction. In the most labile fraction (bioavailable, F1), the contents varied between 8 and 15%. Rubio; Lopez-Sanchez; Rauret (1991), associates the most labile fractions (F1, F2 and F3) as anthropogenic and fraction 4 (residual) associated with lithogenic copper, natural copper of the environment.

Evaluating 32 vineyard soils in the Iberian Peninsula, 72% of the soils had total copper contents above 100 mg kg^{-1}. Non-exchangeable fractions are dominant (approximately 99% of total Cu). The more mobile fractions (exchangeable and available) ranged from 0.6 to 21.8 mg kg^{-1}. The most abundant fraction was related to organic matter (28 to 63% of total Cu, with an average of 44%). The management of vineyards that increase the mineralization of organic matter favors the availability of copper, increasing the degree of toxicity of the crops (GÓMEZ-ARMESTO et al., 2015).

The forms in which the copper is found in the soil vary according to the type of soil, depth and content of organic matter. In more sandy soils, copper is mostly bound to carbonates and in the residual fraction. When surface soils are evaluated, organic matter is the main Cu binder, followed similarly by residual fractions and carbonates (DUPLAY et al., 2014).

Analyzing the soil in the row and in the interweaving of vines using 3 fractions: total copper (aqua regia), extractable copper (ammonium and nitrate) and exchangeable copper (DTPA), the highest levels (extractable and exchangeable) were detected between plants in line than between the lines. There was a negative effect on total carbon at points of higher copper concentration. The biological activities at these points are reduced and with the passage of the years there is less production of organic material, which will cause a modification in the distribution of copper, which may increase its bioavailability (MACKIE et al., 2013).

Water is an important altering factor for the compartmentalization of copper in the particles. In soils that suffer flooding compared to those that do not suffer, copper was bound to the residual fractions (40% vs 4%), organic (25% vs 48%), reducible (23% vs 24%), respectively. In the soil control the other fractions (soluble, exchangeable and carbonate bound) presented 4% together. In the sediments, copper was mainly associated with 49% residual copper (DAMO et al., 2006). Copper bioaccumulation in mangrove roots increases with the increasing concentration of the labile forms of Cu in sediments. Also, the copper dissociation rate of the sediments influences the accumulation of copper in the roots. This study shows that the concentration of labile forms of copper and dissociation rates may be good indicators of copper bioavailability for sediments in mangroves (CHAKRABORTY et al., 2014). In order to evaluate the different nutrient patterns in the soil-leaf-grape system (Ca, Mg, Fe, Mn, Cu, Zn, K, Cd, Pb, Cr, Hg) in the leaves and Fe in the grape (VÁZQUEZ; CID; SEGADE, 2016). Analyzing the copper content in the roots, was verified that this parameter can be used as an indicator of soils contaminated by copper, although it does not serve as an indicator of phytotoxicity in plants, since some plants have mechanisms that do not allow the translocation of the element in (GIROTTO et al., 2014).

Changes in the compartmentalization of copper in soils are common and frequent in soils cultivated for long periods. Casali et al. (2008) studied the fractionation of Tessier et al. (1979) in a Neosol and Cambisol, both contaminated by copper. In both soils the highest amount of copper was bound to the mineral fraction, even in the layer with the highest content of organic matter (0 to 20 cm). If the amount of copper associated with the mineral, organic matter and residual fractions together added up to 89% in the Cambisol and 92% in the Neosol, similar behavior to that found by Brunetto et al. (2014) in another region of southern Brazil wines. However, the higher concentrations of copper were associated with mineral fraction (~ 23 and 75 mg $kg^{-1}$of copper, respectively). However, the area without cultivation obtained the highest concentration of copper associated with residual and organic fraction (3.18 and 0.86 mg kg^{-1}, respectively).

The association of the copper with different particles and the biding energy are factors that controlling the pollution potential of the soil and sediments copper charged. Thus, the sequential chemical fractionation technique is a fundamental practice that must be adopted in studies with contaminated particles that involved environmental risk.

3.5 Soil and sediments: sorption kinetics of Cu

In this study, the term ion sorption will comprise the ability of a soil or sediment to adsorb or desorb ions. In soils contaminated with copper, both behaviours (adsorption or desorption) are fundamental because the adsorption determines the maximum copper retention capacity that the soil or sediment can reach. Desorption represents the behavior in the release of copper in contact with a solution or liquid in the environmental.

The adsorption occurs with the retention of ions by the clay, organic matter and other particles. The term ion adsorption represents the ability of a soil to accumulate an ion at the interface between a solid and the solution (SPOSITO, 1989). The adsorption of metals is governed by the different mechanisms that compose it, either in the form of non-specific adsorption (external sphere), specific adsorption (internal sphere), ion exchange or complexation with soil organic matter (CAMARGO et al., 2001). The most important mineral fractions involved in the sorption of heavy metals are phyllosilicates, oxides and hydroxides, carbonates and phosphates (SPARKS, 2005).

Desorption occurs when the ions are released to the soil solution or when in sediments ions are released into the aquatic environment. The desorption of ions varies depending on the content of the element in the solution, the soil pH, the temperature, the amount of the adsorbed element and the time the soil and the solution are in contact. When we have a more acidic pH, a higher desorption may occur due to the higher concentration of H^+ in the exchange sites (GAO et al., 2003; MCBRIDE, 1989). The pH is the main determining factor in the sorption of ions into organic and inorganic particles (UREN, 1992).

The presence of organic material and its constituents - the functional groups (carboxylic, phenolic, etc.) - generate reactivity with several metals. Reactions between metals and functional groups range from inner sphere (coordinate bonds) to outer sphere (electrostatic attraction) bonds. Density, a type of reactive groups, location of clusters, size of molecule (the higher the molecular mass, the greater its complexation), characteristics of the solution (pH, ionic strength and temperature) all influence the stability of organometallic bonds. The stability of the organometallic bond can reach a point at which a chelate is formed. These structures of great stability are dependent on the types of bonds involved and the number of bonds, always resulting in a ring structure with metal incorporated (SBCS, 2007). The strong bond of Cu^{2+} (present in samples of waters of the Amazonian rivers) with the dissolved organic matter (humic acids added) was explained by the authors as being the result of the lower ionic radius of this ion in relation to the other ions (Cd and Pb) evaluated. Such interactions can occur through adsorption, cation exchange reactions and complexation. The reactions affect the geochemistry of the ions, being the complexation the reaction that causes greater alteration, modifying its solubility, load and redox potential (BEZERRA; AKIYAMA.; BEZERRA, 2009).

Valence, hydrated ray size, electronegativity and polarizability are characteristics of the metal that alter its affinity with the functional groups (SPARKS, 2005). The stability constant of the fulvic-metal complex (for example) is maximum and decreasing for $Fe^{3+}>Al^{3+}>Cu^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}>Fe^{2+}>Mn^{2+}$ (SCHNITZER; KHAN, 1972). The electron configuration of Cu ([Ar] $3d^{10}4s^{1}$) and $3d^{9}$ $4s^{2}$ gives it high reactivity with the functional groups of organic matter, which contain S and N, besides the carboxylic and phenolic groups (CROUÉ et al., 2003). Using the X-ray analysis technique (XANES), it was evidenced that in the tests there was complexation of Cu^{2+} by internal sphere in the natural organic matter and the result suggest that copper is complexed by one or two members of the chelate ring involving possible combinations of amino, carboxyl and carbonyl functional groups. Less than 0.2% of the total copper was in free form (Cu^{+2}) in the samples with pH 4.8 to 6.3 (KARLSSON; PERSSON; SKYLLBERG, 2008).

Soils and sediments are extensively studied for their sorption capacity (adsorption and desorption), mainly of metals and pollutants. In order to calculate the maximum adsorption capacity of ions the adsorption isotherms are use, being the most common to the ones of Langmuir and Freudlich. The Langmuir adsorption isotherm shows a monolayer adsorption, configuring a material with homogeneous surface and identical adsorption sites, this means one ion per surface site. However, the Freundlich adsorption isotherm says that the adsorption surface is heterogenous (BARKHORDAR; GHIASSEDDIN, 2004; FOUREST; VOLESKY, 1996; WALLACE et al., 2003).

In a comparative study between Cu and Zn sorption using Langmuir and Freuclich models, two limestone soils where used at only the clay fraction (without organic material). In this study, the maximum Cu and Zn adsorption using the Langmuir equation was 45,454 mg kg^{-1} and 50,000 mg kg^{-1}, compared to the Freudlich model (2,777 mg kg^{-1} and 2,764 mg kg^{-1}). The Q parameter (Langmuir) indicates that zinc has higher sorption energy in the soils, which can be explained by the absence of organic material (which has higher affinity with Cu) and predominance of the more reactive mineral fractions of clay. The highest desorption occurred for Zinc, which allows to infer that its potential for damage is higher (BAGHERNEJAD; JAVAHERI; MOOSAVI, 2015).

Carrying out adsorption tests in alkaline soils of Russia, containing 1:1 minerals (kaolinite, quartz) and 2:1 (ilite and montmorillonite) Minkina et al., (2017) found a significant correlation between clay content and silt with the parameters $C\infty$ (maximum copper adsorption capacity) and KL (affinity constant) of Langmuir model. As for the strength with which the copper is adsorbed, it is dependent on the chemistry and mineralogy of the adsorbent. Structural X-ray analysis (XANES) showed interactions of Cu^{2+} with soil humic acids, resulting in the formation of complex chelates. In this same work, Minkina et al. (2017) raised the possibility of Cu^{2+} displacing Al^{3+} from within the octahedron of clay minerals, replacing it. The possibility of neoformation of minerals, or even the dissolution and neoformation of these minerals can not be excluded, but their possibility of occurrence based on the experimental conditions of the article should be better discussed.

In a non-competitive system in a soil contaminated with Cu, the maximum copper adsorption was 997 mg kg^{-1}. However, in a competitive system with Zn there was a reduction of 14.7% in its adsorption. When soil is saturate with Zn, and copper is add to it, in this situation, there was a reduction of more than 70% in Zn adsorption, due to the high affinity of copper for the organic material present. The Zn adsorption occurred mainly in the mineral fraction, although the copper adsorption occurred in the organic matter. The Zn addition to copper-contaminated soils did not reduce copper toxicity but added zinc toxicity to the soil as it remained in more bioavailable forms (TIECHER et al., 2016b).

The attempt to reduce the toxicity of copper in soil using industrial waste has also generated countless works. The wine industry itself produces a waste containing large amounts of the mineral bentonite. This waste was tested for copper contamination reduction. After bentonite addition, the parameters of maximum adsorption of Cu, the adsorption at low concentrations and the energy of binding of copper with the soil increased significantly. Additionaly, copper desorption in short periods was very low in all cases (<6.5%), which may reduce the bioavailability of copper in the environment, being a good use indicator of this waste (FERNANDEZ-CALVIÑO et al., 2015).

Wheat straw used as mulching in vine areas proved to be an excellent material with Cu and other ions adsorption. When its sorption capacity was evaluated in a competitive system (Cu, Pb and Cd), the average copper adsorption in all concentrations was approximately 76% of the total copper available, however it desorption did not exceed 9%. When evaluated in a non-competitive system (Cu only), wheat straw reached practically the same average adsorption (76% approximately), although it desorption was more than 15%. This low desorption rate is the result of the affinity of copper to the organic functional groups constituent of the straw, being recommended by the authors their use in areas contaminated with copper (COELHO et al., 2016).

The use of mining waste has been study for use as a copper toxicity reducer in soils. Testing the competitive adsorption of Cu and Zn in pure minerals (ilite, montmorillonite and kaolinite) compared to a hydrothermal basalt powder (metabasalt), the author verified that there was a greater adsorption of Cu than Zn. On average, more than 99% of Cu added was adsorbed on both doses (3,000 and 6,000 mg kg^{-1}). For Zn only 61% of the added zinc was adsorbed. The basalt powder adsorbed more Cu than pure minerals and showed a slower desorption, reaching the lowest levels of Cu and Zn readily and potentially available according to Mckean and Warren model (1996). This behavior suggests its use as adsorbent material of Cu and Zn in contaminated areas, and the author suggests its possible use as a gradual release fertilizer for soils with deficiency of these nutrients (DALLACORTE, 2017).

The sorption behavior of sediments and soils contaminated are important aspects that must be investigate in environmental studies. The use of kinetics model may help researcher understand the potential damage of particles contaminated with copper.

3.6 Soil and sediment contamination with Cu

The term contaminated soil should be used when the nutrient contents found are higher than those naturally occurring in those soils without anthropogenic action. Contamination of soils by copper occurs mainly in superficial layers. This soil layer is very reactive, and the metal can react in various forms (complexation, precipitation/dissolution, sorption/desorption and oxidation) with the most different organic or inorganic soil constituents (SPOSITO, 1989).

The natural Cu contents may differ significantly among soils. In 5 soils developed on different materials of origin in southern Brazil (Rio Grande do Sul) the authors found copper levels in soil ranging from 8 to 309 mg kg^{-1} (using 0.1 M L^{-1} HCl). Soils developed on basalt have higher natural contents, on average 100 ± 78 mg kg^{-1} Cu when compared to other soils developed on other materials of origin that reached on average 10 ± 12 mg kg^{-1} Cu (ALTHAUS et al., 2018).

Contamination of sediments with copper may come from a variety of sources. Collects carried out in the Salt River in Taiwan found 501 mg kg^{-1} of Cu in the sediments along the river, whereas their spatial distribution revealed that the main sources of contamination are the industries and the municipal discharge of waste along the course of the river (CHEN; CHEN; DONG, 2012).

In Brazil, the Conama Resolution N°420/2009 established the guiding values of trace elements in soils and waters (BRAZIL, 2009). It is divided into 3 limits: Quality

Reference Value (QRV), Prevention (QRP) and Interference (QRI). QRV is the natural value that can be found on that soil. QRP is the maximum content in which a soil can be used for agricultural practices. QRI indicates the concentration of an element above which there is a potential risk to human health. Acording the Chemical soil fertility Boarding of South Brazil, several studies indicate that Cu (extracted by Mehlich 1) ranging between 30 and 60 mg kg^{-1} of sandy soils and between 100 and 150 mg kg^{-1} of Cu for clayey areas, already have negative effects on plantations (CQFS, 2016). Table 2 shows the values for Cu in some countries.

Table 2 - Reference values for Cu metal in contaminated soils from diverse locations. Passo Fundo, 2019

Location	Cu levels (mg kg^{-1})	Source
Brazil	>60	Brazil (2009)
Rio Grande do Sul	203 (basalt)	Althaus et al. (2018)
Rio Grande do Sul	17 (other source materials)	Althaus et al. (2018)
Australia/New Zealand	>60	ANZECC/NHMRC (1992)
European Comunity	50-140	Council Directive 86/278/EEC (1986)
Italy	>100	Italy (2006)
The Netherlands	>36	Mackie et al. (2012)
Czech Republic	60-100	Komárek et al. (2008).

Source: author data.

The enormous variation between the natural contents found in the soils of Brazil, and even within only one state (Rio Grande do Sul), it is clear the need for more characterization works for the definition of the natural values of reference to the soils, from which we determine what are and where contaminated soils are within the national territory.

Soils with long history of grapevine production worldwide suffer from high levels of copper caused by the application of copper fungicides. In sandy soils of southern Brazil with grapevine production, it was detected that levels above 65 mg kg^{-1} of Cu already harm the development of grasses in the line of vines, which causes less root development and green mass, increasing the soil erosion and possible water contamination by Cu-rich sediments. The bioavailability of copper (extracted with EDTA) in these soils reached 75% of the total copper (BRUNETTO et al., 2011). Comparatively evaluating a copper contaminated area with a native forest area, Girotto et al. (2014) found little difference in exchangeable copper, however more than 3 times the percentage of copper in the mineral fraction (potentially available), and more than 5 times the proportion in the residual fraction in the contaminated area.

The high bioavailability of copper in soils contaminated with sandy texture causes copper accumulation in the root system of grasses sown under the vineyards (TIECHER et al., 2016a; GIROTTO et al., 2014). However, the antioxidant enzymatic activity of the grasses was high, but was not sufficient to reduce the oxidative stress caused by copper toxicity (GIROTTO et al., 2016). In soil contaminated with Cu, a low growth rate, leaf chlorosis and copper accumulation is detect in the roots, causing damage to the establishment of new vineyards in contaminated areas (MIOTTO et al., 2014).

In order to remediate contaminated soils with metals, there are several techniques, such as immobilization by pH alteration, addition of organic material, removal, sequestration, active mixtures and phyto-extraction (MACKIE et al., 2012). The use of phytoremediation plants in contaminated soils is being evaluate in southern Brazil. Tiecher et al. (2016a) saturated a soil contaminated with Cu with Zn to evaluate the effects on maize plants and their responses to oxidative stress caused by metals. The increase of Zn in the soils had no effect on the dynamics of the Cu in the solution and on the possible reduction of its polluting potential. In samples with high zinc content, there was a reduction in the development of the roots and aerial part of the corn. However, in soil with low levels of Zn and contaminated with copper corn planting can help in the extraction and phytoremediation of this soil.

Peanut (*Arachis pintoi*) is a perennial plant with high factor of bioaccumulation of copper, reaching to accumulate 2.5 kg ha^{-1}. The most accumulated part is found in the roots, having a translocation factor for the lower area (ANDREAZZA et al., 2011). Bioaccumulator plants compartmentalize excess copper in the root apoplast or organelles such as the vacuole. The absorption of copper by bioaccumulating plants reduces its availability in the solution (CHAIGNON; HINSINGER, 2003).

Ferreira et al. (2018a) used 3 soil correctives (limestone, calcium silicate and vermicompost) aiming at reducing the toxic effect of copper on vine shoots planted in contaminated soil (87.5 mg kg^{-1} Cu). The use of vermicompost (aerobic composted grape bagasse and decomposed by earthworms) at a dose of 30 g C kg^{-1} increased the accumulation of biomass in the seedlings by 89%, reducing the free copper content in the solution. There was an increase in the photosynthetic rate, reduction of the activity of peroxidase and superoxide dismutase enzymes and increase in the amount of fine roots. The vines seedlings replanted in contaminated areas showed a defense mechanism, accumulating the Cu and Zn in the roots, reducing its translocation to the aerial part, reducing its toxic effects (TIECHER et al., 2017a).

The use of limestone, calcium silicate and organic compounds (vermicompost) used in soils with high copper content (87.5 mg kg^{-1}) reduces the bioavailability of copper for vine shoots when replanted in these areas. The vermicompost presented better performance due to its high contents of organic molecules of low molecular weight that have great affinity for copper, reducing its bioavailability. These molecules associate with the Fe and promote a greater availability of the plants, which resulted in greater development of the seedlings (FERREIRA et al., 2018a).

The addition of P to the contaminated soils proved to be a viable tool in reducing the toxicity of Cu vines. The mechanism by which the reduction of toxicity occurs is that need to be further explored, since the available Cu contents were not modified by the addition of P. However, the best nutritional status was the one of the plant with high doses of P (100 mg P kg^{-1} soil), which resulted in increased plant biomass and root growth in contaminated soils (BALDI et al., 2018).

The inoculation of *Mucuna cinereum* with arbuscular mycorrhizae associated with the application of phosphorus doses reduced the phytotoxicity of copper and improved the physiological indexes of development of Mucuna, a plant used for the recovery of copper contaminated areas, shortly after vineyard cutting (FERREIRA et al., 2018b).

Some agricultural practices may be used to reduce the solubility or concentration of toxic metals in the soil. The addition of lime (raise pH in acid soils), use phosphate fertilizers (Zn and Cu precipitation), addition of organic material (Cu fixation), copper extraction via bioaccumulating plants, and the promotion of symbiosis between mycorrhizal fungi and plants (BRUNETTO et al., 2016a), are important actions in the reduction of contamination process. In addition, the use of rock dust containing minerals or clay minerals capable of adsorbing metals has been studied (DALACORTE, 2017). The use of bentonite in vineyard soils caused positive effects reducing bioavailability and increasing Cu adsorption (FÉRNANDEZ-CALVIÑO et al., 2015).

3.7 Transfer of Cu from soil to aquatic systems

The transference of particles rich of copper from vineyards to aquatic systems has frequently occurred in the past years. In order to infer the potential of copper transfer to aquatic systems, it is necessary to understand where this copper is bound and with which binding energy, so that the bioavailable potential can be evaluated (CASALI et al., 2008).

There are an important dynamic associate with the particle that must be understood, relationship to the particle size and its reactivity. The transfer of copper in systems is dependent on numerous factors that occur from the choice of the Cu formulation to the sedimentation of the particles. Using an artificial rain simulation, the authors found that the Bordeaux curd applied to the leaf exhibited the lowest total copper content lost compared to two other forms of copper (oxychloride and oxychloride with propylene glycol). The drop size and the fungicide dosage strongly influenced the percentage of losses (PÉREZ-RODRÍGUEZ et al., 2015).

Estimates of sediment sources are difficult to obtain using traditional monitoring techniques, but in recent years the set of techniques known as FingerPrinting has been shown to be a valuable alternative (COLLINS et al., 2017). Using a common δ^{65} Cu isotope in the fungicides applied on the leaves of the vines in a French watershed, with 15% slope, the authors verified that the copper contents exported to other environments vary according to the size of the soil particles, mainly its mineralogy, being more found associated to the finer clay and the organic matter of the soil. In more intense rainfall events, copper can be carried in particles of larger size, but still less frequently than in clays. The copper that underwent surface runoff corresponded to 1% of the mass of copper applied in the growing season, and 84% was found in suspended material particles (BABCSÁNYI et al., 2014).

Using a copper soil transfer factor (total) for the plant, it was verified that Cu and Zn obtained the indexes of 66% and 71% respectively, demonstrating that when there is a green cover on the soil, a large part of the copper applied to be extracted by plants and their reduced availability in the system (DUPLAY et al., 2014). The plants are capable to absorve and accumulate copper in root system. In a soil enriched with Cu and Zn, an accumulation of these metals was verified in the root system, with reduced mobility to the aerial part of the transplanted grapevine, which is a defense mechanism of the plant that allows its development in contaminated soils. However, at higher doses, there are physiological problems that reduce root development, photosynthesis reduction and changes in gas exchange (TIECHER et al., 2018a).

Evaluating the percolated water at a depth of 1 m of highly contaminated copper soils Mirlean et al. (2007) verified distinct copper concentrations varying according to soil type. More sandy soils percolated more copper, having reached 70.5 mg L^{-1}, while more clayey soils were found to contain 3.5 mg L^{-1}. Besides the texture, the greater acidity of the sandy soils in this region contributed to a greater percolation and contamination of the water table.

Monitoring the annual flow of sediment from 132 rivers to the Atlantic, Pacific, and Gulf of Mexico oceans in the United States, Horowitz et al. (2012ab) found Cu in high concentrations in more than 55% of the samples. This high concentration of sediment-associated metal is often associated with industrial areas and large urban centers. Urbanization is one of the major sources of sediment-related contaminants. When rainfall occurs in large urban centers, usually at the beginning of rainfall, the concentration of suspended sediments is low, the sediments are fine grain size (≤63µm), and the concentration of associated elements tends to be higher. As the event proceeds, the concentration of suspended sediments increases, the average particle size becomes larger and as a result the concentration of elements associated with the particles falls, however this may vary as a function of the sediment flow. Even if the concentration of associated elements falls, the sediment flow can increase, generating a growth in the total discharge of contaminated sediments (HOROWITZ, 2009). The table 3 presents the copper content found in particles in the USA.

Table 3 - Copper contents (average) found in soil, bottom sediments and suspended sediments in the USA. Passo Fundo, 2019

	Shacklette[1]	NAWQA[2]	World	Atlantic	Gulf	Pacific	River average[5]
	USA Soils	BS [3]	SS[4]	SF	SF	SF	SF
Cu (mg kg^{-1})	25	24	75	55	19	46	42

Source: Adapted from Horowitz et al., 2012ab.

1: Schacklette and Boerngen, 1984; 2: National Water Quality Assessment; 3: Bottom Sediment (BS); 4: Sediment Suspension (SS); 5: Average of American rivers discharging into the Atlantic Ocean, Gulf of Mexico and Pacific Ocean.

The occupation rate of large centers is a preponderant factor in the concentration of copper associated to bottom sediments of the rivers. Demographic densities between 0 and 3 people per km^{-2} resulted in copper contents averaging 21 mg kg^{-1}. Density between 83 and 186 people per km^{-2} reached average levels of 36 mg kg^{-1} of Cu. Large centers easily reach the density of 558 up to 2,284 people per km^{-2}, which generated sediments loaded with 48 mg kg^{-1} of copper (HOROWITZ et al., 2012ab).

Suspended sediments and their associated chemical constituents have spatial and temporal variability, even under constant or non-sediment discharge conditions. The type of sampler, the interval between collections, the vertical and horizontal location of the collection equipment within the rivers can substantially affect the determination of the amount of suspended sediment and its chemical characteristics. The fraction below 63 µm located on the surface of the bottom sediments (1 cm) serves as an estimate of the chemical concentration of suspended sediments for the main elements and trace elements, but it is not as accurate for nutrients and carbon (HOROWITZ, 2008).

There was a broad perception that land use, its mineralogy/petrology and (geology) could have substantial influences on the geochemistry of lake or river sediments. Most land use categories (agriculture, forest, and natural pastures) appears to have little effect on the chemical composition of bottom sediments. However, human activities have a significant influence on the chemical composition of the sediments. Copper was the 6th element that had its contents enriched in the places with the largest population (HOROWITZ; STEPHENS, 2008).

3.8 Final considerations

The review of the articles allows us to infer about several techniques and actions importants related to sediments and soils contaminated with copper. Below there are five items listed as important during the review of the articles:

Association of strategies with the use of soil correctives (limestone in acid soils), fertilization with phosphorus, organic fertilization, use of minerals (rock dust), mycorrhizal symbioses, phytoplankton plants or phytoremediation plants are strategies with success in the literature, which intend to reduce the bioavailability of copper in contaminated areas.

The dissolved copper is in different forms, but all of them potentially polluting. Determining solution-soluble copper and in river waters can assist in monitoring ideal and limiting levels. National-scale studies are needed to determine the ideal content levels and limits for the definition of contaminated areas. The use of total contents does not portray soil toxicity in soils. The determination of toxic thresholds of copper levels in the soil bioavailable in the different soil classes is fundamental for actions to be taken. The use of indicator plants should be better understood as they provide accurate information on the bioavailability of copper in soils. The copper content in the crop root system that is developed in areas of high copper contamination can serve as an indicator of bioavailability to the environment.

The selection of the best method of chemical fractionation of elements should observe the degree of soil weathering and its natural pH and the presence of carbonates. Fractionation and chemical speciation methods should be standardized and adjusted according to the type of soil or sediment being used, so that the generated data can be compared and discussed.

Sandy, carbonaceous, acidic, clayey soils, among other characteristics provide different behavior and distribution to copper forms, making it more or less bioavailable to the environment. Soils with alkaline pH (> 7.0), Cu fixation in oxides and hydroxides (Fe, Mn and Al) tend to increase comparatively to this same fraction in acid pH soils. Soils at this pH usually have high carbonate content, and in many studies, this fraction is disregarded, or the fractionation method does not contemplate this specific fraction, overestimating other fractions. Several works did not account for the effect of high P content of grape or fruit production soils. P has an important role in the fixation of metals, such as Cu and Zn, which may affect the bioavailability of copper in the environment.

Anthropogenic management actions may alter the distribution of copper in different compartments, increasing or decreasing its bioavailability to the environment. Large urban and industrial centers generate sediments rich in metals (especially copper), and monitoring stations must be set up so that continuous data are generated and mitigation actions can be carried out in a short time to contain the contamination of the waters by the sediments.

The transfer of copper from the soil to the aquatic systems occurs via sediments, and the potential damage that a rich sediment of copper can cause is dependent on many factors, but two are the main ones: the soil type of the sediment and the degree of anthropization of this environment.

4 CAPÍTULO II

Mineralogy of sediments and copper transfer from a centenary vineyard in a small watershed

4.1 Abstract

Vineyard system transfers easily sediments to water bodies. The objective of this study was to evaluate qualitatively the sediment mineralogy and the copper forms presents in the water bodies and its relationship with the sediment mineralogy. Suspended sediment samples were collected in a centenarian vineyard (VY), a riparian forest (RF: control), and in two points of stream (US: upstream and DS: downstream) of five representative rainfall events. A rich mineralogical assemblage from VY and DS was composed of mica, kaolinite, illite, rutile, hematite, quartz, calcite, magnesite, albite, anorthite and a Cu-bearing mineral. Centenarian vineyard produced suspended sediments with high Cu concentration, in their total (9.16 mg L^{-1}), exchangeable (2.81 mg L^{-1}) and soluble (1.2 mg L^{-1}) forms. However, the suspended sediment in downstream was rich only in total Cu, while exchangeable and soluble Cu forms were much lower. The vineyard is enriching soil particles with copper, producing copper-rich sediments, as well as promoting a favorable environmental to the formation of copper-bearing minerals. Such sediments are being discharged into the stream. The mineral greatest diversity and highest concentration of copper in the sediments present at the DS comes from the vineyard. Therefore, the soil use modified the mineralogical composition of suspended sediments. In the suspended sediments found at the stream, the greatest amount of copper was in it total form, with low bioavailability. Bioavailable forms have been found in small concentrations. Thus, the suspended sediments when entering the stream are increasing the total copper stock, acting as a source of copper to the environmental. The presence of minerals with high copper affinity, reduce the bioavailability of copper to the environmental. Perhaps, a changed in the environmental may cause a dessorption of the copper adsorbed in the minerals, promoting an increase in copper available forms to biota, causing serious environmental damage.

Key words: 1. Cu-bearing mineral. 2. Ion sorption. 3. Suspended sediments. 4. Copper forms. 5. X-ray diffraction.

4.2 Introduction

In south Brazil, the viticulture is concentrated in two regions (Campanha and Serra Gaúcha) that present different environmental conditions. The Campanha is the most recent wine production region located in the frontier with the Uruguay, which presents relief plan and soils with medium deep and well drained. The Serra Gaúcha presents vast and ancient areas of grape production under traditional crop systems. Some farmers, mostly Italian immigrants, have maintained vineyards over than 100 years. Besides, the region has a subtropical climate regime and a mountainous relief presenting predominantly shallow and fragile soils (Regosols). Thus, the combination among several environmental and agricultural factors is characterized as a fragile agroecosystem. For instance, there is a great risk of soil erosion due to the high precipitation intensity, high soil declivity and the absence of cover crops in the vineyards (VANACKER et al., 2019; XU et al., 2014). These conditions favor the pollutant transfer from terrestrial to aquatic bodies (BORTOLUZZI et al., 2013). The Serra Gaúcha region covers an area drained by important rivers, such as, Jacuí, Caí, Passo Fundo, Rio das Antas and others, which are all tributaries of the Guaíba Lake, which is the water source for more than 2.2 million people in South Brazil (SEMA-RS, 2019). Recent studies have shown that there is evident sediment contamination with P, Cu and other heavy metals in margins of the Lake Guaíba (ANDRADE et al., 2018b).

In Southern Brazil, the traditional vineyard systems use mainly Cu-based fungicides, such as Bordeaux mix ($Ca(OH)_2+CuSO_4$), to control fungal diseases (TIECHER et al., 2016). It is estimated that from 20 to 80 kg Cu ha^{-1} $year^{-1}$ has been applied on the vineyard canopy along the decades (NACHTIGALL et al., 2007; MIRLEAN et al., 2007; CASALI et al., 2008). The consequence of that is the soil Cu accumulation reaching more than 3,200 mg kg^{-1} (MIRLEAN et al., 2007; BRUNETTO et al., 2016a; BORTOLUZZI et al., 2019). Although the natural Cu concentration may reach 203 mg kg^{-1} for soils originated from basalt rock (ALTHAUS et al., 2018), these values are much higher than those established by the Brazilian legislation (60 mg kg^{-1}) as critical prevention value (BRAZIL, 2005; BRAZIL, 2009).

In brief, Cu accumulates in the soil by three main mechanisms: i) by forming outer and inner sphere complexes onto clay minerals, ii) by ion exchange or ion complexation by the organic matter (SPOSITO, 1989; CAMARGO et al., 2001); iii) Cu precipitation in bearing mineral (BORTOLUZZI et al., 2019). In fact, minerals present high affinity with Cu, mainly expandable 2:1 clays (DALACORTE; ESCOSTEGUY; BORTOLUZZI, 2019) and calcic minerals (TESSIER et al., 1979). Besides, pH controls metal availability in the soil and environment (BRADL, 2004; NOGUEIROL et al., 2010; TIECHER et al., 2018a; DUPLAY et al., 2014). On the other hand, Cu accumulation in soil affects the development of other species that cohabit the vineyards such as the cover crops (BRUNETTO et al., 2016ab; GIROTTO et al., 2016), as well as when absorbed by plants may accumulate in vine products, such as vine and juice (HUMMES et al., 2019). However, the Cu exportation by these mechanisms seems low. As vineyard areas are often exposed to the intense erosion process in a mountainous relief with high rainfall intensity and shallow soils, the Cu-transfer risk to water bodies is higher (LONDERO et al., 2018). These factors once acting together result in a very complex crop system with controversial agronomic efficacy and high environment damage potential.

Understanding environmental and agronomic aspects of vine production is fundamental to an adequate vineyards management in the territory, mainly concerning the sustainability over decades. The ancient vineyards received large quantities of Cu based fungicides result in high Cu input and accumulation in soil profile increasing the risk of Cu transfer to water bodies. The quantitative aspect of vineyard erosion is relatively well known and described in the literature, however, studies about how Cu transfer occurs from centenarian vineyard areas to water bodies and its relationship with sediment mineralogy is lacking. Thus, sediments originated from centenarian vineyard may be Cu-rich and generate high anthropogenic pressure on the watershed landscape and becomes a major agronomic and environmental issue. Besides, the mineralogy of sediment may control the availability of Cu fractions in the sediment (FERNÁNDEZ-CALVIÑO et al., 2008abc). Hence, the mineral characterization of centenarian vineyard suspended sediments may clarify how the sediment works concerning metal transfer from terrestrial to water bodies. This approach may help future soil and vineyard management in order to ensure sustainability of agroecosystem worldwide.

The present study aimed to identify mineral assemblage in suspended sediments from a centenarian vineyard and to evaluate different copper chemical fractions associated to suspended sediments in a small watershed stream in order to discuss the vineyard contribution to Cu-rich sediment production.

4.3 Material and Methods

4.3.1 Study area

The study was carried out in a small watershed (29°6'32.70"S and 51°28'3.77"W) located in the municipality of Pinto Bandeira, in Rio Grande do Sul State, south Brazil. The climate is humid subtropical with mean annual rainfall of 1,850 mm and mean annual temperature of 17.3°C. The rainfall is well distributed along the year, and associated to the high air humidity, it promotes fungal diseases in the vines. The geology is based on the basalt and rhyo-dacite rocks. The watershed has a mountainous relief with more than 20% of declivity, and the soil is classified as Regosol in the soil World Reference Base (Table 4).

Table 4 - Soil profile description† under vineyard and riparian forest. Passo Fundo, 2019

Soil Sites	Horizon	Depth	Munsell color	Consistency			Texture Classes
		cm	moist	wet	moist	dry	

Vineyard	Ap	0-27	10YR 3/3 dark brown	slightly plastic	friable	hard	loam
	CR	27-60	7.5YR 3/4 dark brown	plastic	friable	very hard	loam
	R	+ 60					
Riparian Forest	A	0-35	5YR 3/3 reddish brown	slightly plastic	friable	slightly hard	loam
	C	35-60	7.5YR 4/3 brown	plastic	friable	slightly hard	clay loam
	R	+ 60					

Source: Adapted from Korchagin et al. (2018).

† Soil description based on Food and Agriculture Organization - FAO (2006).

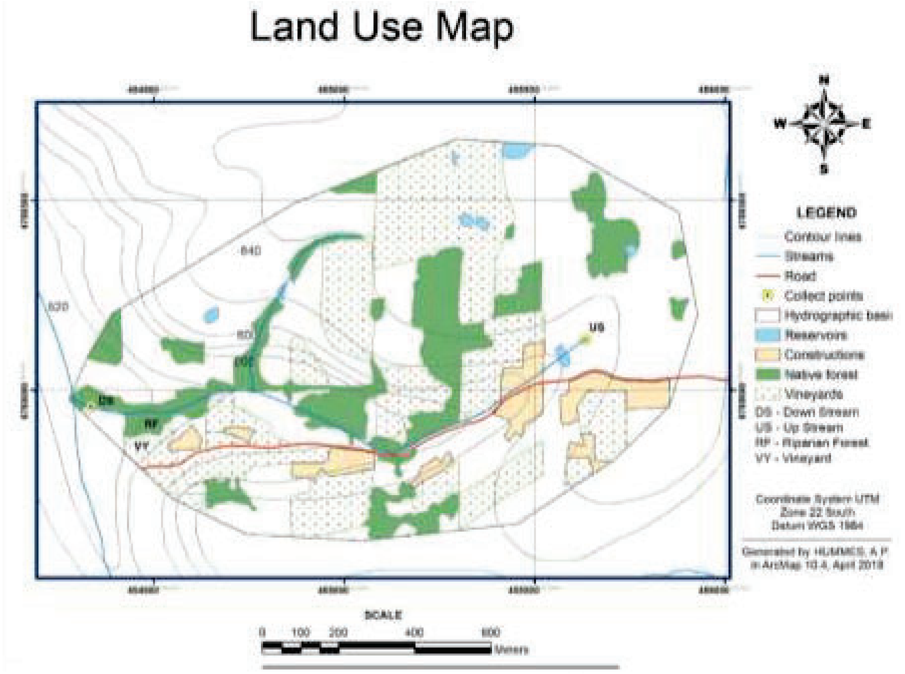
The total surface area of the watershed is 124.5 ha and the main soil uses are: old vineyards with more than 20 years of cultivation (19.6 ha), young vineyards with less than 20 years (22.9 ha), other perennial orchards (29.7 ha), and the lowest anthropogenic uses consist of forest and prairie (21.2 and 16.6 ha respectively) while high anthropogenic uses, including buildings, roads and water basins represents about 5.0, 1.0, and 0.6 ha, respectively (Figure 1). Centenarian vineyard relicts were found, one of then with 1.2 ha started in 1890. The old vineyard areas are cropped using a tendon system, while the young one uses trellis system. Both systems are consisted of frequent copper-based fungicide applications. Total Cu applied in one crop season was estimated in ~48 kg Cu ha^{-1} (1.2 kg Cu 100 L^{-1} of water).

The study site present a relief mountainous, where the vineyard occupied the upper position over the riparian forest. In order to reduce the soil runoff from vineyard to riparian forest, there was build a physical barrier of stones. After many years, the soil from vineyard was continuous accumulating in the barrier, and nowadays the barrier has nom effect in reduce sediments transfer from vineyard, through riparian forest until be deposit in stream water. The riparian forest has a very declivous relief, which not allow the sediment from vineyard or it owns be deposit or accumulated (Figure 2).

4.3.2 Soil sampling

Ten soil subsamples from a centenarian vineyard (VY) and riparian Forest (RF) sites were taken from a layer of 0 to 0.10 m. After drying the soil samples at 50^{o}C and sieving at 2 mm, the following analyzes were performed: soil pH; potential acidity (H+Al) estimated by SMP solution; available phosphorus (P), potassium (K) and copper (Cu) were extracted by Mehlich 1 (TEDESCO et al., 1995). After extraction, Cu content was determined by atomic absorption spectrophotometer (AAS), using acetylene gas, P was dosed using spectrophotometer V-Visible device, and K was dosed using an absorption flame spectrophotometer working with natural gas. Calcium, Mg and Al were extracted using 1.0 mol L^{-1} KCl solution. Ca and Mg were dosed in an AAS, while Al was dosed by acid base titration. The cation exchange capacity (CEC) was then calculated by the sum of H+Al, Ca, Mg and K. The soil organic carbon was estimated by humid digestion method using a digestion block (RHEINHEIMER et al., 2008).

Figure 1 - Land use map and areas of landscapes that compound the microbasin of the centenary vineyard. Passo Fundo, 2019



Land uses	Area (ha)	%
Buildings	6.2	5.0
Forest	21.2	17.0
Water basins	1.3	1.0
Roads	0.8	0.6
Old vineyards	19.6	15.7
Young vines	22.9	18.4
Other orchards	29.7	23.9
Prairies	16.6	13.3
Annual crops	6.2	5.0
Total	124.5	100

Source: author data.

4.3.3 Soil sampling

Ten soil subsamples from a centenarian vineyard (VY) and riparian Forest (RF) sites were taken from a layer of 0 to 0.10 m. After drying the soil samples at 50°C and sieving at 2 mm, the following analyzes were performed: soil pH; potential acidity (H+Al) estimated by SMP solution; available phosphorus (P), potassium (K) and copper (Cu) were extracted by Mehlich 1 (TEDESCO et al., 1995). After extraction, Cu content was determined by atomic absorption spectrophotometer (AAS), using acetylene gas, P was dosed using spectrophotometer V-Visible device, and K was dosed using an absorption flame spectrophotometer working with natural gas. Calcium, Mg and Al were extracted using 1.0 mol L^{-1} KCl solution. Ca and Mg were dosed in an AAS, while

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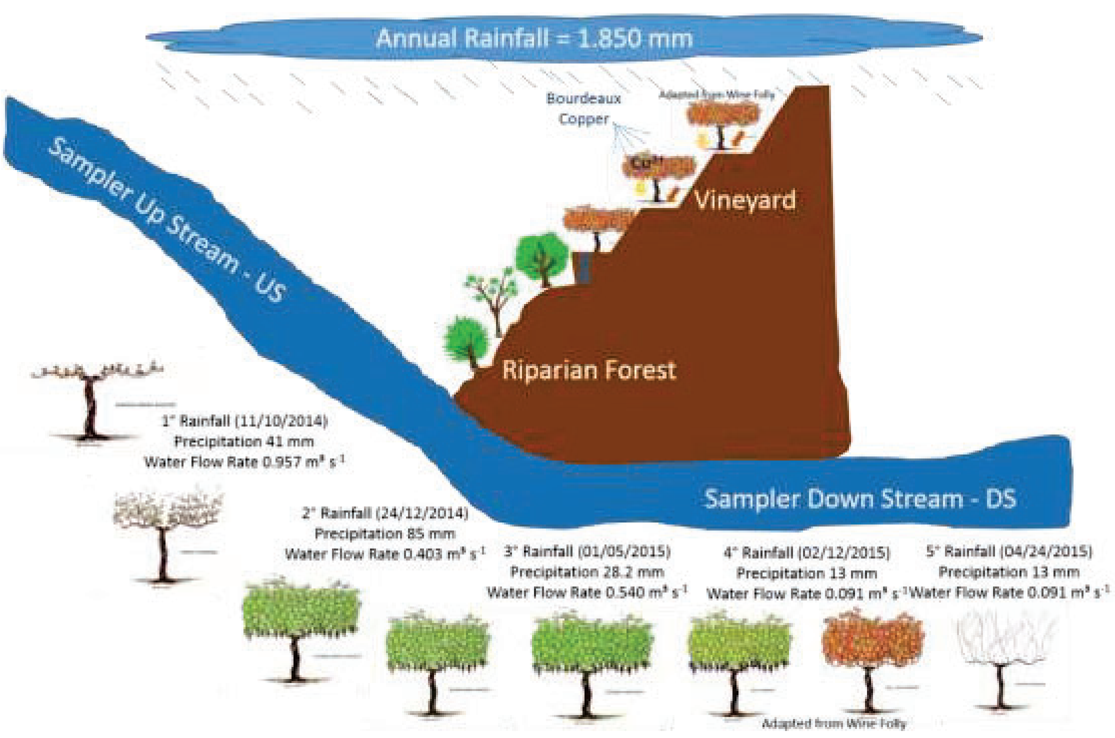
4.3.4 Sediment sampling strategy

Suspended sediment samples were collected using manual samplers in two conditions: i) two soil uses centenarian vineyard (VY) and riparian forest (RF) and ii) in the watershed stream: upstream (US) and downstream (DS) (Figure 2). The samplers at RF and VY were place in the soil level, in order to collect the surface water + suspended sediments eroded after each rainfall event. In the watershed downstream channel, the sampler consisted of one vertical ascending level sampler built according to the specifications of Umezawa (1979) which is able to collect samples at six vertical layers from the water natural level (0.0-0.10, 0.10-0.20, 0.20-0.30, 0.30-0.40, 0.40-0.50 and 0.50-0.60 m). In the watershed upstream channel, the manual sampler collect the water + suspended sediments from the ascending water level (0.0-0.10 m).

Suspended sediments from five representative rainfall events of vineyard crop season were taken of 27 monitored between 2014 and 2015. The rainfall varied from 13 to 105.2 mm while water flow rates in the stream at DS point varied from 0.091 to 0.957 $m^3 s^{-1}$ (Figure 2). After sampling, the water plus sediment sample were maintained at temperature of 5 to 8°C until the analyzes.

Figure 2 – Precipitation data, landscapes and samplers positioning in the vineyard, riparian forest and stream channel in the microbasin. Passo Fundo, 2019



Source: author data.

4.3.5 Sediment characterization

a) Mineralogical analysis

In order to guarantee little mineral alterations and maintains original sediment conditions, the organic matter oxidation was not performed (BORTOLUZZI; SANTOS; VILLETTI, 2010). The sediment samples were split in two aliquots: i) one was Ca-saturated using 0.5 mol L^{-1} $CaCl_2$ solution and, ii) another was K-saturated using 1,0 mol L^{-1} KCl solution. Samples were then washed five times to eliminate salt excess. Sediment suspensions (1.0 mL) were deposited onto slide glass to produce an oriented sample. The Ca-saturated samples were stored in X-ray diffraction (XRD) between 5 and 70° 2θ at room temperature (air-dried) and after ethylene glycol (EG) solvation. K-saturated samples were stored at the same XRD amplitude, but after there were heating treatments at 250 and 550 ^{o}C. The diffractometer used was a Bruker model D2 Phaser operating with Cu-Kα radiation at 30 kv and 15 mA. The XRD patterns were analyzed using EVA$^{®}$ software. The method used to the mineral identification was realized through the comparison of at least one peak (*00l*) in the XRD patterns and their intensities.

b) Chemical properties and copper fractions in sediment samples

Electric conductivity, pH, and sediment concentration (SC) were immediately analyzed after sediment sampling. Available phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), zinc (Zn) and copper (Cu) were determined in SSC according Tedesco et al. (1995). Concerning Cu fractions: the total copper (Cu_T) was determined using 17.5 mL of water plus sediment sample adding 2 mL of sulfur acid in tubes using a digester block, previously heated to 130 °C. Copper was dosed in AAS. Soluble Cu was determined using Whatman filter n° 42 (Cu_S). The exchangeable Cu (Cu_E) was extracted using cation exchange resin (CER), hereafter named as bioavailable Cu. Additionally, seven Cu successive extractions were performed using $NaHCO_3$ saturated CER membranes with 2.5 cm^2 surface area, as described by Bortoluzzi et al. (2013). Each extraction consisted of 16 h of CER contact with sample under mechanical agitation at temperature of 20 °C (±2 °C). After each extraction, Cu was dosed in AAS. The first Cu extraction was considered as Cu easily available while the sum of all Cu extraction is the Cu recovered from the total. The assay was performed in six VY and RF replicates, which presented enough sample quantity. The stream samples did not present enough sample quantities. All extractants was analyzed by AAS.

4.3.6 Statistical analyses

The average data was calculated using triplicates. The mineralogical analyses were made from a representative sample composed from three subsamples. A main component analysis (PCA) was performed based on correlation matrix using all variables that showed themselves significant to the Mann-Whitney non-parametric test ($p<0.10$). Pearson coefficients were also calculated.

4.4 Results

4.4.1 Chemical properties from the vineyard and riparian forest soils

In the VY soil, the available Cu, P and K were 50, 15 and 3 times greater than in RF, respectively. The pH H_2O value found in the VY (6.7) was higher than the RF (5.5). Exchangeable Ca and Mg concentration found in VY soil were 12.8 and 5.3 cmolc kg^{-1}; these values were higher than those found in RF. However, the values of CEC, H+Al and Al^{3+} found in RF were higher than those found in VY (Table 5).

Table 5 - Soil atributes from Vineyard and Riparian Forest in the microbasin. Passo Fundo, 2019

Soil parameters	Centenarian Vineyard	Riparian Forest
pH	6.7	5.5
Ca, cmol$_c$ kg^{-1}	12.8	14.8
Mg, cmol$_c$ kg^{-1}	5.3	3.9
Al, cmol$_c$ kg^{-1}	0.0	0.15
K, mg kg^{-1}	224	675
P, mg kg^{-1}	301	19.7
Cu, mg kg^{-1}	1,753.7	30
†SOM, g kg^{-1}	38	47
H+Al, cmol$_c$ kg^{-1}	2.0	6.6
‡CEC$_{pH7}$, cmol$_c$ kg^{-1}	20.7	27.1

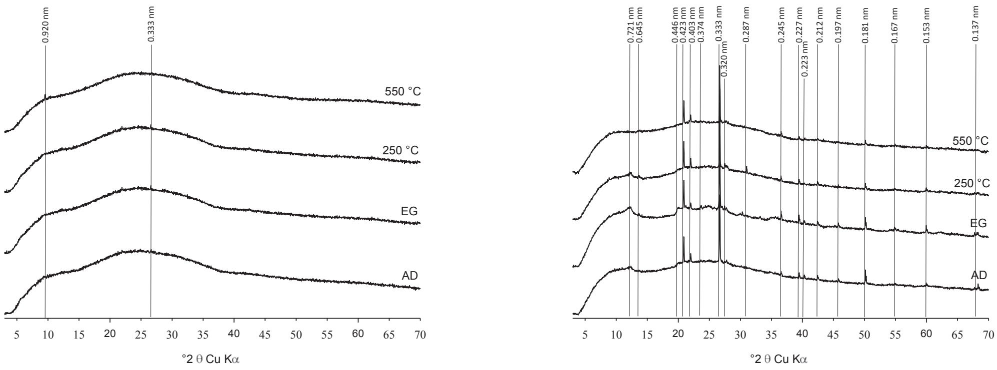
Source: Author data.

†SOM = soil organic matter, ‡ CEC = cation exchange capacity.

4.4.2 Mineralogical analysis

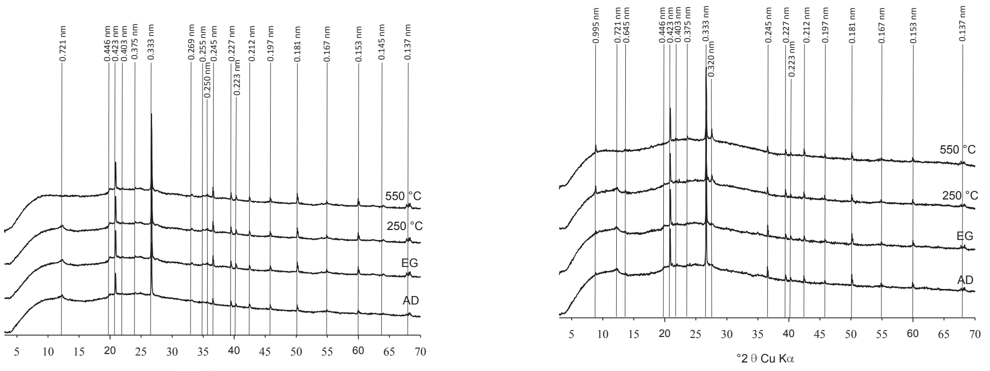
The suspended sediments presented twelve different minerals according the soil use and stream points (Table 6). Three distinct mineral groups were identified: clay minerals (mica, kaolinite and, illite), oxides (rutile and hematite), primary grain minerals (quartz, calcite, magnesite, albite and, anorthite). Besides, four XRD peaks were found (0.64, 0.40, 0.37, 0.42 nm), and they are compatible with two Cu-bearing mineral that may formed in soil (wooldridgeite and cyanochroite) (Appendix 1, Figure 3).

Figure 3 - DRX from 3^{th} rainfall at US, DS 0-10, RF and VY. Passo Fundo, 2019



January 5, 2015.US

January 5, 2015.DS.0.0-0.10



January 5, 2015.RF

January 5, 2015.VY

Source: author data.

Comparing the VY to RF site, several minerals were observed but in a similar assemblage, regardless the rainfall events. The VY suspended sediment was composed of mica, kaolinite, quartz, calcite, rutile, magnesite, albite, and illite. However, RF did not present mica and Cu-bearing minerals but hematite instead.

A poorest mineral assemblage composed of kaolinite, quartz and, anorthite was observed in the suspended sediment from US site, which represents low anthropogenic pressure. Two rainfall events presented only one mineral (quartz).

In the DS site, that represented high anthropogenic pressure, different mineral assemblage was observed according to the water flow levels and rainfall events (Table 6). In DS site, sediment sampled at the water level between 0 and 0.10 m, mica was not presented in the mineral assemblage while hematite was present. At the water level between 0.30 and 0.40 m, mica was absent in the suspended sediments after the 5th precipitation. Concerning the Cu-bearing minerals, wooldridgeite (0.645 and 0.403 nm) and cyanochroite (0.37, 0.42 and 0.40 nm) were identified in all DS and VY sediment samples (Table 6). The Cu-bearing minerals occurrence in sediment is compatible with their presence in vineyard soils (BORTOLUZZI et al., 2019).

4.4.3 Chemical characteristics of sediments

The sediment concentration (SC) varied from 0.016 to 0.915 mg L^{-1} in the vineyard and riparian forest sites (Tables 7 and 8). The VY site produced the highest SC, while the RF produced the lowest one. Rainfall showed a positive correlation with SC, with $r = 0.65$ ($p<0.05$). However, the higher rainfall volume did not produce higher water flow discharge. Considering the 5 days preceding each rainfall where sediments were collected, the first rainfall present a precedent of 22 mm, and the fifth rainfall present a 60.4 mm rainfall precedent. The second, third and fourth rainfall there was no one rainfall precedent. This precedent rainfall has great influence in the soil runoff. A rainfall with small intensity when it occurs in a humid soil (precedent rainfall), the capacity of soil runoff is increase.

The RF sediments presented low values of pH, available P and exchangeable Ca and Mg, compared to the VY area (Table 6). Especially in the VY, values of Cu_T, Cu_E and Cu_S varied from 1.69 to 9.16, 0.99 to 2.81 and 0.20 to 1.20 mg L^{-1}, respectively. In the RF the Cu_E contents varied from 0.00 to 0.50 mg L^{-1} and Cu_S was not observed. As expected the total Cu was low in the RF area. The rainfall showed a negative correlation with Cu_T. The pH values of sediments showed a positive correlation with Cu_T, Cu_E, and Cu_S, with $r = 0.62$, $r = 0.66$ and, $r = 0.62$, respectively.

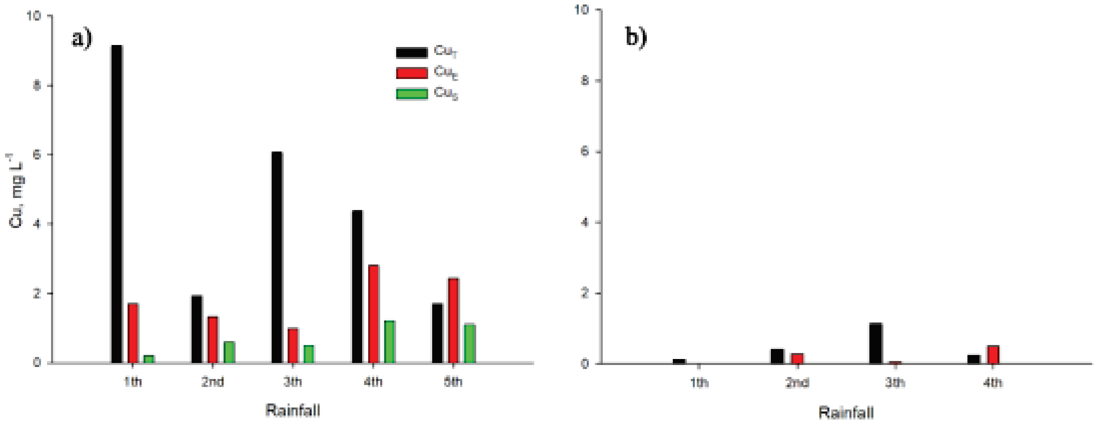
Table 6 - General physical and chemical parameters and copper forms of soil sediments from two soil uses in a Brazilian microbasin. Passo Fundo, 2019

Rainfall events	Sediment parameters							
	SC †	pH	EC ‡	P	K	Ca	Mg	Zn
	mg L^{-1}	Um	µS cm^{-1}	------------- mg L^{-1} -------				
---Vineyard site---								
1th	165.0	6.80	132.50	4.65	8.84	36.51	6.47	1.21
2nd	392.0	6.56	190.10	5.89	10.94	44.60	6.38	0.58
3th	39.0	6.63	94.40	2.68	16.06	29.12	4.48	0.47
4th	206.0	6.71	122.20	3.31	31.07	30.96	5.07	0.35
5th	915.0	6.77	54.20	6.89	25.60	21.51	4.45	2.60
---Riparian Forest site---								
1th	78.0	6.61	23.94	0.47	4.07	14.81	2.25	0.00
2nd	137.0	6.35	61.20	1.37	9.08	22.48	3.10	0.38
3th	Nd	6.32	73.40	0.54	7.45	16.30	4.00	0.43
4th	97.0	6.03	98.70	2.35	12.22	21.72	2.94	0.00
5th	16.0	-	-	-	-	-	-	-

Source: author data.

†SC = sediment concentration, ‡ EC electrical conductivity; – data lost; nd = not determined.

Figure 4 - Copper forms suspended sediments from Vineyard and Riparian Forest in a Brazilian small watershed. Passo Fundo, 2019



Source: author data.

a = vineyard, b = riparian forest, Cu$_T$ = total copper, Cu$_S$ = soluble copper, Cu$_E$ = exchangeable copper.

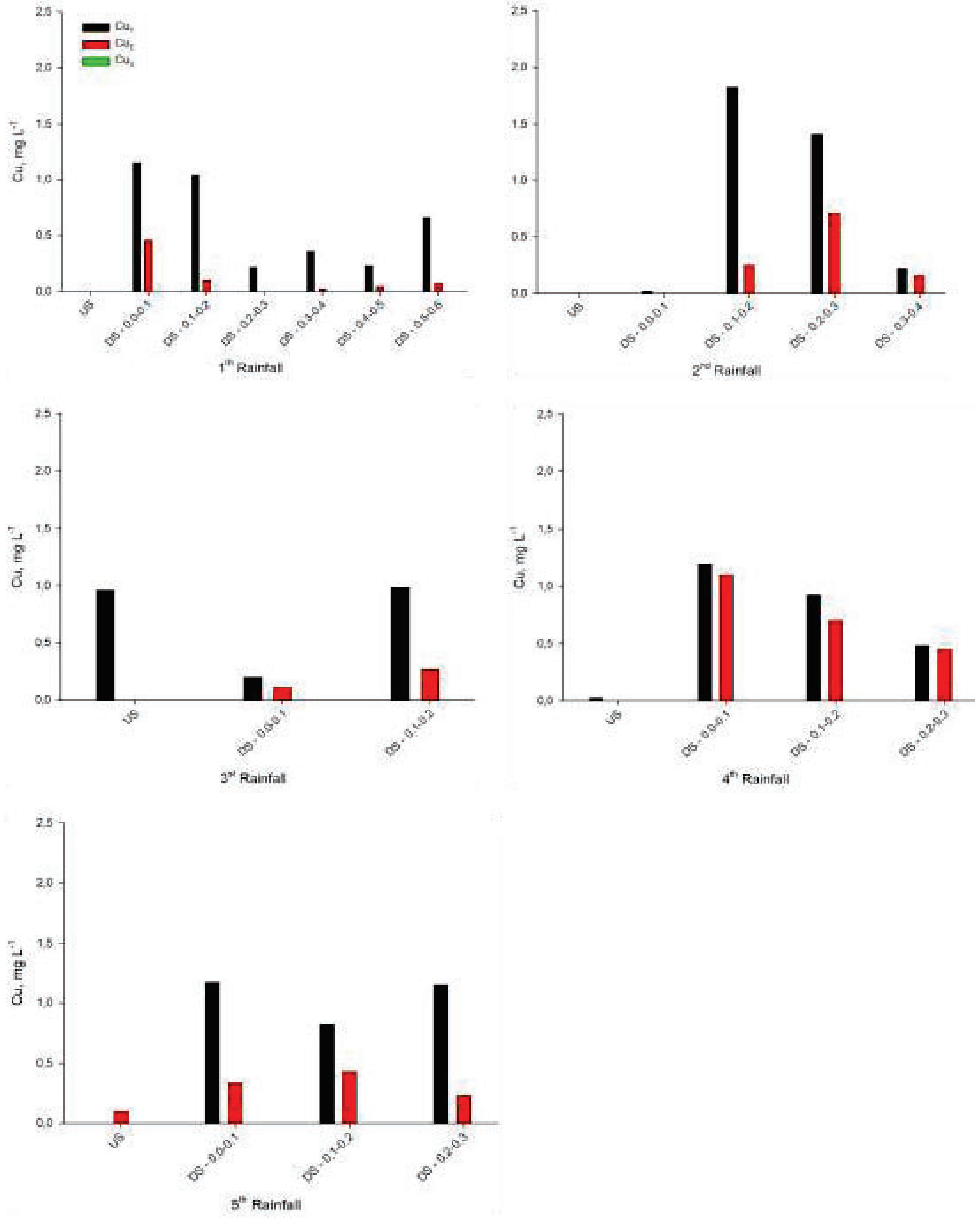
In the US site, all Cu forms presented low contents, except one rain event (3th rain event Cu_T = 0.96 mg L^{-1}). In the DS site, that represent all soil area of watershed, the Cu_T varied from 0.02 to 1.82 mg L^{-1}, while Cu_E varied 0.00 to 1.10 mg L^{-1}. Cu_S was not observed in the rainfalls monitored. The first, third and fourth rainfall events presented high Cu_T contents due to Bordeaux mix application season coincidence. Low rainfall presented high Cu_E values. However, the high precipitation volumes resulted in low Cu_T and Zn contents as a response to the dilution process of sediment concentration in the stream.

In the DS site, the suspended sediments presented high contents of all elements analysed, while the US site low ones (Table 8). Besides, the magnitude of chemical contents in the DS varied according to the chemical element type, rainfall event and water level collected in the DS sampler (height points).

The easily available Cu (first extraction) was of 234 and 13 mg L^{-1}, for VY and RF sites, respectively (Figure 6). The Cu recovered after seven extractions represented only 5.5% and 10.4% of total Cu concentration in the VY and RF sites, respectively. Soil attributes from Vineyard and Riparian Forest in a small watershed.

The first and second components for the soil uses (VY *vs* RF) explained data variation of 59.8% and 17.9, respectively (Figure 6A and 6B). Together the components explained ~78% of the total data variation. In addition, the parameters analysed were completely opposite between the soil uses (RF and VY) on the first component. For the Cu_T, Ca, Mg that their concentrations were closed in the three first rain events. While Cu_E and Cu_S were closed to the Zn and K in the 4th rain event.

Figure 5 - Copper forms of suspended sediments in vertical ascending level sampler from catchment stream in a Brazilian microbasin. Passo Fundo, 2019



Source: Author data.

Cu_T is total copper, Cu_S is soluble copper, Cu_E is exchangeable copper; US is Upstream and DS is Downstream.

Table 7 - General physic-chemical parameters of suspended sediments in vertical

ascending level sampler from catchment stream in a Brazilian small watershed. Passo Fundo, 2019

Rainfall events	Water level	Chemical parameters							
		SC†	pH	EC‡	P	K	Ca	Mg	Zn
	m	mg L^{-1}	un	µS cm^{-1}	-------------- mg L^{-1} -------------------				
				Upstream					
1th	0.0-0.1	80	6.32	41.90	0.43	2.09	16.17	2.28	0.11
2nd	0.0-0.1	10	-	-	0.37	2.62	17.03	2.65	0.00
3th	0.0-0.1	10	5.97	46.80	0.20	2.56	17.60	2.82	0.01
4th	0.0-0.1	200	6.17	84.80	0.40	3.03	18.02	3.14	0.00
5th	0.0-0.1	27	6.48	48.20	0.57	2.21	17.67	2.81	0.00
Mean		109	6.24	55.43	0.39	2.50	17.30	2.74	0.02
				Downstream					
1th	0.0-0.1	270	6.62	67.00	0.60	3.61	18.95	2.89	0.11
	0.1-0.2	350	6.53	70.05	0.54	4.54	21.08	3.32	0.21
	0.2-0.3	320	6.18	59.30	0.37	4.42	18.54	2.80	0. 81
	0.3-0.4	200	6.52	56.80	0.54	4.77	19.12	2.84	1.13
	0.4-0.5	280	6.33	42.10	0.50	4.19	19.14	2.75	1.10
	0.5-0.6	30	6.94	64.50	0.55	2.91	18.90	3.11	0.08
Mean		240	6.52	59.96	0.52	4.07	19.29	2.95	0.53
2nd	0.0-0.1	40	5.95	81.1	0.40	5.35	18.17	2.60	0.00
	0.1-0.2	210	6.21	71.3	0.80	5.59	20.50	3.18	0.24
	0.2-0.3	820	6.06	63.70	0.47	6.52	22.76	3.10	0.08
	0.3-0.4	500	6.21	57.00	0.37	5.59	15.72	2.27	0.09
Mean		390	6.11	68.28	0.51	5.76	19.29	2.79	0.10
3th	0.0-0.1	30	6.35	55.30	0.50	4.31	14.95	2.34	0.50
	0.1-0.2	40	6.31	59.90	0.60	7.58	14.48	2.53	0.61
Mean		35	6.33	57.60	0.55	5.95	14.72	2.44	0.56
4th	0.0-0.1	190	6.33	70.80	0.27	4.89	17.07	2.47	0.00
	0.1-0.2	220	6.23	78.80	0.23	5.00	15.04	2.23	0.00
	0.2-0.3	410	6.11	82.40	0.13	4.77	17.97	2.53	0.00
Mean		270	6.22	77.33	0.21	4.89	16.69	2.41	0.00
5th	0.0-0.1	362	6.37	81.40	1.30	8.97	25.81	4.11	0.00
	0.1-0.2	422	6.35	76.20	0.47	8.84	21.28	3.15	0.00
	0.2-0.3	468	6.40	60.30	0.17	6.98	16.90	2.53	0.00
Mean		417	6.37	72.63	0.65	8.26	21.33	3.26	0.00

Source: Author data.

†SC = sediment concentration, ‡ EC electrical conductivity, – data lost; nd = not determined.

Table 8 - Mineralogy of sediments fron soil uses areas and suspended sediment in the Brazilian watershed stream, Passo Fundo, 2019

Rainfall events	Soil uses †	
	RF	VY
1th	Kao^1/Qtz^3/Cal^1/Rut^2/Mag^2/Hem^3/Ill^1/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^2/Alb^3/Ill^1/Woo^2/Cya^3
2nd	Kao^1/Qtz^3/Cal^1/Rut^2/Mag^2/Hem^3/Ill^1/Cya^2	Mic^2/Kao^1/Qtz^3/Cal^1/Rut^2/Mag^2/Ill^1/Woo^2/Cya^3
3th	Kao^1/Qtz^3/Ano^1/Cal^1/Rut^2/Mag^1/Ill^1/Cya^3	Mic^2/Kao^1/Qtz^3/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/ Woo^2/Cya^3
4th	Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Hem^3/Ill^1/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^1/Cal^1/Rut^2/Mag^1/Alb^1/Ill^1/ Woo^2/Cya^3
5th	Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^1/Alb^3/Ill^1/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/ Woo^2/Cya^3

	Suspended sediment in the stream ‡					
	Upstream – US	Downstream – DS				
		0-0.10 m	0.10-0.20 m	0.20-0.30 m	0.30-0.40 m	0.40-0.50 m
1th	Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/ Woo^2/Cya^3	Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^2/Alb^3/Ill^1 Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^2/Alb^3/Ill^1/ Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Ill^1/ Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^2/Alb^3/Ill^1/ Woo^2/Cya^3
2nd	Kao^1/Qtz^2/Ano^1	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Hem^3/Ill^1/ Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Ill^1/ Woo^2/Cya^3	Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^2/Ill^1/Woo^2/Cya^3	-
3th	Qtz^1	Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^3/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^3/Cal^1/Rut^2/Mag^1/Alb^3/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^2/Alb^3/Ill^1/ Woo^2/Cya^3	-	-
4th	Kao^1/Qtz^1/Ano^3/Alb^2/ Woo^2	Mic^2/Kao^1/Qtz^3/Ano^1/Cal^1/Rut^2/Mag^1/Alb^1/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^1/Cal^1/Rut^2/Mag^1/Alb^1/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^1/Cal^1/Rut^2/Mag^1/Alb^1/Ill^1/ Woo^2/Cya^3	-	-
5th	Ano^1	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/Woo^2/Cya^3	Mic^2/Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/Woo^2/Cya^3	Kao^1/Qtz^3/Ano^2/Cal^1/Rut^2/Mag^1/Alb^2/Ill^1/Woo^2/Cya^3	-	-

Source: Author data.

†US: upstream, RF: riparian forest, ‡VY: vineyard, DS: downstream, Mic = mica, Kao = kaolinite, Qtz = quartz, Ano = anorthite, Cal = calcite, Rut = Rutile, Mag = Magnesite, Alb = Albite, Ill = Illite, Hem = Hematite, Woo = wooldridgeite, Cya = Cyanochroite, The numbers $^{1\ 2\ 3}$ over the minerals represent the number of peaks identified relative to the mineral.

For both the main components for the stream parameters (US *vs* DS) explained data variation of 67.7% and 16.7% (Figure 6A and 6B), Together they explained ~84% for the suspended sediment in the stream, For the suspended sediment, the variation on the second main component represented the differences from the chemical composition of sediments. The Cu_T and Cu_E were closed to the 2nd, 3th and 4th rain events, probably due to the association to the last rainfall and Cu-application season in vineyards. In addition, Cu_T in the sediment was associated sediment concentration. In general, the sediment characteristics were associated with vineyard areas and Cu-application season.

4.5 Discussion

4.5.1 Relationship between sediment mineralogy and copper fractions

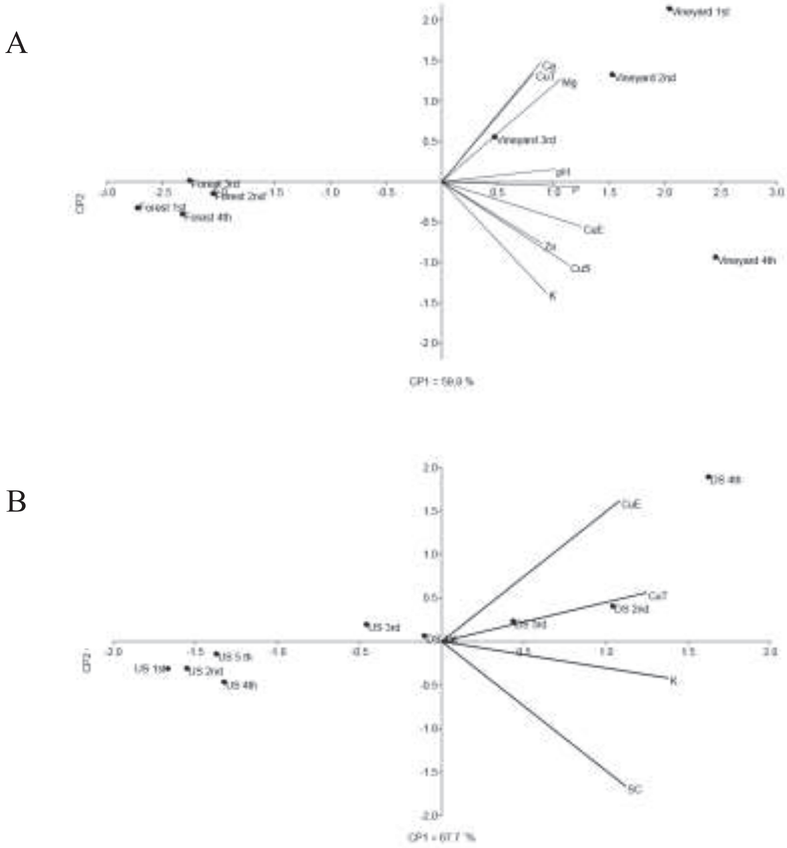
The main differences in the mineral assemblage were due to soil uses (VY vs RF) and soil use contribution in the watershed (US vs DS), Low anthropogenic pressure sites (RF and US) presented a very simple mineral assemblage and low Cu contents because i) the sediment are basically composed of low reactive minerals (Table 8) such as kaolinite, Quartz, anorthite, calcite, rutile, magnesite and albite, and, ii) no Cu applications were made and these areas had low contribution to sediment production in the watershed (Tables 7 and Figure 4).

The VY site yield sediments presenting a rich mineral assemblage which have a high potential of metal adsorption. In this sense, the high level of copper in VY sediment samples was due to factors such as: high Cu accumulation in the soil (Table 5); high affinity Cu-particle and Cu precipitation at high soil pH (BORTOLUZZI et al., 2019) and; the mountainous relief with poor soil cover favoring the sediment transfer from vineyards soil to aquatic bodies (VANACKER et al., 2019) and the occurrence of Cu-bearing minerals in sediments, In addition, high soil pH conditions favored Cu adsorption in soils onto organic matter and mineral fraction (BRUNETTO et al., 2014; FERNÁNDEZ-CALVIÑO et al., 2008 abc; 2015; DALACORTE; ESCOSTEGUY; BORTOLUZZI, 2019). In this study, the mineral sediment assemblage presents great affinity with metals (FERNÁNDEZ-CALVIÑO et al., 2015; DALACORTE;

ESCOSTEGUY; BORTOLUZZI, 2019). The phyllosilicate minerals, oxides and hydroxides, carbonates and phosphates are the most important minerals involved in the metal sorption process (SPARKS, 2005). Besides, clayey soils and sediments have the greatest capacity to adsorb Cu (GIROTTO et al., 2014).

The swelling clay minerals play an important role on the Cu fixation and availability as well (DALACORTE; ESCOSTEGUY; BORTOLUZZI, 2019), However, in the studied sediments, no swelling clay minerals were found, suggesting that the total Cu is associated to particles.

Figure 6 – Principal component analysis from data soil use and principal component analysis from data water stream. Passo Fundo, 2019



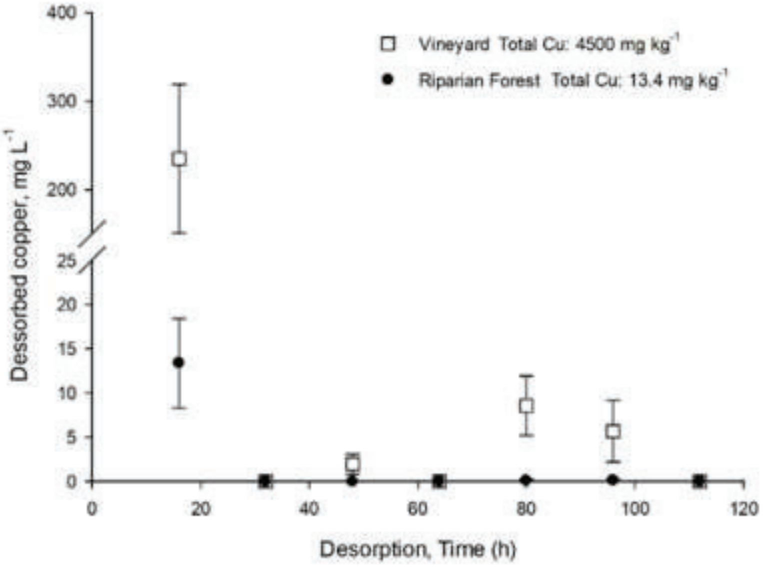
Source: Author data.

A = Principal component analysis from data soil use, B = Principal component analysis from data water stream

Bortoluzzi et al. (2019) suggest the occurrence of Cu-bearing mineral, identified by the X-ray peaks at d=0.64, 0.37, 0.42 and 0.40 nm (Table 8). As these peaks were found at lower intensity in the low anthropogenic sites (RF and US), it is plausible that Cu-rich particles have their origin from the vineyard areas. Furthermore, high amounts of total Cu in the sediment may be associated under high energy with mineral fraction (FERNÁNDEZ-CALVIÑO et al., 2015) such as kaolinite, that can adsorb low amounts of Cu due to the aluminol reactive sites (DALACORTE; ESCOSTEGUY; BORTOLUZZI, 2019). However, as the soil and water pH were higher, the Cu tends to be in a particulate form. In fact, the pH is one determinate factor controling the ion mobility in soil (FERNÁNDEZ-CALVIÑO et al., 2008 abc; BORTOLUZZI et al., 2019).

The interaction of all soil uses in the watershed and rainfall events resulted in a rich Cu-sediment. In this sense, the high Cu-suspended sediment collected in the DS watershed, increased with the flow discharge rates (exception first rainfall) and their mineral assemblage. The variation in SSC may be in part by the particle size of the sediments, and not necessary associated with the rainfall intensities (HOROWITZ, 1991).

Figure 7 - Dessorbed copper from vineyard and riparian forest. Passo Fundo, 2019



Source: Author data.

Rainfalls with small intensities can transfer great amounts of sediments with small particle size. Comparatively to the US point, DS presented a richer mineralogy assemblage because the vineyards contributed greatly to sediment production, besides these areas presented low soil cover and the erosion process may be intense in these conditions (VANACKER et al., 2019; XU et al., 2014). Even low rainfall intensities are capable to transfer sediment particles from contaminated sites to water bodies. This low rainfall intensities can movement small sediment particles (clay and clay minerals), and such particles can present a higher metal sorption capacity (HOROWITZ, 1991), presenting higher environmental potential. Furthermore, the mineral assemblage of DS sediment remained similar at different stream levels suggesting that even low rainfall intensities the Cu-rich sediment production was great. The total Cu contents varied according to the mineral sediment composition, resulting in low exchangeable and soluble Cu contents from the sediments. It may indicate that the stream acted as a sediment mixer get a homogeneity process along the stream.

4.5.2 Vineyard contribution to the Cu-rich sediment production in a watershed

Vineyards areas in the watershed (35% of total surface area), mainly the old ones (15,7%), are characterized as high pressure on the environment, producing high Cu-rich sediments and high risk of Cu-transfer (FERNÁNDEZ-CALVIÑO et al., 2008bc; BRUNETTO et al., 2016ab; YU et al., 2019). As the Bordeaux mix is applied on canopy of vines, their residues fell down on the soil surface enriching soil profile in Cu. Thus, weak precipitations can easily carry out Cu-rich sediments from the vineyard soil to the water bodies. However, in the VY and DS high Cu concentration were found mainly the total Cu that was higher than Cu_E and Cu_S. The high total Cu in sediments was associated to the Cu application while available forms of Cu (Cu_E and Cu_S) were associated to the rainfall after Cu application in the vineyards. It is probably due to the release of Cu from vine falling leaves in the end of crop season (FERNÁNDEZ-CALVIÑO et al., 2013).

In fact, a centenarian vineyard which produced high concentration of Cu-rich suspended sediments after rainfall events compared to the forest site (RF) has given us a piece of new information about how Cu is transferred from the soil to the water bodies. Then, it is plausible that there is in fact a transfer of Cu-nanoparticle from soil to aquatic system, which is according to Cu-bearing mineral observation in vineyards soils (BORTOLUZZI et al., 2019) and high total Cu found in the sediments. Besides, slop and soil cover are the major factor for promoting soil erosion (VANACKER et al., 2019; XU et al., 2014) in particular deep mineralogical changes have been observed under vineyards soil (BORTOLUZZI et al., 2012; 2019). The constant presence of wooldridgeite and cyanochroite in DS, and it low frequency in US, corroborate the hypothesis that such copper minerals are eroded from VY. On the other hand, both control sites i.e. RF and US presented low anthropogenic pressure resulting in none or low pollutant contents.

Centenarian vineyards became rare in the region because new crops are constantly replacing them over these areas year after year. However, these areas are harmed because of a system that has not changed along the years regarding the Bordeaux mix uses. Thus, old vineyard areas represented here a high Cu-rich sediment production capacity as well as high risk of Cu-transfer to the water bodies, hence, environmental quality damage. In this scenario, the productive young vineyards maintain the same or similar Cu inputs along the years increasing the potential to transfer Cu-rich sediments as particulate chemical form to water bodies. Recent assays related the spatial variation in soil Cu concentration in the vineyards, which increased the potential damage (FERNÁNDEZ-CALVIÑO et al., 2013). As strategy to maintain low risk of Cu accumulation in soil may be establish low Cu doses in young vineyards, limiting the crop duration along the time In addition, use cover crops that consists in an efficient agricultural practice to increase soil health (YU et al., 2019), reducing soil erosion and sediment production when middle plant rows are produced (TIECHER et al., 2016a; BRUNETTO et al., 2016ab; MARQUES et al., 2010). On the other hand, soil uses such as orchard (23%) represented low anthropogenic pressure compared to vineyard areas, receiving small or no amounts of Cu compared to the vineyards.

Despite all, under a fragile landscape condition, such as the watershed studied, presenting high erosion process, the soil use and the agricultural practices strongly determine the soil and water quality (YU et al., 2019). In this sense, in the watershed studied the suspended sediment quality was associated to the rainfall events characteristics and the Cu application in the vineyards. As an efficient practice to reduce the Cu-transfer may be to cease or diminish soil erosion process (YU et al., 2019; DUPLAY et al., 2014; VANACKER et al., 2019; XU et al., 2014). The Cu contents associated with the particles of suspended sediments shall be maintained in the soil since erosion process on watershed area will be avoided. Another way to reduce Cu transfer is revisit the fungal control in the vineyard areas and planning the longevity of vines in a watershed. The time in vine cultivation affects total Cu and Cu fractions as demonstrated by several authors in the literature. For instance, the Cu bounded to the crystalline Al and Fe colloids accounted for 21 and 12% of total Cu in old (>30 years) and young (<10 years) vineyards (FERNÁNDEZ-CALVIÑO et al., 2008b).

Finally, Cu-rich sediment loss from vineyard areas reached the water system from the watershed mainly in particulate forms associated to the minerals in the sediment (BORTOLUZZI et al., 2013). The absence of soluble Cu (Cu_S) in the water stream corroborated the interpretation in which the mineral assemblage strongly adsorbed Cu, reducing its availability along its transport in the stream. In addition, the successive extraction was able to extract only 10% of total Cu in the sediment of VY, corroborating the high chemical stability of Cu in the sediment. The sediments originated from vineyard watersheds are bypassing in the watershed stream. However, if they arrive in a redox system, under a benthic environment condition for example, the Cu-rich mineral may release easily Cu to the environment becoming a dangerous issue (BRADL, 2004). This study also highlighted that soluble Cu contents may not be an efficient indicator of the potential pollution (WOJTKOWSKA; BOGACKI; WITESKA, 2016) regardless the prevention value stablished by governmental agencies. Then, a detailed mineralogical behavior must be known in order to establish the role of the major mechanism of metal transfer.

4.6 Conclusion

Vineyards have great potential to produce Cu-rich sediments, and the metal application over time contributing to reduce soil and water quality. We evidenced here in a geographic context presenting old vineyards areas, including a centenarian vineyard, that the Cu-rich sediment is easily produced and transfer to the watershed stream by erosion process. In fact, the traditional vine crop system, i.e. low soil cover, cropping in sloped areas and high Cu-based fungicide application contribute to the scenario.

Concerning the sediment quality, the mineralogy of sediment changes according the soil uses and the stream positions in the watershed. The mineral composition of suspended sediment is based on mica, kaolinite, illite, rutile, hematite, quartz, calcite, magnesite, albite, and anorthite as well as Cu-bearing mineral, also identified in soils in an early study.

Due to the mineral assemblage, the sediment originated from the centenarian vineyard area contains high copper contents in their three chemical forms (total, exchangeable and soluble Cu forms) compared to the low anthropogenic area (Riparian Forest). However, when the vineyard sediment reach the stream in downstream position they presents high total Cu contents, while soluble and exchangeable Cu forms is barely presented, Such behavior is explaint by the high copper affinity minerals found in suspended sediments. The Conama resolution index for copper dissolved in fluvial waters is 0.009 mg L^{-1} for protection of environmental water, value not found in our data analyze (Brazil, 2005).

The suspended sediments have low Cu bioavailability, perhaps, the small vineyard watersheds is a probably temporary deposit for this Cu-rich particles. In case of such particles to be deposit in Lake Guaiba, with differnet environmental conditions (mainly water pH and redox condition), this bioavailability may increase desorbing the copper in the water. In this sense, the suspended sediment is acting as a source of copper for the environment. Thus, mineral sediment composition must be taken into account in environmental quality because the Cu-rich particle was the major factor to the metal transfer from terrestrial to aquatic system. Despite of a traditional vineyard production in the watershed, this agroecosystem remains complex, which agricultural traditional practices such as Cu-fungicides application should be revisited in order to maintain soil and environmental quality.

5 CAPÍTULO III

Phosphorus in sediments and its relationship with the mineralogy: a review

5.1 Abstract

The increase of phosphorus (P) levels in agricultural soils by the addition of organic or inorganic fertilizers enriching the soil particles, creating sediments with great polluting potential. The association between P and soil particles is strongly influenced by the mineralogy of the particles, and each mineral has a specific association with P. The association of P with soil oxides and hydroxides, carbonate minerals, the presence of high reactivity clay minerals, particle size, the biological activities and environmental pH and redox potential are factors that affect the sorption behavior of sediments. Thus, this review sumarizes dozens of researches that highlits associations between soils and sediments rich in P and the mineralogy of the particles.

Key words: 1. Carbonates. 2. Oxides. 3. Clay minerals. 4. Sorption.

5.2 Introduction

Urban, rural and industrial environments are constant sources of sediments, trasnfering ions, inorganic and organic molecules associated. The contribution of agricultural to the production of sediments varies according to the type of soil, vegetation, topography, hydrological aspects, soil use and management practices (MINELLA et al., 2007; BORTOLUZZI et al., 2010; DIDONÉ; MINELLA; MERTEN, 2015). In agriculture sites, the transference of sediments rich in ions is one of the main form of contamination of water bodies. The agriculture sediment transfer to water bodies may be responsible for serius environmental damage, depending it molecule or ion is associated. Phosporus is a main fertilizer applied to soil in world agriculture, how higher the productivity of the crops, higher the doses applied. This particles P rich may be transfer to aquatic system, promoting environmental damage.

The water contamination by enriched sediments containing phosphorous results in changes in biological aquatic relationships (STERNER et al., 2004). Such imbalance in natural habitat can result in eutrophication processes, causing serious damage to the environment. The eutrophication process is complex and is associated not only to the growth of harmful algal blooms but, to all environmental biodiversity. The proportion and form of the nutrients can modify the aquatic biodiversity, so the metric used to measure is important, and the used of metrics isolated (chlorophyll, total content (N) and P) some times do not relate to the environmental biodiversity (GLIBERT, 2017).

The monitoring of the sediment yield for both small and large scales is essential to the soil and water conservation. In Brazil, it is estimated that the production of sediments is in the order of 800 million tons a year. In small scales (river basins) the increasing of soil use by agriculture causes significant increases in sediment yields (MERTEN; MINELLA, 2006, 2013; MINELLA; MERTEN, 2011). Monitoring small scales (micro basins) in Southern Brazil (DIDONÉ; MINELLA; MERTEN, 2015) verified big sediment yields in agricultural production system without appropriate soil preservation, reaching a delivery relationship of sediment to the outlet of 18%, Studies conducted in watersheds in the south of Brazil, showed that agriculture (even under direct planting) is responsible for up to 70 to 90% of all sediments contribute to rainwater (TIECHER et al., 2017b; 2018a).

The volume of rainfall and the precipitation intensity are quality and quantity key factors of the sediments that will be freighted. Heavy rainfalls favored the increase in volume of sediments in agricultural areas. The forest barriers near the outlets for soaring of river basins (permanent preservation areas), that occur between the channel and the agricultural production areas are fundamental on the reduction of arrival of sediments to the rivers (TIECHER et al., 2014; TIECHER et al., 2018b).

Even inside the same river basin, the sediments can vary in quantity and composition. The soils and sediments from the same river basin show different mineralogic compositions. This behavior shows distinct relations of sorption of ions, due to different linking forces that exist between ions and particles. Besides the intrinsic differences of sediments, soil use and the type of soil influential in the mineralogical segregation of the particles. Associated with those characteristics there is still the segregation of physical particles, which occurs during a rain with surface runoff. It is natural that particles that are more reactive (that have a smaller size) are swept in the water (BORTOLUZZI et al., 2013). During the transportation of sediments there is the segregation of the particles. Thus, the same sediment source can produce deposits with distinct minerals (PREDA; COX, 2005).

As important as the size of the particles is its reactivity in the environment. Studies of identification of minerals in sediments (mineralogy), tracking sediment sources (fingerprinting), sequential removal process of pollutants, adsorption capacity and desorption of ions in sediments, are fundamental to determine the reactivities of these particles in the environment. Using the fingerprinting technique is possible the tracking of the sediments sources in a river basin. Knowing the origin, it is possible to take some actions that reduce or mitigate the generation of sediments (LACEBY et al., 2017).

Techniques such as sequential and selective extractions of elements (MELO et al., 2002), determination of mineral crystallinity (PELLEGRINI et al., 2008), X-ray fluorescence, X-ray diffraction and Emission Spectroscopy in plasma are frequently used to determine the sediments mineralogy in sand, silt and clay fractions in sediments of different origins (KIRBY; DECKER; MACANDER, 1999). In addition, new techniques that use ultrathin membrane filtration to determine ions bioavailability (i.e. Phosphorus) in sediments and soils are being developed (ZHANG et al., 2014). Studies in sediments are complex because the particles undergo changes due to environmental changes and redox conditions (terrestrial to aquatic). Limitations such as the amount of material in sediment samples (particularly if they are suspended sediments) are common, which sometimes may restrict the application of determined techniques.

In this study, we will revise various technical providing a material to serve as a basis to the studies in sediments contaminated by P, focusing on the sediments mineralogy.

5.3 Soil and water contamination with P

One of the main elements that are found related to sediments is P. The most common sources of phosphorus which load sediments are agricultural areas, urban and industrial areas (HOROWITZ, 1991). P is one of the main nutrients that limit crop productivity, for this reason increases in fertilization with P are being undertaken all over the world. The search for greater productivities in crops means the use of larger amounts of fertilizers present in soil, enriching its particles. The significant increase in fertilization (mainly phosphate) has occurred in all farming systems, mainly in countries such as Brazil which has acid soils and highly intemperate (FINK et al., 2016).

Agriculture and urbanization are key contamination factors of soil and sediments. In urbanized environments as major centers of population, it is possible to find large pollutant concentrations (Zn, Cu, Ni, Pb, P, C and, N) associated with soil or sediments (ANDRADE et al., 2018b).

A survey on the 10 main river basins of China has proved that total levels of P and N in sediments are being changed. In several river basins there was a significant increase in levels of P entre 1990 e 2013 (YANG et al., 2017). Analizing and simultating P scenarios on agricultural soils in China, it is conclusive that the current standard of use is not sustainable for food and environmental security. This occurs due to the considerable sums of P lost because of soil erosion, leaching and laminar erosion, and the insufficient manure recycling of animals and humans (WANG et al., 2011; LI et al., 2015).

The metropolitan region of Porto Alegre (capital of the southernmost state of Brazil), is supplied by the water of the Guaíba Lake, that provides water for more than 2 million habitants (ANDRADE et al., 2018b). Assessing the sediments in Guaíba Lake, the available levels of P (Mehlich I) vary between 10 and 109 mg kg^{-1}, being the largest levels found in channels that pass through the urbanized capital area (Arroio Dilúvio and Cavalhada). In the 12 sampled environments, there was a positive association between P levels and the clay fraction of the sediments (ANDRADE et al., 2018b), demonstrating the importance of this fraction in the performance of P in lakes and dams. Andrade and Giroldo (2014) worked with sediments from Guaíba Lake and determined that the sediments are probably the main source of P in that river, mainly in moments of low hydraulic retention.

Mirim Lake is located in the South of Brazil and it is an important lake that communicates with the Atlantic Ocean. This lake recives sediments of large agricultural regions with production of rice and soybean. The P level in sediments in the lake was considered high (compared to N level) and concerning other ecosystems. This high level seems to be associated with intense use of phosphate fertilizers in contribution basin, besides frequent resuspension of bottom sediments, once that is a lake of little depth (SANTOS et al., 2004).

The movement of dam bottom sediments causes the vertical ascent with transportation of dam bottom thin sediments to the surface, which work as a nutrient source to the aquatic fauna (AMMAR et al., 2015), being able to provide the necessary nutrients to the development of the eutrophication process.

Itaipú dam in the South of Brazil (Paraná state) is one of the greatest hydropower plants of the world, which uses water from Paraná river to generate energy. Monitoring the sediments of beaches around Itaipú dam, the authors detected big differences in total levels of P. The highest concentration of total P was present at the place where there are spills of organic manure from trucks that freight these products on the ferry linking Brazil and Paraguay. According to the authors, this place is considered as highly eutrophicated, having 43 times more phosphate than the point of less concentration (BELO; QUINÁIA, PLETSCH, 2010).

Big cities all over the world are supplied by superficial water (rivers, lakes or dams). The quality maintenance of these waters is a matter of national safety, and keeping the quality of these waters is to keep the life quality for the populations. Many countries have strict laws that administer the occupation of the area near lakes and dams so that to avoid the water contamination via sediments loaded with nutrients. From all the elements, the most common are N and P, once P is easily found associated in sediments.

In 1972 the USA and Canada implemented a P-load reduction program around big lakes (INTERNATIONAL JOINT COMMISSION, 1978), aiming at improving the quality of the main source of potable water in these countries. In the region an indicator that integrates the soil enriched with P was developed, so that the capacity of P desorption on soil, and the transference of sediment to water, provided a map with the likely hazardous location. Based on these pieces of georeferenced information, local action prevention and mitigation of big lakes contamination are adopted, from an environmental to a political sphere (BOCHOVE et al., 2011).

Monitoring group studies of sediments in lakes and dams all over the world must be developed. The frequent monitoring of this flow of nutrients and contaminants is essential to guarantee national security of the territories and their population that uses the water from these lakes.

5.4 Polluting potential of sediments loaded with P

Several factors control the pollution potential of sediments loaded with P. The size of the particles, mineralogy of sediments (type of materials and their reactivity), pH and redox potential of the environment, and a biological activity of the environment are so important that affect the pollution potential of sediments enriched with P. Also, the agricultural and urban environmental are factors which directly affect the pollution potential of sediments loaded with P (ZAFAR et al., 2016).

5.4.1 Size of particles

For classification purposes of a soil-particle size, three classes are determined: sand, silt and clay. The sand fraction is the biggest (>0.05 to 2 mm) being the less reactive compared with others. The silt fraction has an intermediate size of particles (0.002 to 0.05 mm) and with an average reactivity. The clay fraction is the smallest

(<0,002 mm) and with bigger reactivity in the environments (CQFS, 2016). Even smaller than the clay there are the Fe, Al, Mn oxides and Ti oxides, that are particles very reactive with phosphorus. For sediment studies it is common to work with clay and oxides fractions and silt on the same sample (< 63 µm), since they are the most reactive fractions (BORTOLUZZI; POLETO, 2013).

The size of the particle is a characteristic that affects the polluting potential in urban environments (POLETO et al., 2009), since the thinnest particles (clay and silt) have a bigger capacity of loading of associated pollutants (HOROWITZ, 1991). A technique such as the determination of the laser granulometry allows visualization of the particle size distribution in a sample. The association of the laser ganulometry with the mineralogy may improve the konwledge about the relationship of the ion and the particle.

Studying the sediments of paved roads in Brazil and their particle sizes. Poleto et al. (2009) verified a bigger homogeneity and smaller size in suspended particles on the streets rather than the ones placed in drains. As well as sediments, their associated ions tend to be found in smaller particles, although the association of ions to coarser fractions can not be reglected.

Gérard (2016) revised more than 70 years of publications with works of P sorption, and verified that clay minerals, which are fractions of very small sizes, can have the capacity of P sorption close to Fe and Al oxides, varying according to their specific superficial area (reactivity). The size of the particles in a soil sample or sediment is the preponderant factor in water contamination studies.

The results show in a general way that P levels increase with the decrease of the aggregate size. However, the relative distribution and the speciation of the many forms of P were independent from the size of soil aggregates (JIANG et al., 2015). It is important to highlight that even though the sand fraction be excluded from the samples, it can have a significant amount of oxides recovering its particles. Removing sand and the oxides linked to this fraction, we are removing an important and reactive part of the sample (CHEN; HULSTON; BECKETT, 2000; EWAIS; GRANT; ABDEL FATTAH, 2000).

5.4.2 Mineralogy of sediments

In the most reactive fractions of soil (silt, clay and oxides) there are hundreds of minerals that act in a distinct manner, which can be associated to P having bigger or smaller force, desorb (source) or adsorb (sink) P from natural environment. This behavior of source or sink can be estimated knowing the minerals that compose the samples as well as the environment in which it is inserted. The sediment mineralogy is one of the main factors that determine the force in which P is associated to sediments. Techniches are applied to sediments to identify it mineral composition (X-ray diffraction and x-ray fluorescence) (LEMES; FILHO; PIRES, 2003). The identification of minerals is fundamental to understand the behavior of sink or source of the sediment,

The sediments can act as a source (desorption) or sink (adsorption) of P in the water (JIANG et al., 2006). All the phosphorus adsorbed in sediments can thermodynamically be desorbed (BARROW, 1983). The adsorption or desorption of P on soils is strongly influenced by mineralogy, being dependent upon quantity and quality of Fe, Al, Mn oxides and soil organic matter (FINK et al., 2016). Methodologies that quantify the full capacity of ion adsorption (Freudlich and Langmuir) are commonly used in sediment studies, Accordingly, methods that quantify the sediment capacity in ion desorbing are used (MCKEAN; WARREN, 1996).

The minerals not silicated as the Fe, Al, Mn and Ti oxides and hydroxides has huge capacity of P adsorption (BORTOLUZZI et al., 2015). On the other hand, the silicated minerals, clay minerals such as a kaolinite, ilite and montmorilonite, show a smaller P sorption capacity. However, Gérard (2016) revised P sorption works over more than 70 years of history and found reasons that prove that the clay minerals sorption capacity can be close or even bigger than the Fe and Al oxides, depending on the specific superficial area of these minerals constituents of soil.

The adsorption of P in weathered soils varies according to the mineral composition of the clay, mainly the different forms or quantities of Fe and oxides and hydroxides, Soils with the same degree of weathering, but located in different altitudes in the landscape (thermal and rainfall variations) have different mineralogical compositions, having Fe and Al oxides and hydroxides with different crystallinity degrees, which causes different P adsorption and desorption capacities. Studies carried out in soils in the South Brazil, determined that hematite and goethite (Fe oxides) with a high degree of crystallinity are found in regions of lower altitude, Gibbsite and ferrihydrite with less crystallinity are found in regions de higher altitude (BORTOLUZZI et al., 2015).

The crystallinity of a Fe and Al oxide interferes with its capacity of P association (BORGGAARD, 1983). The lower crystallinity Fe and Al oxides (amorphous) present higher adsorption of P in relation to oxides of higher crystallinity. However, Borba et al. (2017) found in his work a tendency where the crystalline Fe oxides (goethite and hematite) had greater association with the P sediments.

The oxides and hydroxides are particles that can be found in sediments or soil covering larger particles. Many studies remove the coarser fraction (sand). However, in this fraction there are significant amounts of Fe, Al and Mn oxides which cover such particles, and these have high affinity with P (CHEN; HULSTON; BECKETT, 2000; EWAIS; GRANT; ABDEL FATTAH, 2000).

Mine waste that contains Fe is being studied for euthropication reduction, lake euthropication (bioavailability reduction of P), Fe^{+3} reduction in the solution caused phosphorus sequestration, and its reoxidation formed hydroxides and iron oxides containing phosphorus or precipitates (CLAYTON; LIEGEOIS; BROWN, 2004). Under anaerobic conditions Fe is reduced and its phosphorus retention capacity is diminished. The reverse oxidation process may increase the P release capacity of sediments (NÓBREGA et al., 2014).

Other important mineral group is the apatite. This group is compound by minerals that contains phosphorus, and they are very common in sedimentary, metamorphic and igneous rocks (FOLLMI et al., 2009). The apatite solubility and dissolution rates increase with the increasing acidity, but at neutral pH the apatite is relatively insoluble (HEINDEL; LYONS; WELCH, 2018; WELCH; TAUNTON; BANFIELD, 2002; DOROZHKIN, 2012).

The apatite dissolutions vary according to its mineral composition (fluorapatite is less soluble than others), specific superficial area and the supply and the chemistry of the weathering conditions solution (FOLLMI et al., 2009; WEI et al., 2013; HEINDEL; LYONS; WELCH, 2018). The action of organic acids on the mineral increases its rate of dissolution (WELCH; TAUNTON; BANFIELD, 2002), then the biological activity may increase the bioavailability of P bound to apatite.

Carbonate is one importante mineral group. The most commun minerals found in sediments are dolomite and calcite. Both minerals have a intimus association with P. Analyzing P forms in sediments using chemical fractioning, the author found significant amounts of P associated with carbonates, noting that such minerals (calcite and dolomite mainly) provided support for the interpretation that authigenic $CaCO_3$ removed P from the water column (WHITEHOUSE, 2007).

Dolomite is recognized as a low cost phosphate adsorbent. The removal of phosphate from the solution by dolomite was rapid (removal rate above 95% in one hour) when the initial phosphate concentration was in the range of 10 to 50 mg L^{-1}. The Langmuir isotherm was more sensitive than Freudlich to describe the adsorption characteristic of phosphate by dolomite, reaching its maximum adsorption of 4.76 mg phosphate for each gram of dolomite (YUAN et al., 2015b).

The retention of phosphate by calcite and dolomite between pH 6 and 7 is mainly attributed to the formation of amorphous calcium phosphates ($Ca_3(PO_4)_2$), dibasic calcium phosphate ($CaHPO_4{\cdot}2H_2O$), and hydroxyapatite ($Ca_5(PO_4)3OH$), Under pH $\geq$ 8, phosphorus immobilization occurs by the formation of complexes on calcite surface followed by calcium phosphate formation (including amorphous calcium phosphate, dibasic calcium phosphate and hydroxyapatite) with increases in P levels (> 2 mg L^{-1}). As a result, at pH ≥ 8 the dolomite shows a higher phosphorus immobilization capacity compared to calcite. Thus, the dolomite serves as a better phosphorus drain than the calcite in the environment (XU et al., 2014). On the other hand, Hanna, Sherief and Abo Elenin (2008) found higher P adsorption in calcite in their study which used a pH range between 7.5 and 12, and found the maximum adsorption at pH 12.

5.4.3 Organic material

The organic matter present in sediments or dissolved in water strongly influences the P availability to the environment. The organisms present in water can absorb the ions, reducing their bioavailability, however as a food source, their multiplication occurs at a higher rate, about 20% of P was accumulated by the organisms present in water (BARTOSZEK; KOSZELNIK, 2016). Inorganic (orthophosphate and pyrophosphate) and organic forms (phosphate monoesters, phosphate diesters and phosphonates) are forms present in many samples (JIANG et al., 2015).

Studying sediments from 7 lakes in China, Zhang et al. (2009) extracted phosphorus with NaOH-EDTA and the solution was analyzed. The authors found the phosphorus predominantly in inorganic forms. The P forms were: orthophosphate (76.7 to 97.4%), monoester orthophosphate (1.8 to 14.3%) and phosphate diester (0.4 to 8.9%), pyrophosphate (0.1 to 0.7%) and phosphonate (0.1 to 0.2%) of total phosphorus extracted from the extract. The authors suggest that the two forms of P in the sediments should be related to the degree of eutrophication of the lake.

Aiming at determining the organic forms of phosphorus, the authors used gel permeation chromatography. The organic phosphorus extracted with NaOH made 18% of the total phosphorus and 79% of the organic fraction. Several organic fractions were observed, from humic and condensed acids to more compact molecules, like fulvic acids that contain the majority of the fossil (GILBIN; GOMEZ; PICOT, 2000).

Organic phosphorus forms in sediments were investigated by the chemical fractionation (Labile - $NaHCO_3$, moderately labile - HCl / fulvic acid, and non-labile - humic acid) used by Ivanoff, Reddy and Robinson (1998) and ^{31}P NMR spectroscopy. The chemical fractionation presented the following ranking: humic acid-P> HCl-P> fulvic acid- P ≈ $NaHCO_3$-P > residual-P. The labile and moderately labile forms, which can be degraded by phytoplankton, comprise 58.7 to 68.5% of the total organic phosphorus. The analysis of ^{31}P NMR spectroscopy suggested the following order of the P species present in the extract: orthophosphate> monoester-P> DNA-P> pyrophosphate-P. Phytate, polyphosphate and phosphonate were not found. The authors demonstrated that the organic forms of P in the sediments probably contributed to the P content in the water column, and consequently, later, to the eutrophication of the lake (DONG et al., 2012).

Several fractions of the organic phosphorus in the sediments were studied via sequential chemical fractionation: P-microbial biomass, P-fulvic residual phosphorus, and the use of ^{31}P NMR, which included monoester orthophosphate, diester and pyrophosphate. The organic P contributed over 50% of the total phosphorus, and the average concentration of the organic phosphorus species decreases from P-fulvic acid-P> humic acid-P and P-microbial biomass. Additionally, the relative proportion of the phosphorus compounds in the sediments decreases in order of the monoester > pyrophosphate orthophosphate (HEZHONG et al., 2017).

5.4.4 The pH and the redox potential of the environment

The pH of a solution is an important factor in the adsorption and desorption process related to phosphate. The efficiency of removal of phosphates from the solution by minerals such as calcite and dolomite increases with increasing of pH, and reached maximum values at pH 12 (HANNA; SHERIEF; ABO ELENIN, 2008).

When rates of phosphorus removal by dolomite were studied, it was found that rates increase to pH 9.5. When the pH is close to this value, HPO_4^{2-} is the dominant form in the solution. Calcium phosphate formation is the predominant mechanism in phosphorus immobilization at high pH (YAN et al., 2007), dolomite dissolves itself and a part of Ca^{2+} reacts with HPO_4^{2-} and PO_4^{3-} forming calcium phosphate. Inhibition of phosphate adsorption can also be explained by the competition of hydroxyl anions (OH^-) with phosphate by the dolomite surface area (YUAN et al., 2015b). Considering that the calcium phosphate precipitation at low pH (acids) is small (YAN et al., 2007), there is a considerable contribution of dolomite as a phosphate adsorbent in solution at pH 3.5 (YUAN et al., 2015b).

The P release characteristics of Taihu Lake sediments were influenced by pH changes. Acidity (pH 2) and alkalinity (pH 9.5 and 11.8) were more beneficial for the release of phosphorus, compared to pH 7.2 (neutral). The amount of phosphorus released from the sediments under alkaline conditions was 4 times higher than in the acidic condition and in the neutral condition when the release of phosphorus tended to be stabilized. The acidic condition favors the release of P associated with Ca. On the other hand, the alkaline condition promotes the release of P associated with Fe (HEZHONG et al., 2009).

The effect of aerobic sediment resuspension on phosphorus release was studied by the authors. In the tests, the concentration of suspended solids and the total phosphorus level increased substantially by the resuspension treatment of the samples. However, the reactive soluble phosphorus was strongly affected only at night, when high pH levels caused a release of phosphorus. During the day at the same period, no reactive soluble phosphorus was detected due to high assimilation by phytoplankton. In this lake a considerable part of the total P is found in the fraction associated with Al-P and Fe-P, which are pH dependent, in other words, if there is resuspension or algae activity they can release significant soluble phosphorus amounts in water (NIEMISTÖ; HOLMROOS; HORPPILA, 2011).

The study showed the main effects during P release in the sediments, redox effect and pH. In both lakes studied, the rates of P release were higher under reduced conditions and with high pH level. The formation of a micro-layer on the oxidized surface under oxidized conditions acts as a protective film, preventing the release of P in the sediments of a lake. On the other hand, the other lake showed a continuous and growing tendency to release phosphorus under various physicochemical conditions, acting as a constant internal source of P (CHRISTOPHORIDIS; FYTIANOS, 2006).

5.5 Forms of P in sediments and in water

P is associated to several particles in the sediments (organic and inorganic ones), thus having forces that determine its adsorption and desorption in the environment. Is important to determine how strongly P is associated with each fraction. In order to determine the forces with which the P is associated with the different fractions of the sediments there are techniques called sequential chemical fractionation.

The determination of the total P level in the sediment is not sufficient to determine its polluting potential (PELLEGRINI et al., 2008). The chemical fractionation of P in sediments is one of the most used techniques that allow us to understand the potential of release of P to the environment. The binding energy of P with the particles is proportional to their ability to be released (to become bioavailable) to the environment. The weaker the binding, the more easily it enters the water column and starts to be incorporated into the biota, contributing to eutrophication.

The P fractionation methodology suggested by Hedly et al. (1982) is widely used in sediment research. Tiecher et al. (2017b) studied the fractionation of P in sediments of a microbasin with no-tillage soil (tobacco production). In the fractionation, it was verified that the most labile fraction of the P increased greatly in the sediments produced during the transplanting of the seedlings, at which time there were fertilizations associated with management actions with soil movement.

With the use of 7 fraction chemical fractionation techniques, described by Paludan and Jensen (1995) and Paludan and Morris (1999), the authors detected that the mangrove contamination by effluents from a shrimp farm was modifying the forms that P was associated with soil particles. In this sense, there was a great contribution of Fe-P in the mangrove affected by the (N-rich) effluent, since it may be alternating the dominance in the reduction of Fe and S in the mangrove soil, resulting in higher oxidation conditions and higher amounts of reactive Fe acting as a drain of P. On the other hand, in the driest season, oxidation conditions and natural acidification occur, increasing the eutrophication process, promoted by the increase of MO mineralization and carbonate dissolution, resulting in the release of P which was associated with these fractions (NÓBREGA et al., 2014).

The sequential extraction suggested by Psenner, Ucsko and Sagher (1984) and adapted by Hupfer, Gaechter and Giovanoli (1995) was used in an Atlantic basin near Spain. The predominant form of P in the sediments was the organic form. Although the inorganic P was predominantly associated with the metal oxides, bioavailable P and total P were significantly related to the specific area of the sediments, such as clay and organic matter (BARRAL et al., 2012).

P in water can have two origins: internal and external. The P of external origin comes from diffuse sources (natural, agriculture) or point sources (industrial or domestic effluents). Sediments deposited in the waters are internal sources of nutrients for aquatic fauna (WANG et al., 2013).

In contrast to many studies, the authors have shown that total phosphorus and reducible phosphorus are at low correlations with available phosphorus. This finding implies that high levels of total and reducible phosphorus in sediments will not necessarily result in a high release of phosphorus under anaerobic conditions. In addition, the authors highlighted that phosphorus release from sediments was greatly suppressed when there were Fe/P> 30 and Fe/S> 6 in the samples (WANG et al., 2018). The authors propose the use of Fe/P and Fe/S as indexes capable of predicting the availability of P in sediments.

The P dissolved in water can occur in different forms. Knowing the P species is essential in water eutrophication studies. When the sediment loaded in P enters the aquatic system, it can be made available to the biota in several ways: i) desorption of the organic or inorganic P attached to the surface of the minerals, ii) dissolution of phosphatic minerals in its crystalline structure, in its precipitated or occluded form (iii) hydrolysis or mineralization of organic matter, (iv) excretion of exudates from macrophyte roots or bacteria, (v) dissociation of phosphorus complexed with humic substances (ORIHEL; BAULCH.; CASSON, 2017).

The variation in precipitation, due to the change of the seasons, can modify the forms of phosphorus dissolved in water. The organic and inorganic forms of P dissolved in water are determined by speciation techniques. Organic forms of P can consist of 50-80% of total phosphorus (NANNY; KIM, 1995). Orthophosphate is one of the most common forms, albeit organic forms are also found, associated with DNA, RNA, polyphosphates and inositol hexaphosphate (BALDWIN; WHITTINGTON; OLIVER, 2003).

Contamination of soils or sediments with organic or inorganic material affects their availability in water. When evaluated the P forms in soils and in the drainage water of areas with loose housing pigs, the organic forms of phosphorus had less mobility and tendency of homogeneity in the space and time evaluated. On the other hand, the inorganic forms (P - Olsen) had the greatest lability, with great variability in space and time, In the drainage waters, total and dissolved phosphorus had great variability, with values above 0.1 mg L^{-1}. This value is considered as the maximum ceiling for the prevention of eutrophication and quality of groundwater by the European Union (HORTA et al., 2012).

Sequential extraction procedures produce fractions which are operationally defined and can not be used to identify the forms present in the samples, but rather to associate the quantities of P attached to each predetermined fraction (WANG et al., 2013), Due to the large number of papers that use such methods, they are widely accepted in the scientific world and they correlate very well with the forms that P is in environments.

New techniques that directly quantify P species that occur in the samples are being calibrated. In a work carried out in a “XANES” (synchrotron-based X-ray absorption near-edge structure spectroscopy) two forms of P (orthophosphate and inositol hexakphosphate) were added in associations with the main constituents of soils capable of adsorbing phosphorus: Fe (ferrihydrite, goethite, hematite) oxides and hydroxides of Al (boehmite) oxide and hydroxide, carbonates (calcite and dolomite), saturated montmorillonite with Ca or Al and organic matter of the soil saturated with Ca and Al, P inclusion via orthophosphate and inositol hexakisphosphate in several pedogenic minerals (ferrihydrite, boehmite and Al-montmorillonite) or organic matter of the soil saturated with Al or Ca-phytate as predictor components in addition to the traditional use of P free-spectra forms was positive and with an increase in accuracy in P free-forms speciation of P forms (PRIETZEL et al., 2016).

The authors used the Mossbauer spectroscopy to characterize Fe forms in soils and to associate their occurrence with P retention. The authors detected a greater isomorphic substitution in goethitem, indicated by doublets of spectra at 298 K 15, which seems to hamper the phosphorus adsorption, most likely by the decrease of OH groups surfaces (CURI et al., 2008). In the association of oxides with P, the identification of mineral forms and crystallinity using Mossbauer spectroscopy is a promising technique that may greatly help in the studies with such interactions.

The use of the ^{31}P nuclear magnetic resonance spectroscopy analysis has contributed greatly to the debates related to phosphorus contained in sediments, helping to differentiate the P forms in the sediments (SHINOHARA et al., 2017; ZHANG et al., 2009; AHLGREN et al., 2005). This technique is able to distinguish phosphate compounds (orthophosphate, pyrophosphate, polyphosphate, monoester orthophosphate, diester and phosphonates), based on their specific resonance frequencies (ZHANG et al., 2009).

5.6 Final considerations

The study of sediment mineralogy provides important information about the adsorption or desorption behavior of P. These studies allow the inference of the potential pollutant of each sediment in the environment.

Whether in the identification of mineral sources of P (apatite) or sink of P (oxides, hydroxides, calcite, dolomite, minerals 2:1), mineralogy contributes significantly in the understanding and estimation of the pollution potential of the particles. The entry of P-enriched sediments into the aquatic environment increases the algae proliferation capacity. Although substantial amounts are not bioavailable, small modifications of redox and pH potential can make P available to the aquatic biology. The organic fraction to which P is associated may also undergo partial hydrolysis and release P to ambient. Constant evaluations of the dissolved P levels in water are necessary for us to understand the P cycle. Periods of higher P input in the system, with periods of higher P consumption by biota are common and must be determined so that a management plan can be performed.

The work proposed by Wang et al. (2018) brings up the relations between elements as indexes capable of predicting the release behavior of P in the sediments, thereby it is plausible that further studies in this sense are carried out and such relationships corroborated and calibrated compared to methods that are already widely accepted by researchers. The speciation of the P-forms in the synchrotron is a very promising technique (PRIETZEL et al., 2016) that needs to be calibrated so that the results are compared to the traditional processes of speciation already enshrined. Mossbauer spectroscopy should also be considered in the planning of studies related to the fixation and release of P in the sediments. The use of ^{31}P nuclear magnetic resonance spectroscopy can be well exploited in sediments (ZHANG et al., 2009), associating it with sequential chemical fractionation and other techniques to identify P forms in sediments and water. The use of new techniques or even the innovation in the use of old techniques is necessary within the area of sediments and pollutants.

The P cycle in the terrestrial-aquatic system is complex, and the mineralogy of the particles which carry P must be better understood. From soil with high levels of P, through the sediment being transported, going to water, being desorbed or adsorbed, or incorporated by biota and returning to its organic form, all of this is controlled by factors that change with anthropic actions and climate change. Thus, P-loaded sediment storages within lakes and rivers affect and are potential sources of pollution to surface waters.

All in all, it is salutary that we encourage the creation of continuous research networks in all national territories so that the water quality of a nation can be monitored and controlled, being a matter of security and national sovereignty.

6 CAPÍTULO IV

Geochemistry and mineralogy of Southwestern Lake Superior sediments with an emphasis on phosphorus lability

6.1 Abstract

The lability of phosphorus in sediments from Lake Superior and its relationship with sediment mineralogical and geochemical characterization remains poorly understood. The purpose of this study is to provide information about Southwestern Lake Superior (SLS) sediment P-lability and relate this information to the mineralogical composition and geochemical characterization of these sediments. Samples were collected from riverbed (input load), shoreline erosion (input load), and lake bottom. Thirteen samples were submitted to P sequential extraction and nine were submitted to mineralogical and geochemical analysis to evaluate P lability. The sediments were composed of non-clay minerals of low P-reactivity (quartz, augite, calcite, dolomite, anorthite, microcline, and magnesite) and minerals with greater P-reactivity such as oxides (rutile and hematite) and clay minerals (kaolinite, smectite/vermiculite, chlorite, mica or illite, and interstratified clays). The total P concentration in the lake sediments, input load and shoreline erosion sediment groups (average of 1,151, 945 and 837 mg kg^{-1}, respectively) was very high. However, labile P [extracted by NH_4Cl (P-loosely sorbed) and $NaHCO_3$ (P-redox sensitive)] represented less than 10% of the total phosphorus. More than 80% of P in the sediments was associated with organic compounds and carbonates with low availability to biota. Findings indicate that input load, shoreline and lake sediments contain very low concentrations of P available to aquatic biota due to the presence of minerals with high chemical reactivity with potential to adsorb P, such as poorly-crystalized iron oxides, clay minerals like chlorite, and 2:1 clay minerals with hydroxy-aluminun interlayered minerals. These results suggest that sediments in SLS may act as a long-term sink for P, which helps to explain the very low concentration of P found in the SLS aquatic system.

Key words: 1. HIM. 2. Lake sediments. 3. Oxides. 4. Phosphorus sequential fractionation. 5. P-remaining.

6.2 Introduction

Phosphorus (P) is a nutrient that sustains and often limits primary productivity in freshwater bodies, Its concentration depends on external inputs (natural, agricultural, industrial and domestic effluents) and internal loads, while its availability is dependent on its chemical forms, Soluble orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}) is considered the form of P most assimilable by aquatic biota, while various chemical forms of particulate P associated with organic matter and sediments are varyingly less accessible. Sediment can act both as a sink where P can be stored, or a source that can release P (JIANG et al., 2006).

The amount of orthophosphate released by sediments to the overlying water depends on exchanges between dissolved-P and P adsorbed onto solid phases, with this process regulated mainly by pH, redox potential and anions in solution able to displace the adsorbed phosphate from sediments into the aqueous phase (STUMM, 1985). The adsorption/desorption on the sediment surface is considered a main mechanism (along with biotic uptake and regeneration) that controls dissolved P. Depending on the binding capacity of the sediment surface, P is more or less available to fuel production.

P sequential extraction has been used to define operational schemes to evaluate the binding energy of P sorbed in sediments (HEDLEY; WHITE; NYE, 1982; PSENNER; PUCSKO 1988; RUBAN et al., 1999; KOPACEK et al., 2005; LUKKARI; LEIVUORI; HARTIKAINEN, 2007; LUKKARI et al., 2007; WANG et al., 2013). In general, the operational schemes consider that inorganic forms of P are sorbed in three main sediment geochemical pools, which are: (i) labile pool, which is considered the P absorbed with low binding energy, easily releasable and available for aquatic biota; (ii) redox sensitive pool, considered the P associated with Al, Fe, and Mn oxides and hydroxides; and (iii) Ca-P pool, associated with Ca-bound compounds such as apatite $[(Ca_5(PO_4,CO_3)_3(F,Cl,OH)]$, Organic forms of P in sediments mainly composed of microbial P, humic- and fluvic-associated P, and residual-P (YUAN et al., 2015a).

The dynamics of P-forms in aquatic environments largely depend on the mineralogical composition and geochemical caracteristics of the sediments. Generally, non-silicate minerals (such as hematite, gibbsite, magnetite, ferrihydrite, and lepidocrocite) present higher P sorption capacities than silicate-minerals (such as kaolinite, montmorillonite and illite) (BORTOLUZZI et al., 2015; GÉRARD, 2016).

Additionally, the specific surface area (SSA) and the crystallinity of non-silicate minerals (oxides) are also important characteristics controlling phosphate release capacity (BORGGAARD, 1983).

6.2.1 Dynamics of P and mineralogy in sediments from Lake Superior

Lake Superior is an oligotrophic lake where the total dissolved P in the overlying water is very low, 0.02 to 0.06 mmol L^{-1} (BAEHR; MCMANUS, 2003) and the pH is 7.8 to 7.9 (COONEY et al., 2018). In part because of elevated nitrate concentration (STERNER, 2011). The P is considering the primary limiting nutrient in Lake Superior (ROSE; AXLER, 1997; STERNER et al., 2004). The main inputs of external P are from soil erosion that occurs in the northwestern Wisconsin shoreline area (HESS, 1974; SYDOR, 1976) and related sediment flux from the Nemadji River (BAHNICK, 1977; ROBERTSON, 1997; ROBERTSON; SAAD, 2011). Shoreline erosion occurs especially when north-easterly winds exceeding 5 m s^{-1} and waves of 1.5 m abrade the toe of the shore. Sediment flux from the Nemadji River occurs especially during high flow. The magnitude of P potentially released by sediments into SLS from shoreline erosion and from the Nemadji River is about 240 and 63 metric tons yr^{-1} of orthophosphate P, respectively, according with Bahnick (1977) and Bahnick et al. (1978).

The overt characteristics of sediments from shoreline erosion and from the Nemadji River include red color and a fine texture (BAHNICK; ROUBAL, 1975; MENGEL; BROWN, 1976). The fine particles (< 2 mm) confer a high P-sorption capacity and allow these sediments to be transported long distances before deposition (HORTON et al., 1971; BAHNICK et al., 1978). Once these sediments are deposited in shallow depths (less than 20 m), they can be resuspended during episodes of strong north-easterly winds when wind velocity exceeds 8 m s^{-1} for 10 or more hours, Stortz et al. (1976) estimate an annual sediment resuspended load of around 1.6×10^{6} metric tons yr^{-1}. According with Bahnick et al. (1978), this amout of sediment potentially results in an input of orthophosphate of 100 (±40) metric tons yr^{-1}.

The origin of shore erosion and the Nemadji River sediments is glacio-lacustrine red clay deposits located mainly in northern Wisconsin. These sediments are composed mostly of clay minerals (52%) such as illite, chlorite and mixed-layer which present a basal distance of d=1.00-1.40 nm, and non-clay minerals (48%) such as quartz and plagioclase feldspar (DELL, 1973). The total organic carbon (TOC) content in sediments varies between 0.01 to 3.9% (THOMAS; DELL, 1978).

Although sediment input into Lake Superior is documented (BAHNICK, 1977; KEMP et al., 1978; ROBERTSON, 1997; RIEDEL et al., 2010; ROBERTSON; SAAD, 2011), the lability of P and its relationship with sediment geochemical composition remain poorly described. Therefore, our hypothesis is that the use of sequential chemical fractionation of P in sediments, combined with a detailed analysis of the mineral and geochemical solid phase, may improve our understanding of the lability of P in SLS.

6.3 Materials and Methods

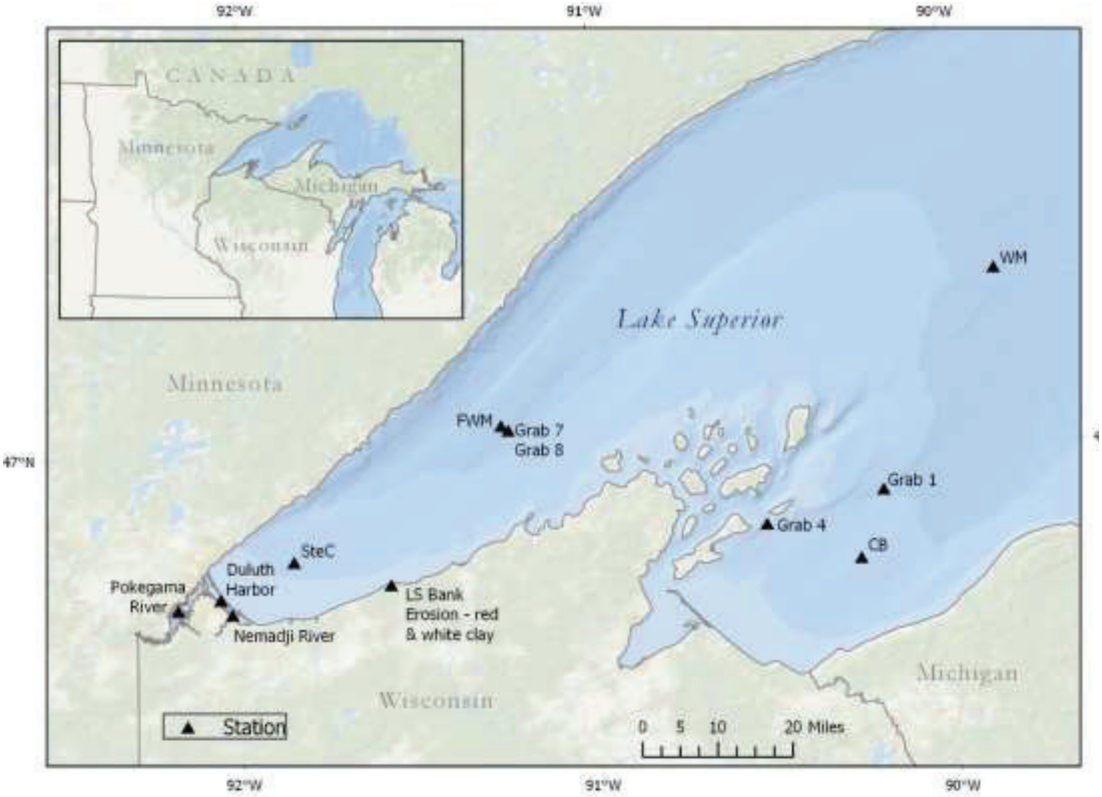
6.3.1 Site location and sediment sampling

Sediment sampling sites are presented in Figure 8.

Sediment sampling was carried out at thirteen sites, representing different sediment sources: rivers (Pokegama and Nemadji) and the Duluth Harbor, shoreline erosion (LS Bank Erosion Red Clay and LS Bank Erosion White Clay), and lake sediments (FWM, CB, SteC, WM and Grab 1, 4, 7 and 8) (Figure 8).

Pokegama, Nemadji, and Duluth Harbor samples were taken from submerged sediments, whereas the bank sediments came from the shoreline just above the waterline. Pokegama and Nemadji River samples were collected close to the respective river mouths. Bank sediments were collected on the shoreline, the Red Clay sampled in soil horizon A and the White Clay sampled in soil horizon C. Lake submerged sediments were collected from boats, using equipment described in Table 9, and were kept frozen until analysis. Before the analyses, the entire set of samples was air dried, homogenized by grinding, and passed through a 63 µm sieve (silt/clay fractions). P fractionation analysis was carried out on the entire set of samples, while the mineralogical composition and geochemical characterization analysis was completed for just nine samples representing the three main sediment groups (lake, input load and shoreline erosion sediments). Grab samples 1, 4, 7 and 8 were not submitted to mineralogical and geochemical analysis based on the assumption that these samples were similar to the other lake sediment samples (FWM, CB, SteC and WM).

Figure 8 - Map of Lake Superior showing the lake and input sediment sample sites used in this study. Passo Fundo, 2019



Source: Author data.

6.3.2 Grain size (D_{50}) and total organic carbon (TOC)

The sediment grain size analysis was evaluated using laser diffraction sizing technique (BORTOLUZZI et al., 2010) where the organic matter was previously removed from sediments using pre-treatment with H_2O_2 5% at 40°C.

Total organic carbon in the sediments was determined in dried sediments acidified using a LECO CR-412 carbon analyzer according to the procedure recommended by Bernard, Bernard and Brooks (2010).

Table 9 - Description of three different lake sediment samples. Passo Fundo, 2019

Code sample	Identification	Coordinates Latitude (N)	 Longitude (W)	Sample type	Water depth (m)
		Lake sediments			
1	FWM	47,0573	91,2643	core (0-2 cm)	100
3	CB	46,7855	90,2608	core (0-2 cm)	96
5	SteC	46,8016	91,8525	core (0-2 cm)	41
7	WM	47,3351	89,8602	core (0-2 cm)	167
8	Grab 1	46,9175	90,1919	ponar	20
9	Grab 4	46,8560	90,5225	ponar	40
10	Grab 7	47,0482	91,2441	ponar	102
11	Grab 8	47,0482	91,2441	ponar	100
		Input load sediments			
17	Pokegama River	46,7107	92,1787	ponar	8
23	Nemadji River	46,8022	92,0653	ponar	12
26	Duluth Harbor	46,7308	92,0591	ponar	11
		Shoreline erosion sediments			
30	LS Bank Erosion - Red clay	46,7552	91,5809	grab	ED
32	LS Bank Erosion - white clay	46,7552	91,5809	grab	ED

Source: Author data.

ED= exposed clay deposit.

6.3.3 Al and Fe forms

Poorly- and well-crystallized Fe and Al forms were extracted from sediment samples. Poorly-crystallized Fe and Al forms (Feo and Alo) were extracted using ammonium oxalate 0.2 mol L^{-1} at pH 3 (BLAKEMORE; SEARLE; DALY, 1987) while well-crystallized forms (Fed and Ald) were extracted using dithionite-citrate-bicarbonate (DCB) (MEHRA; JACKSON 1960). The Al and Fe concentrations in these extracts were measured by atomic absorption spectroscopy. For these analyses, only one replication was made due to the small quantity of sediment.

6.3.4 Mineralogical analyses

To provide mineralogical qualitative analyses, the sediment samples were separated into two aliquots with and without organic matter (pre-treatment with H_2O_2 5% at 40 °C). In the sediment samples with organic matter, the mineralogical sediment composition was determined on air-dried bulk sediment samples according to methods detailed by Bortoluzzi et al. (2010). Powdered samples were randomly oriented and placed in an acrylic powder sample carrier and X-ray diffraction (XRD) patterns were scanned in a range of angles spanning 15–65° 2θ.

For the sediments without organic matter, the air-dried sediment samples at room temperature were re-suspended in water. Sediment samples were then separated into two sub-samples: one sub-sample was Ca-saturated using 0.5 mol L^{-1} $CaCl_2$ and the other was K-saturated using 1 mol L^{-1} KCl, Ca and K saturation was performed three times following centrifugation and removal of supernatant. After this procedure, the sediment samples were washed using water following agitation and centrifugation to remove excess salts. This process was performed four times before samples were tipped onto glass slides. Care was taken to use similar mass of all sediment samples (1 mL of sediment suspension per slide). For Ca-saturated samples, XRD patterns were recorded between 5–70° 2θ at room temperature (air-dried) and after ethylene glycol (EG) solvation. For the K-saturated sediment samples, the XRD patterns were recorded after heating at 110 °C, 250 °C and 550 °C at the same scan, X-ray diffraction patterns were produced using a Bruker diffractometer model D2 Phaser (Cu-Kα radiation, operating at 30 kv and 15 mA).

The XRD patterns (Ca-saturated under air-dry condition) were analyzed using EVA® software. A semi-quantitative phase analysis was performed on the same XRD patterns using DecompXR software on the 5–17° 2θ angular range after subtraction the background (LANSON, 1997). The surface area of each peak presented in XRD was calculated according to the intensity and full width at half maximum (FWHM) of each experimental peak (HUGHES; MOORE; GLASS, 1994). Thus, the relative surface area of each peak corresponds to the relative proportion of the mineral in the sample (MOORE; REYNOLDS 1997; VELDE, 2001).

The identification of mineral occurrence in a given sample was performed according to the coincidence of at least three peaks (00l) in the XRD patterns and their intensities using the peak distances of minerals of reference (BRINDLEY; BROW, 1980).

6.3.5 Specific surface area (SSA)

Sediment samples (with and without organic matter) were solvated with ethylene glycol monoethyl ether (EGME) at controlled temperature ($20 \pm 1^{o}C$) to provide a total particle surface covering according to the specific surface area method (CARTER; HEIMAN; GONZALES, 1965). The amounts of EGME absorbed in monolayer onto the particles corresponded to the SSA of the sample ($m^2\ g^{-1}$).

6.3.6 Cation exchange capacity (CEC)

The effective cation exchange capacity (CEC) of the sediments without organic matter was determined using 1 mol L^{-1} $MgCl_2$ followed by 1 mol L^{-1} ammonium acetate exchange, according to the adapted method by Righi, Terribile and Petit (1995). The NH_4^+ displaces Mg^{2+} and is measured by atomic absorption spectrometry corresponding to the CEC of mineral fraction of sediment ($cmol_c\ kg^{-1}$).

6.3.7 P chemical fractionation analysis

Sediment samples were subjected to a sequential P fractionation scheme, as proposed by Engstrom and Wright (1984), Engstrom (2005), Psenner and Pucksko

(1988), and Kopacek et al. (2005). Briefly, duplicates of 0.02 g dry sediment samples were fractionated according to the following sequence (Table 10): (i) 20 mL of 1 M NH_4Cl, which extracts the available P or loosely bound-P (PLS); (ii) 20 mL of 0.11 M $NaHCO_3$¸ which extracts labile P (PRS) adsorbed onto Fe oxyhydroxides (released under low redox conditions); (iii) 25 mL of 0.1 M NaOH, which extracts moderately labile P adsorbed to Al and Fe oxyhydroxides (P-exchangeable with OH); (iv) 24 mL of 0.1 M NaOH + Persulfate, which extracts labile organic P; and (v) 2 N of HCl solution¸ which extracts the mineral-bound P in calcite and apatite (P-bound with carbonates). After extraction, the P contents were determined using a UV-Vis spectrophotometer, according to the method proposed by Murphy and Riley (1962).

Table 10 - Extraction schemes for determining the fraction composition of sediment phosphorus. Passo Fundo, 2019

Extraction/fraction	Code	Proposed fraction
1.0 mol L^{-1} NH_4Cl	F1	P_{LS} (P-loosely sorbed)
0.11 mol L^{-1} $NaHCO_3$ + 0.1 mol L^{-1} $Na_2S_2O_4$	F2	P_{RS} (P-redox sensitive)
0.1 mol L^{-1} NaOH	F3	P_{OH} (P-exchangeable with OH)
0.1 mol L^{-1} NaOH extraction followed by hot persulfate digestion	F4	P_O (P-organic)
2.0 mol L^{-1} HCl	F5	P_{Ca} (P-bound with carbonates)

Source: Author data.

6.3.8 P-remaining

For the P-remaining analysis, representing a single point in the adsorption isotherm (BACHE; WILLIAMS, 1971), the SLS sediment samples were saturated with 5 ml of a solution containing 60 mg L^{-1} of P that was stirred (30 rpm) for 60 hours at constant temperature (20±1°C). In the next step, the samples were centrifuged for 10 minutes at 6000 rpm and an aliquot of 2 mL of supernatant was withdrawn. From this aliquot, a volume of 0.5 mL was placed in snap-cap and 7 mL^{-1} of ultrapure water was added (ALVAREZ et al., 2000). From this solution, a volume of 3 mL was used to estimate the P-remaining in solution, according to the method proposed by Murphy and Riley (1962). P-remaining method directly evaluates the potential for P immobilization by the sediments, where the higher the concentration of P-remaining in the solution, the lower the potential for P immobilization by the sediments.

6.3.9 Statistical analyses

The P-chemical fractionation analysis and geochemical characterization of SLS sediments was submitted to the Kruskall-Wallis H-test, a nonparametric test (LEVIN, 1999). The Pearson correlation was used to provide a correlation matrix between sediment geochemical properties and P forms resulting from P-fractionation analysis.

6.4 Results

6.4.1 Mineralogical composition of sediments

The nine samples of Lake Superior sediments were composed, in general, of grain minerals (quartz, augite, calcite, dolomite, albite, anorthite, magnesite and microcline), oxides (rutile and hematite) (Figure 7A), and clay minerals (kaolinite, smectite, kaolinite/smectite, mica-illite, chlorite, hydroxy-Al interlayered mineral and interstratified clays) (Figure 7B and in Appendix 1 - supplementary material).

Regarding the mineral occurrence (Figure 7a), it was observed that: (i) quartz, kaolinite, albite, and rutile were present in all sediments (minimum three peaks for each mineral identified in the XRD patterns); (ii) dolomite, calcite, and hematite were present in at least one sample (two peaks for each mineral identified in the XRD); and (iii) magnesite, augite, and microcline were probably found in at least one sample (probably because only one peak was identified in the XRD patterns).

Calcite was present in sample 32 (LS Bank Erosion-white clay) and it was likely present in sample 1 (FWM) and sample 5 (SteC). Dolomite was present in samples 5 (SteC), 7 (WM), 23 (Nemadji River), 26 (Duluth Harbor), 30 (LS Bank Erosion-red clay), and 32 (LS Bank Erosion-white clay), and there was probable occurrence in samples 1 (FWM), 3 (CB) and 17 (Pokegama River). Magnesite and augite had a probable presence in sample 1 (FWM), 3 (CB) and 26 (Duluth Harbor) because two respective peaks of these minerals were found in the XRD patterns (Table 10). Microcline, Albite and Anorthite, minerals that contain K, Na and Ca in their structure, have been reported in the literature as common in SLS sediments (DELL, 1959). Augite (peaks at d=0.43, 0.163 and 0.299 nm) had a probable presence in sample 26 (Duluth Harbor) (Figure 7A and Table 3). The peak at d=0.83 (Figure 7a) likely corresponds to mixed layer clay (e.g. interstratified chlorite/kaolinite) that was identified in all sediment samples, consisting of a very common clay mineral present in SLS sediments.

Hematite (peaks at d=0.27, 0.17 and 0.25 nm) was present in five samples: sample 1 (FWM), 17 (Pokegama River), 23 (Nemadji River), 26 (Duluth Harbor), and 30 (LS Bank Erosion-red clay) (Figure 7B and Table 10). This oxide was not present in sample 3 (CB), and there was probable occurrence in three other samples: sample 5 (SteC), 7 (WM), and 32 (LS Bank Erosion- white clay).

Figure 7b (X ray diffraction air-drier Ca-saturated) highlights phyllosilicate clay mineral composition (2:1 and 1:1 crystallography structure). Kaolinite and mica were identified in all samples (Table 10, Figure 7b and Appendix 1). True chlorite was identified in samples 3 (CB), 7 (WM), 17 (Pokegama River), 26 (Duluth Harbor) and 32 (LS Bank Erosion-white clay) (Appendix 1). Chlorite peak did not vary with any solvation or heating treatments.

Smectite, an expandable clay mineral, was identified in all samples with the exception of sample 3 (Appendix 1) and varied in proportion among the samples (Table 10). The peak at d~1.4 nm corresponded to smectite, as part of this peak was sensitive to solvation with ethylene glycol (expandable interlayers) and heating treatments (shrinkage interlayers) (Appendix 1).

In addition, the XRD patterns for samples 1 (FWM) and 5 (SteC) present peaks varying from d=0.90-0.93 nm, corresponding to mixed-clay, probably a kaolinite-smectite clay mineral (Figure 7B). This peak was displaced after ethylene glycol solvation and disappeared after heating to 550 ^{o}C (Appendix 1). In addition, samples 5

(SteC), 17 (Pokegama River), 23 (Nemadji River), and 26 (Duluth Harbor) presented peaks at d=0.88-0.89 nm which were insensitive to ethylene glycol solvation, but disappeared after heating at 550 °C, indicating an interstratified kaolinite-chlorite clay mineral (Figure 7B and Appendix 1). All XRD patterns under air dried conditions (at room temperature and Ca-saturated) presented two peaks at d=0.83 nm and d=0.63 nm, probably corresponding to the presence of kaolinite-chlorite, as these peaks remained unaltered after ethylene glycol solvation and heating treatments (Figure 7b). Thus, there are two populations of mixed layers in the samples (Table 10).

In samples 1 and 32, one peak was observed at d=0.63 nm in the XDR patterns of power preparation (Figure 7A) suggesting the presence of a P-bearing mineral [e.g. vivianite, identified in Lake Superior sediment by Dell (1972ab)]. These findings suggest that the presence of P-bearing minerals in Lake Superior should be studied in greater depth in the future.

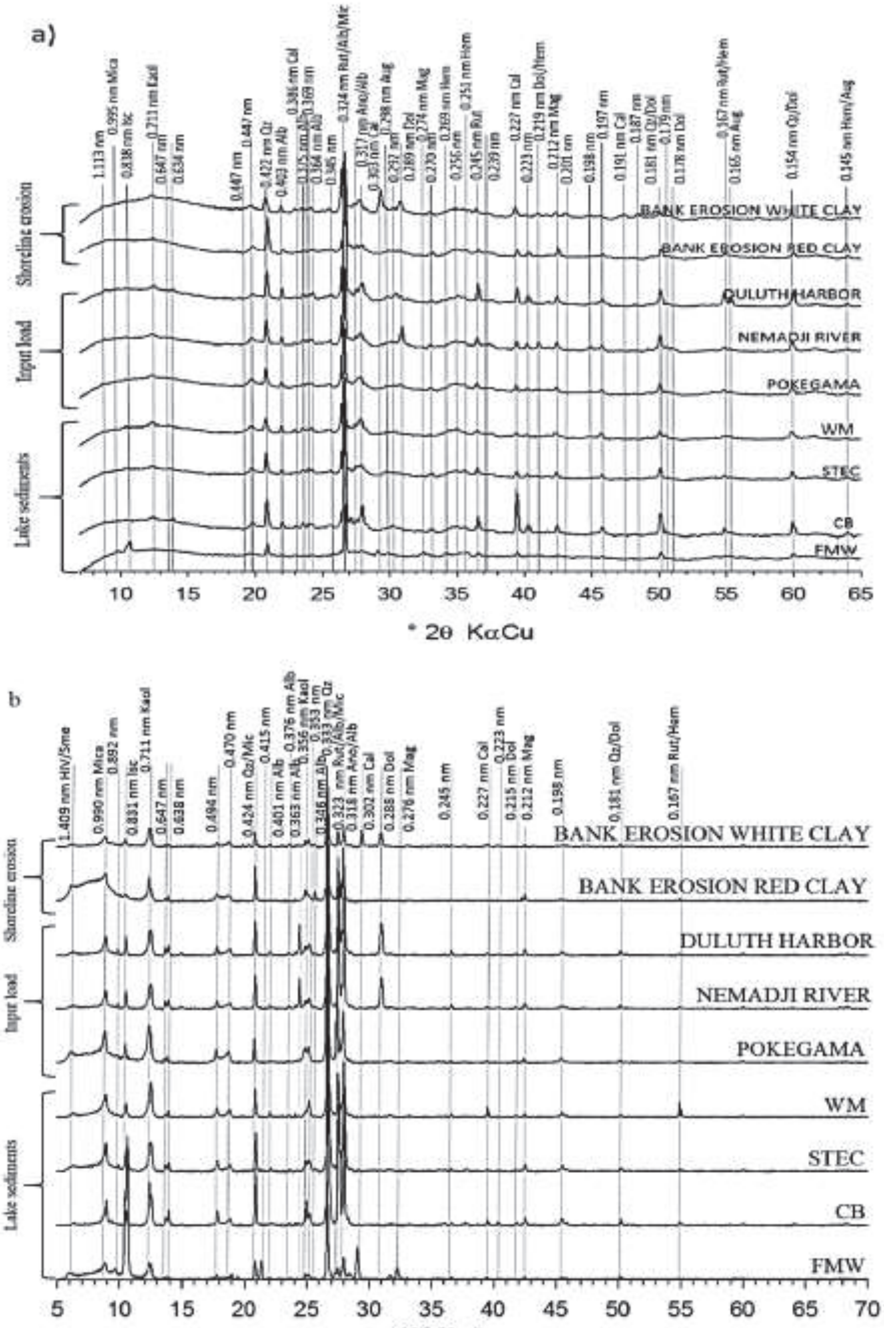
Regarding clay minerals, kaolinite and mica represented the main components of the sediment samples. Their relative proportions ranged from 11 to 53% and 9 to 38%, respectively (Table 10). Mica was found in lower proportions in the shoreline erosion sediment group.

The hydroxy-Al interlayer mineral (HIM) presented a higher relative proportion, around 70% (sample 30-LS bank erosion red clay) and 36% (sample 17 Pokegama River). As chlorite and HIM have similar behavior after mineralogical treatments, the relative proportion of these minerals can be presented by its sum, In the lake sediments group, the HIM was found only in samples 5 and 7, with 18 and 23%, respectively (Table 10). The decomposition of the peak at d=1.40 nm contains part of a peak that was displaced after EG solvation (Appendix 1), corresponding to smectite. Smectite occurred in all samples of input load sediments and shoreline erosion, and in three samples from the lake sediment group (1-FWM, 5-SteC and 7-WM).

6.4.2 P-forms, physical-chemical sediment characterization, and P-rem

The total P-sediment concentration (Table 11) ranged from a minimum of 572 mg kg^{-1} (sample 3 CB) to a maximum of 2,146 mg kg^{-1} (sample 11-Grab 8), with an average of 978 mg kg^{-1} (Table 11).

Figure 9 - X-ray diffraction patterns of sediment samples from lake and input load sediments under two preparations: (a) powder preparation – randomly oriented particles and, (b) air-dried Ca-saturated sediment samples – oriented particles samples. Passo Fundo, 2019



Source: author data.

Mic = mica, Kao = kaolinite, Qtz = quartz, Ano = anorthite, Cal = calcite, Rut = Rutile, Mag = Magnesite, Alb = Albite, Ill = Illite, Hem = Hematite, Aug = augite, Dol = dolomite, Sme = smectite, Isc = interstratified.

Table 11 - Occurrence of minerals observed in powder by X-ray diffraction patterns from SLS sediments. Passo Fundo, 2019

Minerals		Sediment sources								
		Lake sediments				Input load sediments			Shoreline erosion sediments	
		1	3	5	7	17	23	26	30	32
Grain minerals	Quartz – Qz [SiO_2]	*	*	*	*	*	*	*	*	*
	Calcite – Cal ($CaCO_3$)	**	-	**	-	-	-	-	-	*
	Magnesite – Mag [$MgCO_3$]	**	-	-	-	-	-	-	-	-
	Dolomite – Dol [$CaMg(CO_3)_2$]	**	**	*	*	**	*	*	*	*
	Microcline – Mic [$KAlSi_3O_8$]	**	**	**	**	**	**	**	**	**
	Albite – Alb [$NaAlSi_3O_8$]	**	*	*	*	*	*	*	*	*
	Anorthite – Ano [$CaAl_2Si_2O_8$]	-	-	-	-	-	-	-	-	-
	Augite – Aug [$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$]	-	-	-	-	-	-	**	-	-
	Messelite [Ca2Fe2+0.75Mn2+0.25(PO4)2 2(H2O)]	**	-	-	-	-	-	-	-	**
	Meyerhofferite – Mey [$Ca_2B_6O_6(OH)_{10}$•$2(H_2O)$]	*	*	*	*	*	*	*	*	*
Oxides	Hematite – Hem [α-Fe_2O_3]	*	-	**	**	*	*	*	*	**
	Rutile – Rut [TiO_2]	*	*	*	*	*	*	*	*	*
	Greigite - Gre [$FeIIFeIIIS_4$]	**	-	-	-	-	-	-	-	-
Relative proportion of surface area of phases (%)										
Clay minerals	Kaolinite	29	53	35	37	28	42	43	11	45
	Mica/illite	38	34	30	33	21	29	31	9	20
	Smectite	17	0	7	4	11	9	8	6	8
	Hydroxy-Al interlayer mineral (HIM)/chlorite	0	0	18	23	36	9	7	73	8
	Other clay minerals (i.e. mix-layer minerals)	6	11	8	3	4	8	8	1	19

Source: Author data.

*Present; ** probably present; - not found. Sample 1- FWM; Sample 3- CB; Sample 5-SteC; Sample 7-WM; Sample 17- Pokegama River; Sample 23 Nemadji River; Sample 26- Duluth Harbor; Sample 30- LS Bank Erosion-red clay; Sample 32- LS Bank Erosion- white clay.

Table 12 - Phosphorus forms of three different lake sediment sources. Passo Fundo, 2019

Sediment sources	Identification	Phosphorus forms					
		TP	F1	F2	F3	F4	F5
		mg kg^{-1}					
Lake sediments	1-FWM	1,299	24	110	93	348	724
	3-CB	572	14	90	35	265	168
	5-SteC	1,038	17	249	92	364	316
	7-WM	863	17	90	107	371	278
	8-Grab 1	727	8	43	36	497	143
	9-Grab 4	942	6	94	80	416	346
	10-Grab 7	1,623	9	309	212	691	402
	11-Grab 8	2,146	19	192	149	1,223	563
Input load sediments	17-Pokegama River	972	6	62	70	502	332
	23-Nemadji River	830	10	72	54	307	387
	26-Duluth Harbor	1,032	8	86	72	526	340
Shoreline erosion sediments	30 - LS Bank Erosion - red clay	852	7	35	39	586	185
	32 - LS Bank Erosion - white clay	822	10	19	8	419	366
Lake sediments	Mean	1,151	14	147 a	101	522	368
Input load sediments	Mean	945	8	73 ab	65	445	353
Shoreline erosion sediments	Mean	837	9	27 c	24	502	276
Kruskal-Wallis H-test	H-value	1.48	2.76	7.18	4.05	0.66	0.22
	p-value	0.476	0.264	0.028	0.131	0.719	0.895

Source: Author data.

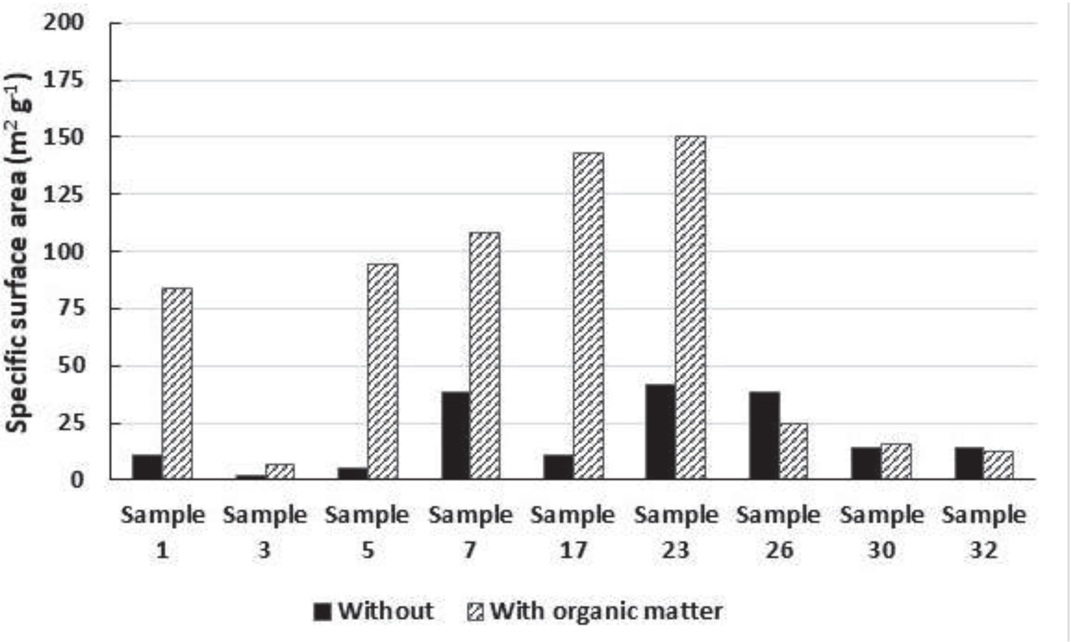
$^*p<0.1$; TP= F1+F2+F3+F4+F5.

The overall average of total P-sediment concentration, comparing the three different sediment groups (lake, input load and shoreline erosion), were 1,151, 945 and 837 mg kg^{-1}, respectively. Except for the P form F2, for which the shoreline erosion sediment group presented a lower P concentration when compared with lake and input load sediment sources, all different P forms (PT, F1, F3, F4 and F5) were very similar ($p<0,1$) between sediment sources.

With respect to physical-chemical sediment characterization properties, the Kruskall-Wallis H-test showed discrimination between the three sediment groups for D_{50} ($p<0.029$), TOC ($p<0.046$), Al_d ($p<0.040$) and Al_2O_3($p<0.040$) (Table 12). The input load grain size was smaller (clay is the predominant class) when compared with the lake sediment group (where silt is the predominant sediment grain size class). TOC in the shoreline sediment erosion source was lower (0.3%) when compared with input load (2.8%) and lake sediment (2.0%) groups. The total organic carbon was exceptionally high in sample 26-Duluth Harbor (3.8%) considering that this is a zone of high primary production. The presence of Al_d minerals was higher in the input load group when compared with lake and shoreline erosion groups, Al_2O_3 in the sediments was very low (<2.8%), indicating poor concentration of Al-bearing minerals. Comparing the three sediment groups, the percentage of Al_2O_3 in the input and shoreline sediment groups was two times higher than for the lake sediments. This finding is consistent with the mineralogical analysis, considering that the presence of HIM/chlorite (which has an Al-surplus in the interlayer structure) was higher in the input load sediment group (Table 8).

The specific surface area (SSA) was exceptionally high in samples 23-Nemadji River (150 m^2 g^{-1}) and 17-Pokegama River (143 m^2 g^{-1}), and very low in samples 32-LS Bank Erosion-white clay (12 m^2 g^{-1}) and 30-LS Bank Erosion-red clay (16 m^2 g^{-1}) (Figure 9). Figure 9 compares SSA for the mineral and organic phases and shows how closely SSA corresponds with the presence of organic matter. The concentration of well crystallized iron (Fed) ranged from 7.3 to 21.5 g kg^{-1} (Table 12), while the concentration of poorly crystallized iron (Feo) ranged from 10.0 to 24.6 g kg^{-1}. The Feo/Fed ratio higher than 1 means that the poorly crystallized forms predominate over the crystallized forms. The only exception was for sample 30 (LS Bank Erosion – red clay), where the Feo/Fed ratio was lower than one. The Fed content in the samples corresponded to the hematite oxide in the XRD. The poorly crystallized Fe form may appear on samples as ferrihydrite, however it is difficult to identify through the XRD method.

Figure 10 - Specific surface area from sediments with and without organic matter. Passo Fundo, 2019



Source: Author data.

Lake sediments= 1 (FWM), 3 (CB), 5 (SteC), 7 (WM), Input load sediments=17 (Pokegama River), 23 (Nemadji River), 26 (Duluth Harbor), 30 (LS Bank Erosion- red clay) and 32 (LS Bank Erosion-white clay).

The P-remaining (P-rem) was very low in samples 23-Nemadji River (14 mg L^{-1}) and 17-Pokegama River (23 mg L^{-1}), demonstrating that these two samples present a very high capacity to adsorb P, explained by the very high SSA found in both samples (Table 12).

Table 13 - Geochemical substrate characterization and P fractionation analyses of SLS sediment samples. Passo Fundo, 2019

Sediment sources	Identification	D_{50}* mm	SSA $m^2\ g^{-1}$	CEC cmolc kg^{-1}	TOC* %	Fe*d* g kg^{-1}	Fe_2O_3 %	Al*d** g kg^{-1}	Al_2O_3* %	Fe*o* g kg^{-1}	Fe*o*/Fe*d*	P-rem, mg L^{-1}
Lake sediments	1-FWM	4.4	83.9	22.8	1.66	19.49	27.87	0.54	1.01	24.56	1.26	31.4
	3-CB	12.8	7.0	15.9	2.43	11.79	16.87	0.18	0.34	17.61	1.49	34.5
	5-SteC	10.4	94.4	16.1	2.14	21.52	30.77	0.64	1.2	24.16	1.12	27.1
	7-WM	7.5	108.4	24.5	1.84	8.15	11.66	0.77	1.45	16.82	2.06	30.9
Input load sediments	17-Pokegama River	2.5	143.3	43.3	2.21	14.63	20.92	1.47	2.77	18.37	1.26	22.8
	23-Nemadji River	3.5	150.3	48.8	2.47	13.42	19.19	1.43	2.7	15.58	1.16	14.2
	26-Duluth Harbor	3.5	24.5	21.8	3.71	13.01	18.61	1.08	2.05	20.18	1.55	31.8
Shoreline erosion sediments	30 - LS Bank Erosion - red clay	0.9	15.7	31.7	0.45	16.79	24.01	0.94	1.78	14.69	0.87	39.0
	32 -LS Bank Erosion - white clay	0.9	12.2	61.0	0.21	7.34	10.5	1.1	2.08	10.00	1.36	21.4
Lake sediments	Mean	8.8	73.4	19.8	2.0	15.2	21.8	0.5	1.0	20.8	1.5	31.0
Input load sediments	Mean	3.2	106.0	38.0	2.8	13.7	19.6	1.3	2.5	18.0	1.3	22.9
Shoreline erosion sediments	Mean	0.9	14.0	46.3	0.3	12.1	17.3	1.0	1.9	12.3	1.1	30.2
Kruskal-Wallis H-test	H-value	7.12	3.30	4.20	6.14	0.40	0.40	6.44	6.44	4.51	0.83	1.08
	p-value	0.029	0.192	0.123	0.046	0.818	0.818	0.040	0.040	0.105	0.662	0.583

Source: Author data.

Notes: * $p<0.1$ Statistical difference between sediment sources using the Kruskal-Wallis H-test.

D_{50} is the median sediment grain size; SSA is the specific surface area with organic matter; CEC is the cation exchanged capacity; TOC is total organic carbon; Fe*d* and Al_d are extracted using dithionite-citrate-bicarbonate (DCB); Fe*o* is extracted using ammonium oxalate; P-rem is the phosphorus remaining method.

6.4.3 Geochemical correlations

According to the Pearson correlation matrix analysis (Table 14), the total P presented a strong correlation (r = 0.81**) with the F5 P-form (associated with the Ca phosphate mineral) and with Fe_d and Fe_o (r = 0.63* and r = 0.64*, respectively), The loosely sorbed P (F1 P-form) presented a negative relation with Al_d (r = –0.68**) and a positive relation with Fe_o (r = 0.60*), suggesting that well crystallized aluminum (Al_d), found in the Al-sheet of HIM and chlorite, plays an important role in reducing P availability.

The P-redox sensitive fraction (F2) presented a significant positive correlation with Fe_o (r = 0.78**). The F3 P-form (P exchangeable with OH) showed a positive relation with Fe_o (r = 0.76**). The F4 form (P-organic) presented a negative relation with D_{50} (r = –0.68**). The Ca phosphate P-form (F5) did not present any relation with the physical-chemical parameters analyzed in this study.

Regarding grain size distribution, the D_{50} presented a negative relation (r = –0.75**) with Al_d, indicating that the presence of Al is associated with very small particles and higher SSA (Table 14), In addition, Al_d presented a negative correlation with P-rem (r = –0.65*), with the latter presenting a strong and negative correlation with CEC (r = –0.69**), SSA (r = –0.62*) and Al_d (r = –0.65*).

6.5 Discussion

Lake, input load and shoreline erosion sediments in southwestern Lake Superior are very heterogeneous in terms of mineralogical composition and geochemical characteristics (Table 10 and 12), which likely reflects the sedimentary processes that have occurred in SLS from late glacial to postglacial eras. Dark gray or brown clays, deposited after ice retreat, represent the upper unit, with sands overlying, especially in the nearshore zone and deep waters. Silty clays (calcareous varved) represent the lower unit, deposited while the glacier was still within the lake's drainage basin. These two deposits of sediments are underlain by glacial till (THOMAS; DELL, 1978).

This complex geochemical substrate is associated with chemical and mechanistic processes that drive the P lability in the sediments and the magnitude of adsorption/desorption processes that occur on the surface sites of sediments (P-sorption capacity). Sediment grain size (D50), surface area (SSA), mineralogical compositon, and geochemical substrate (Fe and Mn oxides, reactive Fe, organic matter and type of clay minerals) are the most important mineralogical and geochemical factors that control P adsorption/desorption in the sediments.

The mineralogical analysis of SLS sediments allowed identification of three types of minerals: granular (non-clay) minerals, Fe/Al oxides, and clay minerals (Table 10). Similar results were found by Dell (1973), who described the mineralogical composition of the clay fraction (<2 mm) of late-glacial and postglacial Lake Superior sediments. According to this author, the most abundant clay minerals were illite (10-41%) and mixed-layer 1.00-1.40 nm clay minerals (7-29%), while quartz (3-28%) and plagioclase feldspar (4-21%) were the most abundant non-clay minerals. Additionally, Dell (1973) observed a diagenesis process occurring within the lake sediments (and on lake basin soils), with increased mixed-layer clays and quartz accompanied by a decrease in illite and feldspar.

In terms of the P-sorption capacity (or sediment reactivity to P), Fe/Al oxides and clay minerals are the reactive constituents of sediment. There is a consensus that Fe/Al oxides play a more important role than clay minerals (MANNING; GOLDBERG, 1996; CUI; WENG, 2013; PEREZ et al., 2014). However, a current study presented by Gérard (2016) shows that the P-sorption capacity of clay minerals may be close to or even higher than that of Fe/Al oxides, depending on the SSA of these minerals, In fact, high P adsorption was observed in samples 17 (Pokegama River) and 23 (Nemadji River) from the input load sediment group because they present the highest SSA and Al contents (Table 12). The Al content can made part of hydroxy-Al interlayer of 2:1 clay minerals found in great proportion in sample 17 (Table 10). This Al form is normally poorly crystalized, presenting a very high P-sorption capacity (BORTOLUZZI et al., 2013; 2015; Gérard (2016).

Table 14 - Person correlation matrix of the sediments attributes. Passo Fundo, 2019

	TP	F1	F2	F3	F4	F5	SSE	D_{50}	CEC	TOC	Fe*d*	Fe*o*	Al*d*	P-rem
TP	1.00													
F1	0.52	1.00												
F2	0.36	0.53	1.00											
F3	0.59	0.55	0.61*	1.00										
F4	0.12	-0.62*	-0.35	-0.11	1.00									
F5	0.81**	0.65*	0.12	0.31	-0.32	1.00								
SSE	0.40	0.12	0.26	0.57	-0.23	0.39	1.00							
D_{50}	-0.25	0.50	0.66*	0.31	-0.68**	-0.20	-0.03	1.00						
CEC	-0.11	-0.50	-0.64*	-0.58	0.16	0.15	0.16	-0.71**	1.00					
TOC	-0.05	-0.01	0.37	0.45	-0.18	-0.18	0.27	0.39	-0.47	1.00				
Fe*d*	0.63*	0.31	0.65*	0.40	0.07	0.34	0.21	0.14	-0.46	0.12	1.00			
Fe*o*	0.64*	0.60*	0.78**	0.76**	-0.18	0.38	0.28	0.45	-0.75**	0.53	0.77**	1.00		
Al*d*	0.07	-0.68**	-0.41	-0.14	0.47	-0.01	0.47	-0.75**	0.74**	0.02	-0.18	-0.39	1.00	
P-rem	-0.05	0.18	0.04	0.12	0.31	-0.30	-0.62*	0.24	-0.69**	-0.08	0.19	0.24	-0.65*	1.00

Source: Author data.

Notes: Statistical significance for the Pearson matrix coefficients $**P<0.05$; $*P<0.10$.

SSA is the specific surface area; D_{50} is the median sediment grain size; CEC is the cation exchanged capacity; TOC is total organic carbon; Fe*d* and Al*d* are extracted using dithionite-citrate-bicarbonate (DCB); Fe*o* is extracted using ammonium oxalate; P-rem is the phosphorus remaining method; Total P represents the available +recalcitrant P forms; F1 is the P-loosely sorbed; F2 is the P-redox sensitive; F3 the P-exchangeable with OH; F4 is the P-organic; F5 is the P-bound with carbonates.

Despite the presence of hematite in samples 17 (Pokegama River) and 23 (Nemadji River), this oxide is in a highly crystallized form, and thus presents a relatively low P-sorption capacity when compared to the low Fe/Al crystalized form found in these samples. In this sense, our results show that the sediment samples presenting high P interaction are those that present high HIM and SSA.

Regarding the Fe/Al oxide contents, some sediment samples (5, 1 and 30) contained high levels of well crystallized iron (Fe_d) (Table 12), identified in XRD patterns as hematite (Table 10), However, poorly crystalized iron (Fe_o) was observed to be the main form of Fe in all sediment samples ($Feo/Fe_d > 1$), with the exception of sample 30 (Table 1). This sample, different from all the other samples collected in the subaqueous environment, was taken from an exposed clay deposit located on the lakeshore. Sample 32 was taken from the same location as sample 30, but its Feo/Fed ratio was higher than one, indicating poor drainage on the subsurface (Table 12).

The sediments samples contain proportionally high levels of low reactivity clay minerals, such as kaolinite, with the exception of sample 30 (Table 10). However, these clay minerals present a higher proportion of Al-sheets in their structure when compared with smectite and mica clay minerals, suggesting high P-sorption capacity (GÉRARD, 2016). The HIM clay minerals had great quantities of Al polymers occluded into the interlayer (Table 10), according to the Al_d contents found, especially in samples 17 (Pokegama River) and 23 (Nemadji River) (Table 12). It is known that Al-octahedral sheets of 2:1 clay minerals can contribute to P fixation in soils (GÉRARD, 2016) and this fact explains the negative relation observed between F1 P-form and Al_d presented in Table 6. However, it is important to consider that P-sorption capacity is also pH-Eh dependent, Gérard (2016) shows that clay minerals, depending on the ionic strength and the composition of the clay mineral, tend to show maximum P-sorption capacity between pH 4 and 7, Beyond this pH range, the P-sorption capacity is reduced in relation to the ionic strength and composition of the clay mineral. In Lake Superior, where the pH is approximately 7.8 (COONEY et al., 2018), minerals such as dolomite and calcite play an important role in P-sorption, which can explain why sample 32 presents twice the F5 form of P than sample 30 (Table 11).

Zhang et al. (2016), studying the characteristics of P in surface sediments of a limnetic ecosystem in Eastern China, verified that the concentration of HCl-P (F5 phase in P-sequential fractionation) increases, while labile P-forms decrease with pH elevation (pH 7 to 8), suggesting that P bioavailability would increase if sediment pH decreases (pH < 7). Bahnick (1977), evaluating phosphate releases under aerobic conditions using SLS sediment samples from clay deposits along the Nemadji River and SLS shoreline, observed that P-release from sediments was pH-dependent, Comparing the P-released under pH 7.4-7.8 and pH 5.9-6.0, the latter increased by a factor of 2.

According to Table 11, most of the P found in SLS sediments is likely not available to the aquatic biota (represented by F4 and F5 P-phase in the sediments). The most labile P form (F1) associated with adsorbed sites represents less than 2% of the total P. This potentially explains why the dissolved P in the SLS water column is very low [0.02 to 0.06 mmol L^{-1} (BAEHR; MCMANUS, 2003)] as previously commented. Despite the fact that the TP concentration determined in the three sediment sources can be considered high [minimum of 572 mg kg^{-1} (sample 3 - CB) and maximum of 2,146 mg kg^{-1} (sample 11 - Grab 8) (Table 11)], more than 80% of sediment total-P is associated with the F4 and F5 P-phases, which are considered less available to the aquatic biota, The F4 and F5 P-phases, according to the methodology used in this study, represent P associated with organic matter and Ca phosphate minerals, respectively, where the latter is considered strongly retained by the sediment (LUKKARI et al., 2007; WANG et al., 2013). These results are consistent with P-fraction distribution expected to occur in Inseptisols and Alfisols (the two predominant soil classes in the SLS basin), where more than 80% of total-P is distributed in less labile forms (YANG; POST, 2011). In lacustrine surface sediments, the less soluble P-forms (HCl-P and NaOH-P) are also considered to be the predominant P-forms (FYTIANOS; KOTZAKIOTI, 2005; ABDEL-SATAR; SAYED, 2010; ZHANG et al., 2016).

The different P forms and the geochemical characterization of sediments (Table 13) showed that the F1 (P-loosely sorbed), the F2 (P-redox sensitive) and the F3 (P-exchangeable with OH) phases presented a positive relation with Fe_o, suggesting that poorly crystalized Fe is controlling the P-sorption process, especially in the F2 (r =

0.78**) and F3 (r = 0.76**) phases. With the exception of sample 30 (LS Bank Erosion-red clay), all other sediment samples presented a Fe_o/Fe_d ratio higher than one. Poorly crystalized Fe forms (Fe_o) exhibit higher P-sorption and faster P-sorption rates (WANG et al., 2013; BORTOLUZZI et al., 2013). P release from Fe oxides associated with the F2 phase commonly occurs in eutrophic lakes with anoxic hypolimnia (MORTIMER, 1971), which is different from the highly oxic SLS environment due to low oxygen demand related to subsequent low annual loading of organic matter input (THOMAS; DELL, 1978).

On the other hand, the Al extracted by dithionite (Al_d) presented a strong and negative relationship (r = –0.68**) with the F1 form (P-loosely sorbed). This means that Al_d in the sediments can potentially contribute to remove dissolved P from SLS waters. This interpretation is attributed to the mineralogical composition and geochemical characteristics of sediments (Tables 10 and 12). According to Table 12, the Al_d and Al_2O_2 forms were notably higher in the input load (Pokegama and Nemadji River) when compared with the lake sediments. This suggests that, despite the predominance of aerobic conditions in the bed of the SLS environment, bed sediments are submitted to a diagenesis process such as observed previously by Dell (1972ab). However, different from Dell (1972ab), HIM was found in only two of four bed sediment samples, while Dell (1972ab) verified HIM presence in all sediment samples studied. This suggests that the diagenesis process can occur in different ways or intensities depending on the mineral involved. For instance, clay minerals can be easily altered or formed in response to the chemical elements cycling in mangrove conditions (ANDRADE et al., 2018a).

The F4 phase (P-organic) presented a significant and positive relation with particle size (D_{50}) and no relation with TOC, contrary to initial expectation (Table 13). However, Figure 8 shows that SSA is largely associated with organic matter, where most of the sediment P was found (F4 phase of sequential fraction analysis). This highlights the importance of a better understanding of organic forms of P.

The P-bound with carbonates (F5 phase), which represents 34% of total-P of different sediment sources, was not correlated with any of the five geochemical sediment parameters evaluated (Table 13). However, in the mineralogical study using X-ray diffraction (Figure 7; Table 10), two minerals potentially associated with P were identified. Dolomite was identified in all nine samples, while calcite was observed in samples 1 (FWM), 5 (SteC), and 32 (LS Bank Erosion –white clay), Dell (1973), working with glaciolacustrine sediment in Lake Superior, also identified the presence of calcite and dolomite, whose source comes from red tills surrounding the lake that contain abundant calcite and dolomite derived from Paleozoic rocks (PETERSEN; CHESTERS; LEE, 1966). The bioavailability of P associated with phase F5 (P-bound with carbonates) is unlikely, considering that the dissolution of Ca minerals implies a sharp decrease in pH that is unlikely to occur in SLS waters.

The P-rem showed negative correlation with SSA (r = -0.62*) (Table 13), Low values of P-rem are associated with a high sediment P-reactivity and vice versa. The highest P-rem value (39 mg L^{-1}) was observed in sample 30 (LS Bank Erosion-red clay) and the smallest value (14 mg L^{-1}) was observed in sample 23 (Nemadji River). Most probably, this contrast can be explained by high and low values of SSA (150 m^2 g^{-1} vs, 16 m^2 g^{-1}) verified in sample 23 (Nemadji River) and 30 (LS Bank Erosion-red clay), respectively (Table 12).

The methods utilized in this study (sequential P extraction associated with sediment mineralogical composition and geochemical characterization) show that the bioavailability of P from sediments (defined by the sum of available P and the potential P that can be transformed into available P by natural physical and chemical processes) is very low in SLS. The bioavailability of phase F5 (Ca-P) is not expected to occur without drastic aqueous pH reduction. The bioavailability of organic P is dependent on bacterial mineralization and organic matter decomposition, which has been poorly explored in SLS sediments. On the other hand, bacterial mineralization is also associated with water temperature, which is increasing in SLS (AUSTIN; COLMAN, 2008), suggesting microbiological activity and thus bioavailability of organic P could increase.

Finally, using information about the F1 (P-loosely sorbed) concentration of samples 30-LS Bank Erosion-red clay and 23-Nemadji River [7 and 6 mg kg^{-1}, respectively (Table 11)] and information from the literature about shoreline erosion from the western portion of Lake Superior [around 8 × 106 metric ton $year^{-1}$ (BAHNICK; ROUBAL, 1975; SYDOR, 1976); and Nemadji River suspended sediment flux [around 2.5 × 105 metric ton $year^{-1}$ (SYDOR, 1976)], the potential annual load of P-loosely sorbed from the shoreline and Nemadji River are estimated to be around 56 and 2.5 metric tons, respectively. Considering the P contribution from SLS resuspended sediment [estimated around 1.6 × 106 metric tons $year^{-1}$ (STORTZ; CLAPPER; SYDOR, 1976)], and an average F1 (P-loosely sorbed) concentration of lake sediments of 14 mg kg^{-1}, the potential annual load of P-loosely sorbed is estimated to be around 22 metric tons $year^{-1}$, Adding the three important P sources, the total annual load of P loosely sorbed is around 81metric tons.

6.6 Conclusions

The mineralogical geochemical and P-sequential analyses highlight the role of sediments in the P-cycle in Lake Superior. Despite substantial P input due to shoreline erosion, only a small portion of this P is ultimately available to biota, Labile P forms (F1 and F2) represent less than 10% of the total-P contained in lake sediments, input load and shoreline erosion sediments. Most of the P in the sediment is associated chemically with Ca carbonate (F5 form) and organic matter (F4 form), where P-availability of the first depends on the dissolution of Ca minerals, while the second is poorly understood and depends on microbiological activity to be used by the aquatic biota.

In terms of sediment P reactivity, SLS sediments contain minerals with high chemical reactivity with potential to adsorb P, such as Al oxides, poorly crystalized Fe oxides, and clay minerals (e.g. chlorite, smectite, mix-layer 2:1/1:1 minerals and hydroxy-Al interlayer mineral). In addition, the sediment P reactivity may drastically increase in the presence of organic matter due to its contribution to the SSA. These facts suggest that sediments actually decrease lake P, acting as a sink where P can be stored, which helps to explain the very low concentration of P found in the SLS aquatic system.

7 CONSIDERAÇÕES FINAIS

Uma das grandes preocupações dos pesquisadores quando estudam os sedimentos é qual será seu comportamento no ambiente aquático. Os sedimentos podem atuar como fonte ou dreno de contaminantes? Esse questionamento pode ser respondido com a utilização de técnicas de geoquímica e mineralogia. Neste sentido, a literatura aponta que os estudos sobre sedimentos apresentam grande potencial quando utilizam diversas técnicas geoquímicas e mineralógicas. Nesse sentido aqui, foram aplicados algumas dessas técnicas em dois estudos de campo, um com sedimentos ricos em cobre e outro rico em fósforo.

Os sedimentos em suspensão do Lago Superior dos EUA agem como dreno de fósforo do lago, retirando da água quantidades significantes de P. Esse comportamento de dreno de P é explicado pela composição mineral dos sedimentos (óxidos de Al, óxidos de Fe mal cristalizados, e argilominerais como clorita, esmectita, argilominerais com hidroxi-alumínio entrecamada), esses argilominerais são capazes de prender o P com força suficiente para reduzir sua bioatividade no lago.

Os sedimentos em suspensão estudados do Brasil agem como fonte de cobre para o riacho. Os minerais presentes nos sedimentos (mica, caulinita, ilita, rutilo, hematita, calcita, magnesita, albita e anortita) além dos minerais de cobre (wooldridgeite e cyanochroite) apresentam-se carregados de cobre nas 3 formas estudadas: total (maior concentração), trocável e solúvel (menores concentrações. Apesar dos teores de cobre no riacho estarem abaixo dos níveis indicados elo CONAMA (órgão ambiental regulador), os sedimentos estão carregando altos teores de cobre, formando um estoque perigoso e com altos riscos quando o sedimento for depositado em ambiente reduzido/bentônico. O lago Guaíba é onde os sedimentos transportados por esse riacho serão depositados ao fim de seu deslocamento. Essa mudança de ambiente (potencial redox, pH, temperatura água, etc) pode promover um aumento na dessorção de cobre dos sedimentos, aumentado a biodisponibilidade, e por consequência causando sérios danos a biota. Além disso, o Lago Guaíba é um reservatório de água que abastece a região metropolitana de Porto Alegre, com mais de 2 milhões de habitantes.

A composição mineral dos sedimentos é fator determinante do comportamento dos sedimentos nos ambientes e ajuda explicar o processo de transferência e contaminação de corpos d´água. A utilização de conhecimentos em mineralogia associada à geoquímica dos sedimentos contribui para o entendimento do potencial de poluição dos sedimentos. Esse conhecimento contribuirá de maneira significativa para entendermos quais os sistemas agrícolas de produção que possuem maior risco ambiental e que necessitará de medidas mitigadoras ou mesmo restrições de produção em seus ambientes.

8 CONCLUSÃO GERAL

A agricultura é uma atividade que se destaca no Brasil e nos EUA como fontes primárias de divisas para os países. São gerados bilhões de dólares de arrecadação, milhões de empregos, e ambos países tem sido destaque no mundo todo como os principais países produtores de alimentos.

A alta produtividade das culturas é suportada pelo aumento do aporte de fertilizantes ao solo, e também o aumento da aplicação de defensivos, visando proteger as culturas de fungos, bactérias e insetos principalmente. Ambos os crescimentos estão contribuindo para o enriquecimento das partículas do solo com fertilizantes e defensivos. Essas partículas carregadas quando transferidas das lavouras para o ambiente aquático, podem se tornar fonte de contaminantes (fonte), ou sequestrar da água moléculas ou íons (dreno) estocando tais contaminantes no fundo dos rios e lagos, os quais podem ter sua água utilizada na própria agricultura, indústria ou consumo humano.

Sistemas agrícolas mais intensivos tendem a produzir sedimentos mais carregados. Monitorar com frequência os sedimentos dessas áreas de intensa produção deve ser um preceito básico para manutenção da qualidade dos ambientes próximos. Mais necessário do que as ações de mitigação dos problemas causados pelos sedimentos agrícolas contaminados, é o monitoramento dos solos, dos seus teores máximos de íons e moléculas, para que seja evitada ou reduzida a transferência desses sedimentos para ambientes aquáticos.

Nos EUA existem mapas das áreas de risco de contaminação por sedimentos dos mananciais, tendo um rigoroso controle das atividades ao seu redor. No Brasil é eminente a criação de um sistema de alerta para áreas com maior risco de contaminação das águas pelos sedimentos. Criação de um mapa de risco das atividades agrícolas, urbanas ou industriais próximos aos mananciais de água, que utilizem informações precisas, associando o potencial de erosão do solo, o nível de contaminação das moléculas e íons, e o uso e manejo do território.

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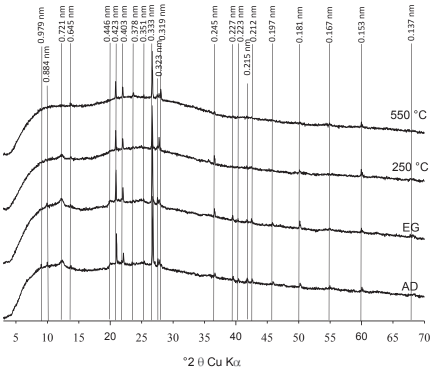
APÊNDICE

APÊNDICE I - X-ray diffraction patterns from oriented sediment samples



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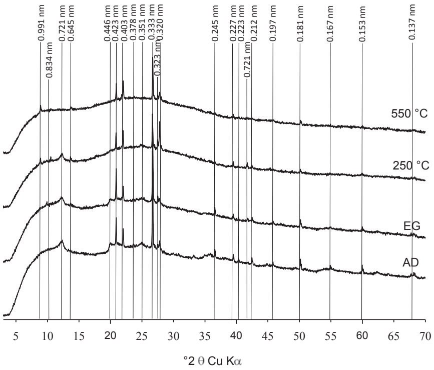

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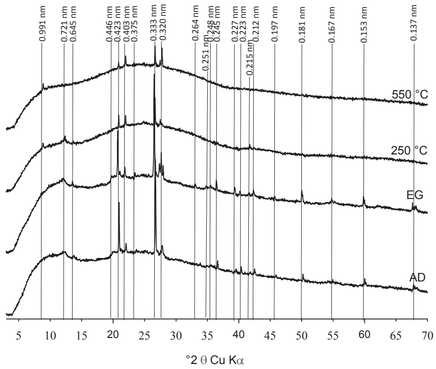

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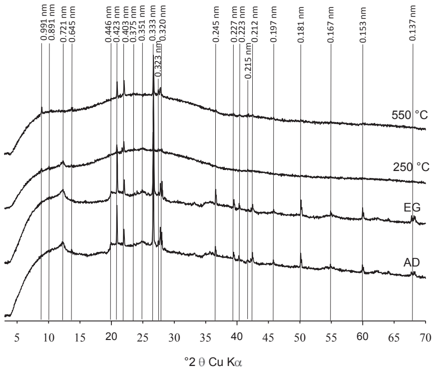

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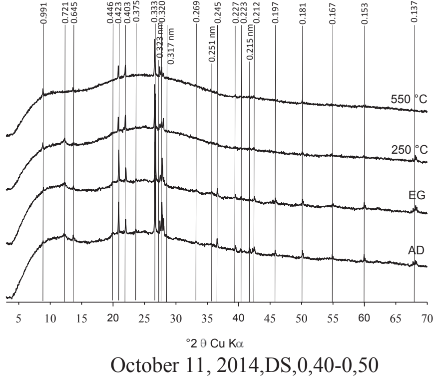

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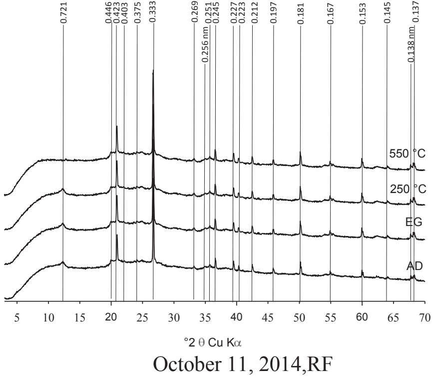

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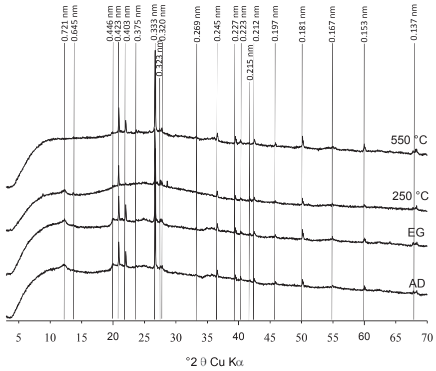

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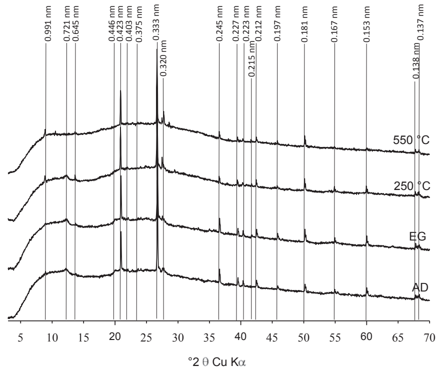

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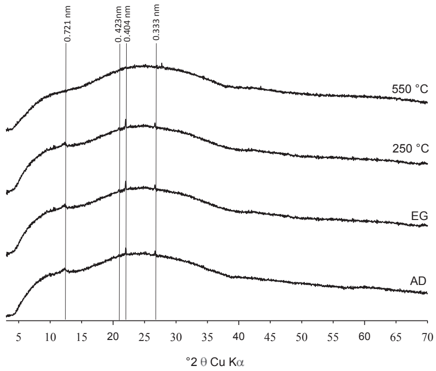

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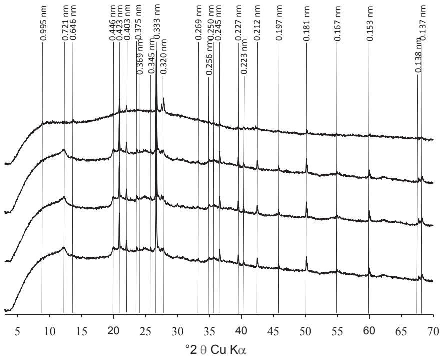

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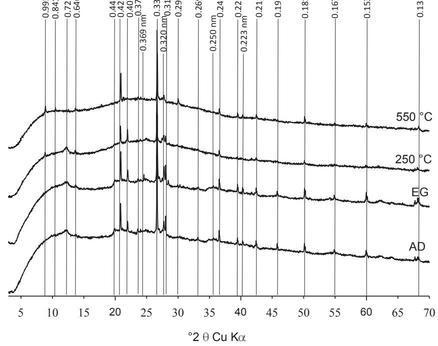

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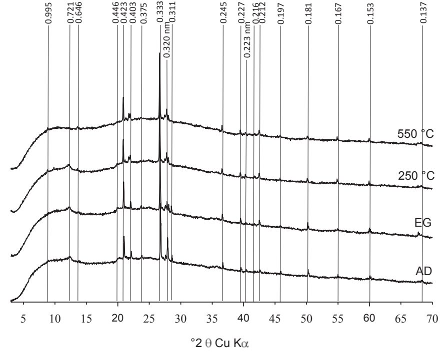

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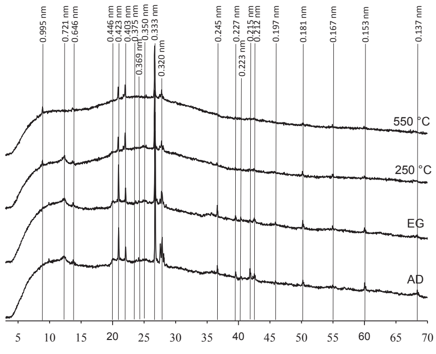

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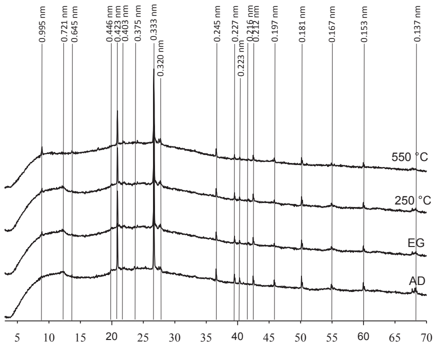

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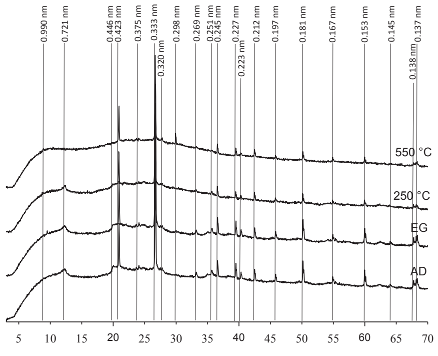

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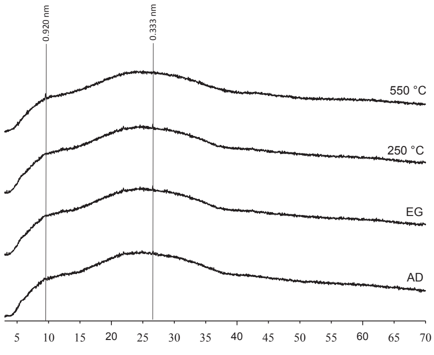

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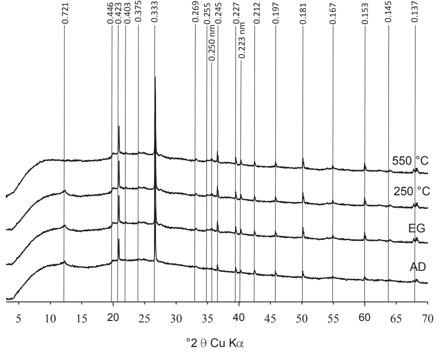

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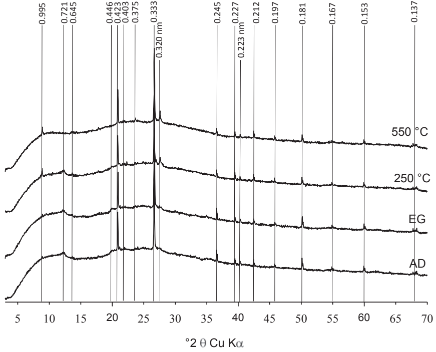

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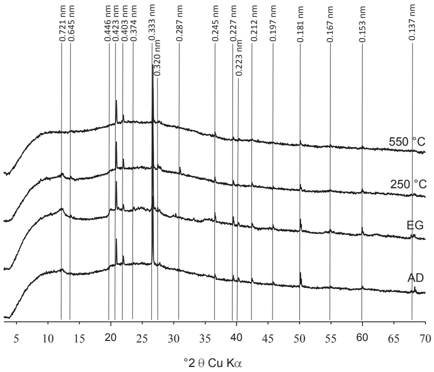

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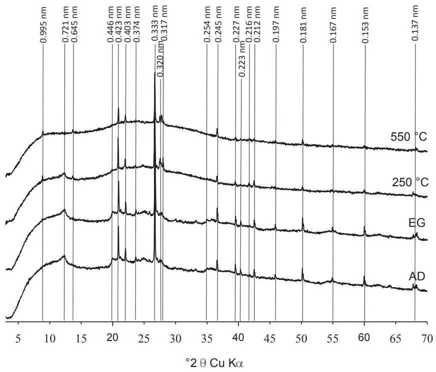

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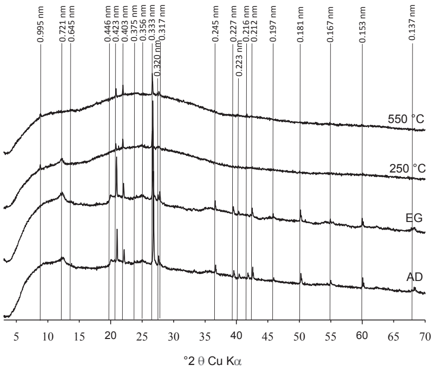

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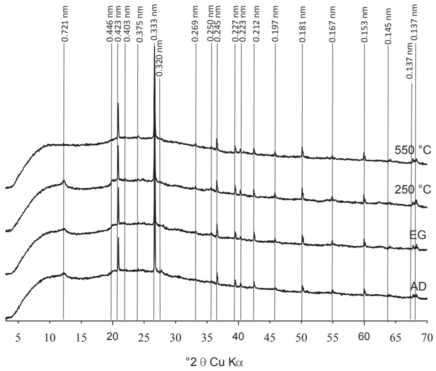

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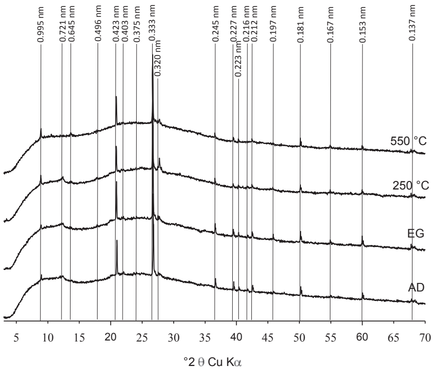

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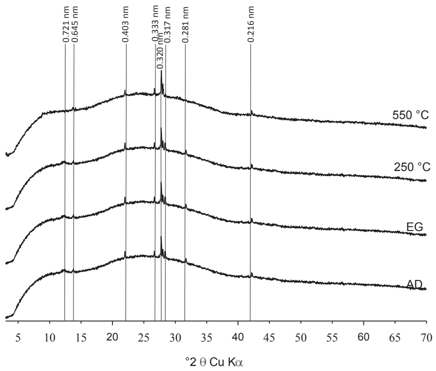

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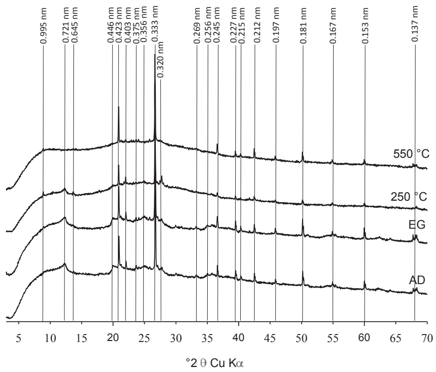

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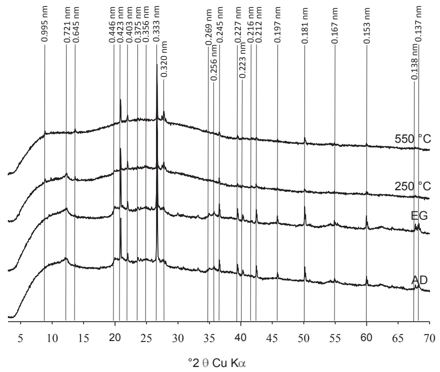

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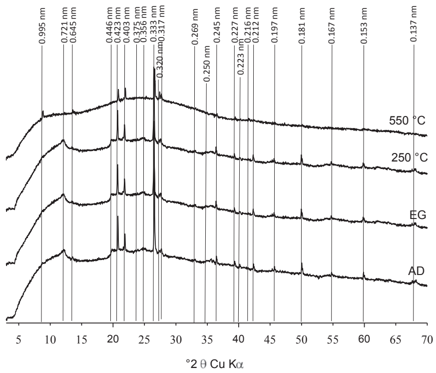

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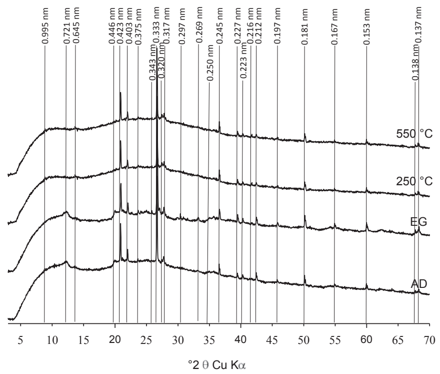

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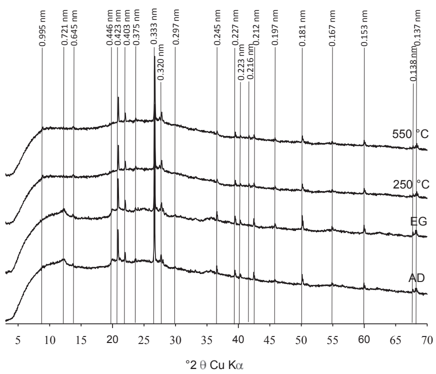

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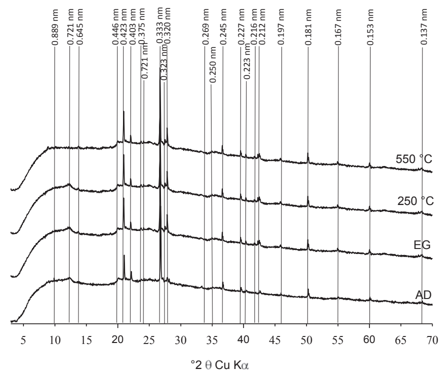

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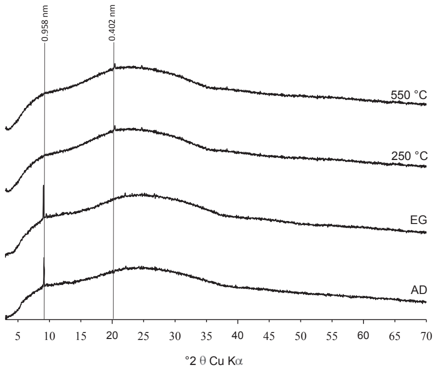

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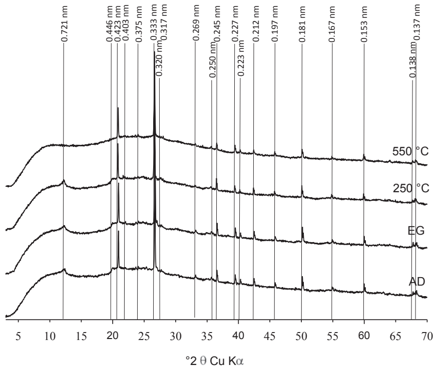

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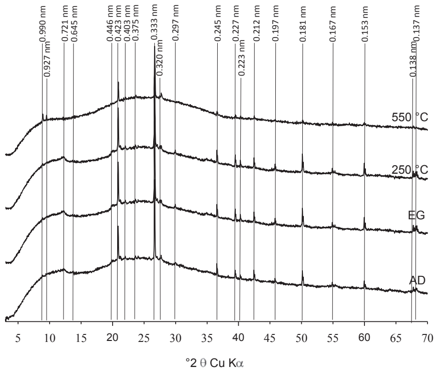

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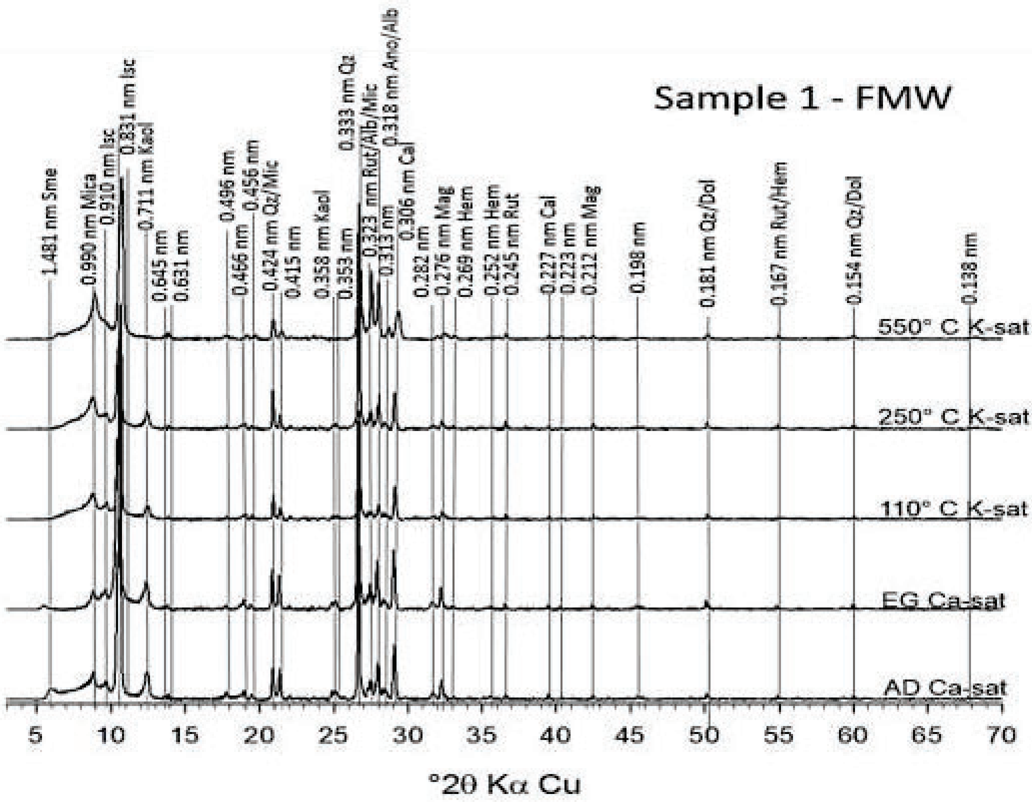

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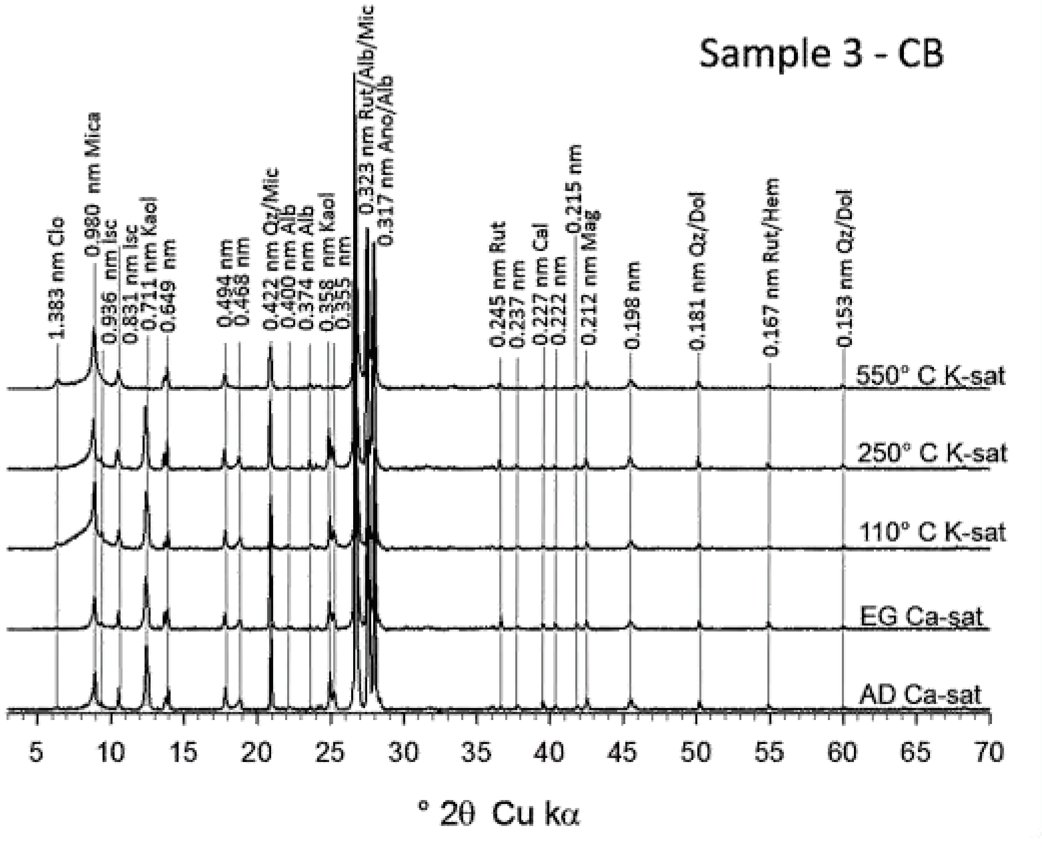

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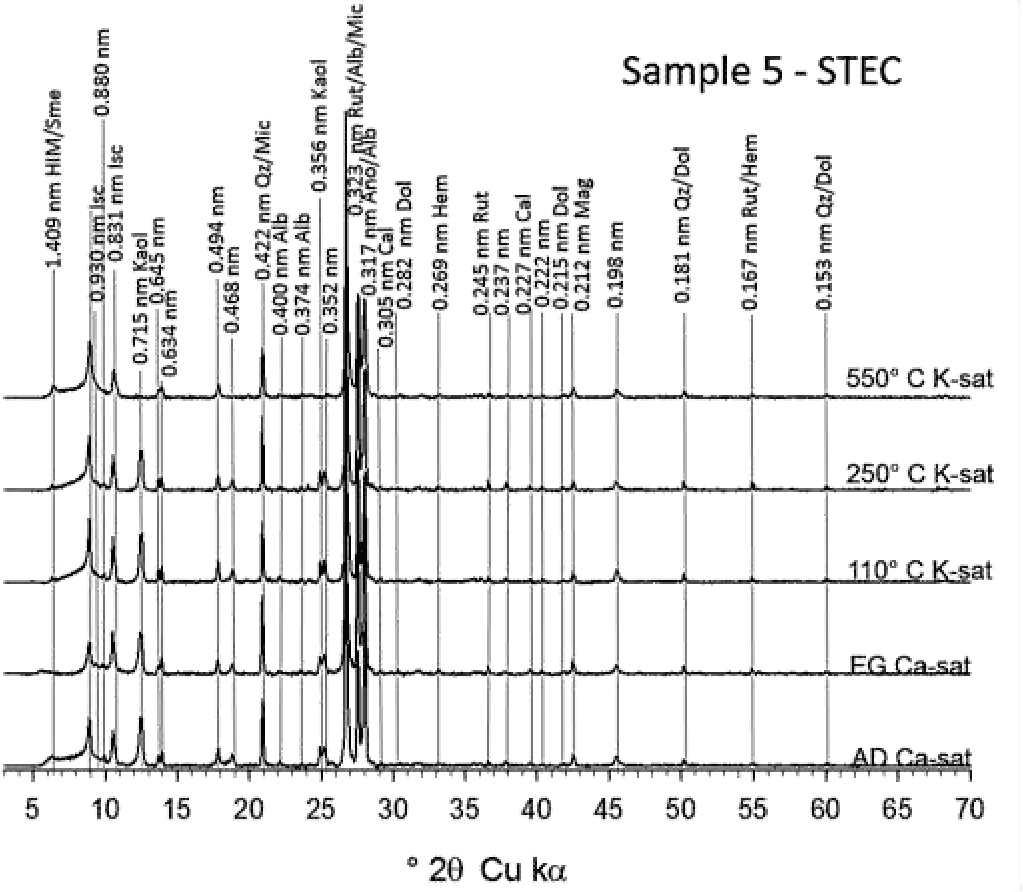
Sample 5 - STEC
1.409 nm HIM/Sme
0.930 nm Isc
0.880 nm
0.831 nm Isc
0.715 nm Kaol
0.645 nm
0.634 nm
0.494 nm
0.468 nm
0.422 nm Qz/Mic
0.400 nm Alb
0.374 nm Alb
0.356 nm Kaol
0.352 nm
0.323 nm Rut/Alb/Mic
0.317 nm Ano/Alb
0.305 nm Cal
0.282 nm Dol
0.269 nm Hem
0.245 nm Rut
0.237 nm
0.227 nm Cal
0.222 nm
0.215 nm Dol
0.212 nm Mag
0.198 nm
0.181 nm Qz/Dol
0.167 nm Rut/Hem
0.153 nm Qz/Dol
550° C K-sat
250° C K-sat
110° C K-sat
EG Ca-sat
AD Ca-sat
5
10
15
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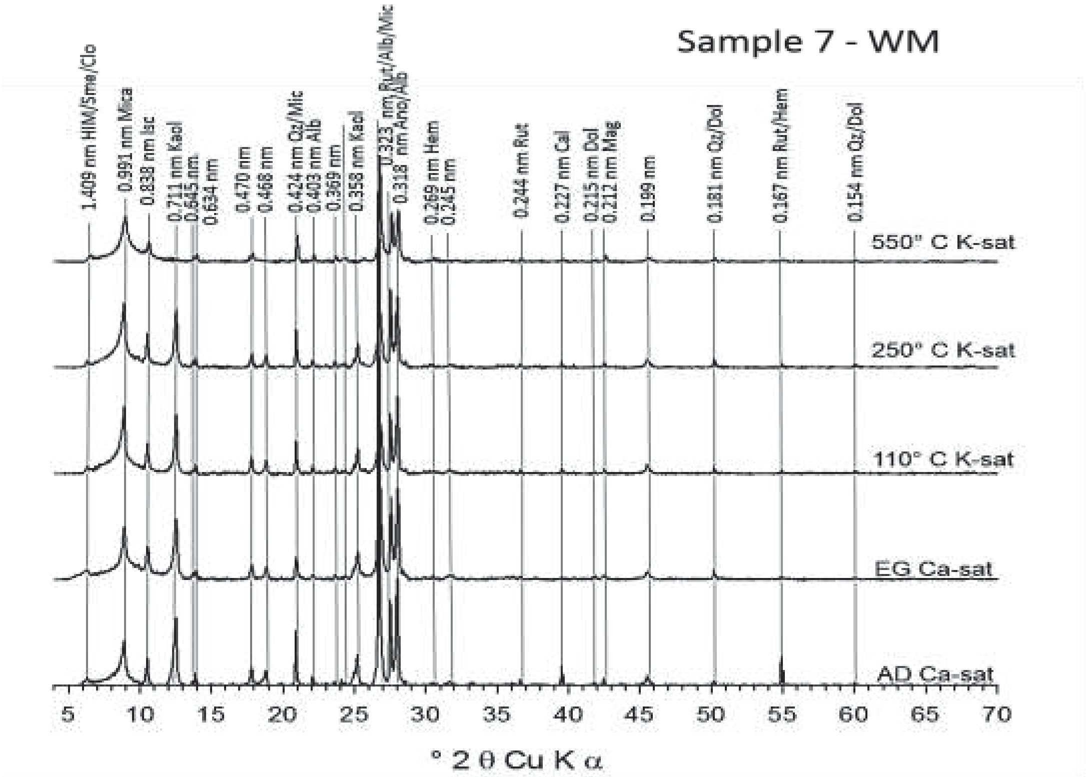
35
40
45
50
55
60
65
70
° 2θ Cu kα


Sample 7 - WM
1.409 nm HIM/Sme/Clo
0.991 nm Mica
0.838 nm Isc
0.711 nm Kaol
0.645 nm
0.634 nm
0.470 nm
0.468 nm
0.424 nm Qz/Mic
0.403 nm Alb
0.369 nm
0.358 nm Kaol
0.323 nm Rut/Alb/Mic
0.318 nm Ano/Alb
0.269 nm Hem
0.245 nm
0.244 nm Rut
0.227 nm Cal
0.215 nm Dol
0.212 nm Mag
0.199 nm
0.181 nm Qz/Dol
0.167 nm Rut/Hem
0.154 nm Qz/Dol
550° C K-sat
250° C K-sat
110° C K-sat
EG Ca-sat
AD Ca-sat
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10
15
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25
30
35
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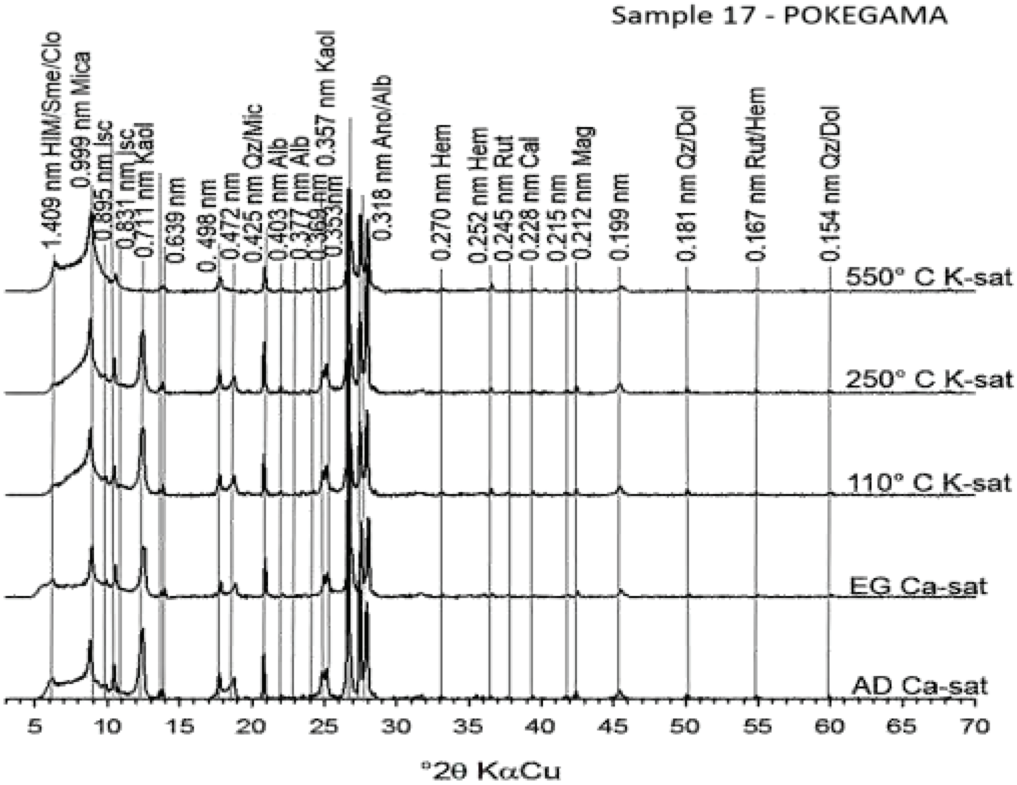
55
60
65
70
° 2 θ Cu K α


Sample 17 - POKEGAMA
1.409 nm HIM/Sme/Clo
0.999 nm Mica
0.895 nm Isc
0.831 nm Isc
0.711 nm Kaol
0.639 nm
0. 498 nm
0.472 nm
0.425 nm Qz/Mic
0.403 nm Alb
0.377 nm Alb
0.369 nm
0.353nm
0.357 nm Kaol
0.318 nm Ano/Alb
0.270 nm Hem
0.252 nm Hem
0.245 nm Rut
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550° C K-sat
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110° C K-sat
EG Ca-sat
AD Ca-sat
5
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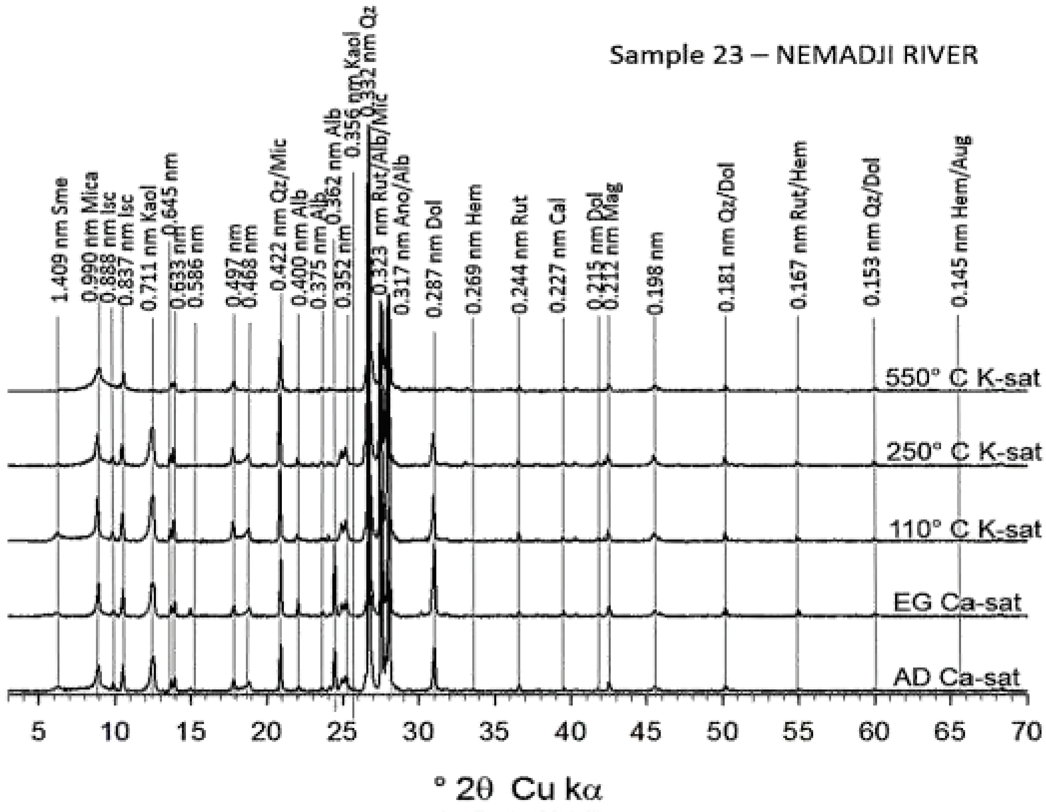
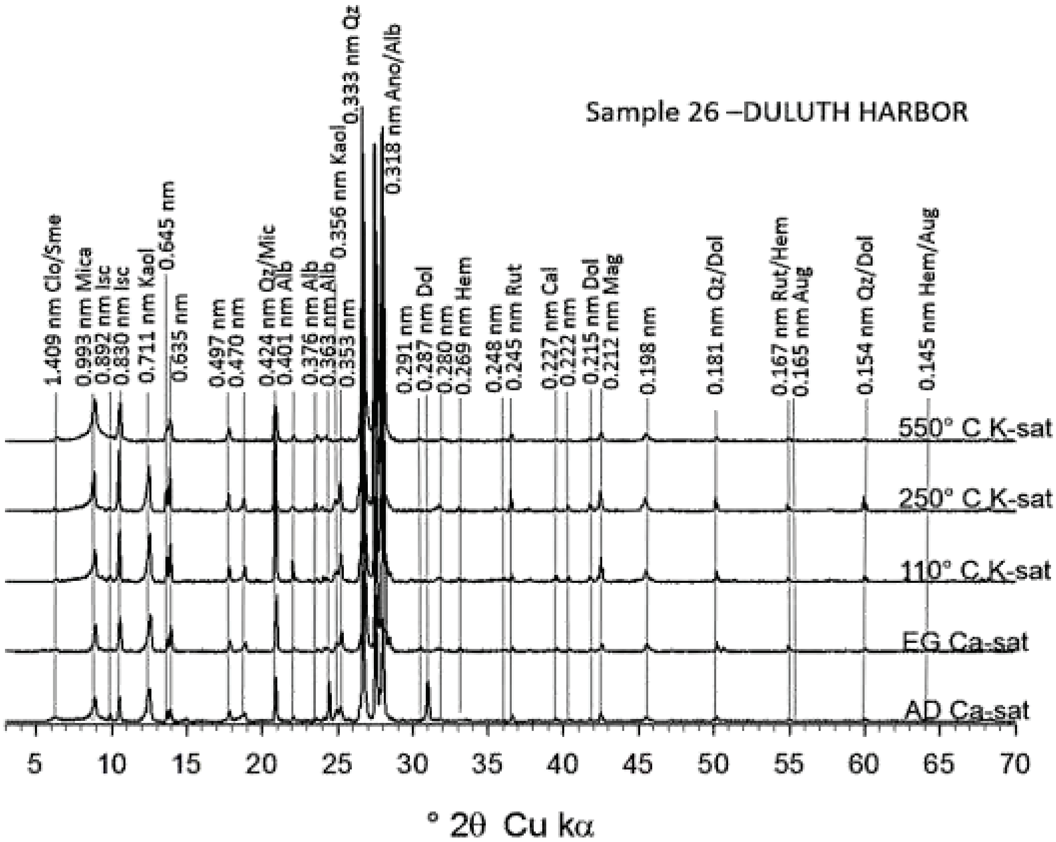
60
65
70
°2θ KαCu


Sample 23 – NEMADJI RIVER
1.409 nm Sme
0.990 nm Mica
0.888 nm Isc
0.837 nm Isc
0.711 nm Kaol
0.645 nm
0.633 nm
0.586 nm
0.497 nm
0.468 nm
0.422 nm Qz/Mic
0.400 nm Alb
0.375 nm Alb
0.362 nm Alb
0.352 nm
0.356 nm Kaol
0.332 nm Qz
0.323 nm Rut/Alb/Mic
0.317 nm Ano/Alb
0.287 nm Dol
0.269 nm Hem
0.244 nm Rut
0.227 nm Cal
0.215 nm Dol
0.212 nm Mag
0.198 nm
0.181 nm Qz/Dol
0.167 nm Rut/Hem
0.153 nm Qz/Dol
0.145 nm Hem/Aug
550° C K-sat
250° C K-sat
110° C K-sat
EG Ca-sat
AD Ca-sat
5
10
15
20
25
30
35
40
45
50
55
60
65
70
° 2θ Cu kα


Sample 26 –DULUTH HARBOR
1.409 nm Clo/Sme
0.993 nm Mica
0.892 nm Isc
0.830 nm Isc
0.711 nm Kaol
0.645 nm
0.635 nm
0.497 nm
0.470 nm
0.424 nm Qz/Mic
0.401 nm Alb
0.376 nm Alb
0.363 nm Alb
0.356 nm Kaol
0.353 nm
0.333 nm Qz
0.318 nm Ano/Alb
0.291 nm
0.287 nm Dol
0.280 nm
0.269 nm Hem
0.248 nm
0.245 nm Rut
0.227 nm Cal
0.222 nm
0.215 nm Dol
0.212 nm Mag
0.198 nm
0.181 nm Qz/Dol
0.167 nm Rut/Hem
0.165 nm Aug
0.154 nm Qz/Dol
0.145 nm Hem/Aug
550° C K-sat
250° C K-sat
110° C K-sat
EG Ca-sat
AD Ca-sat
5
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15
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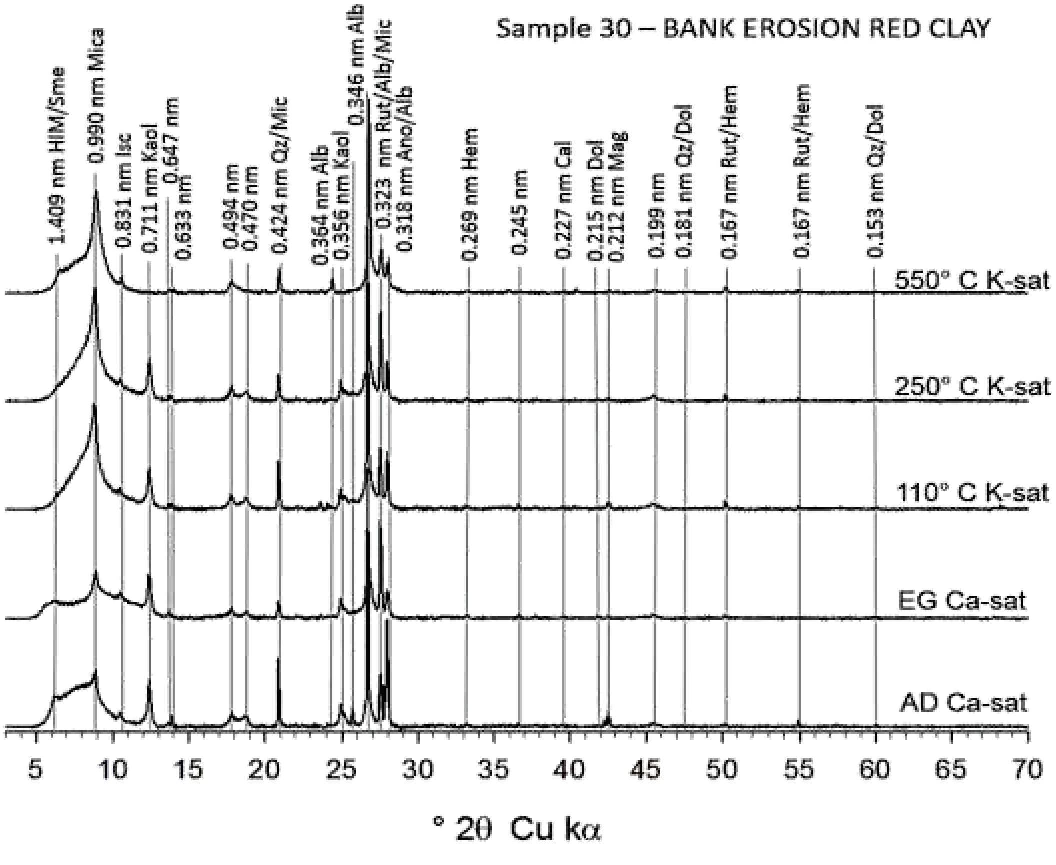
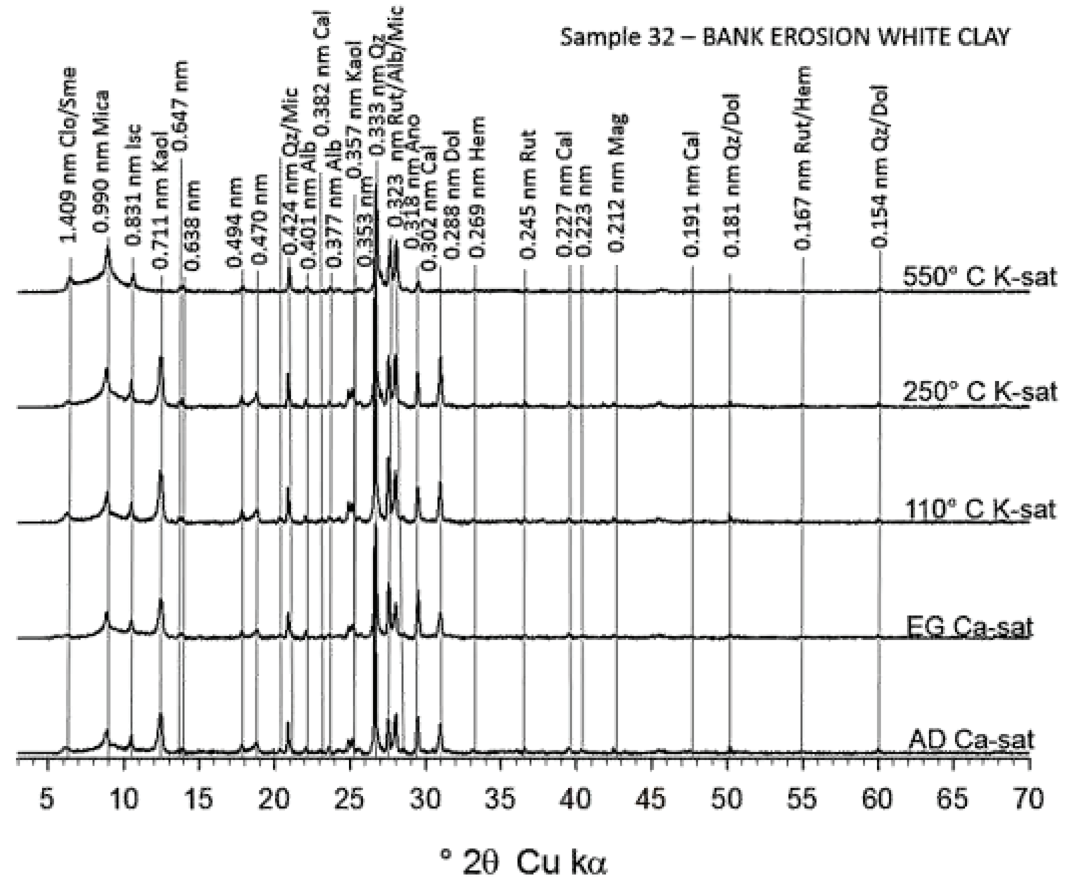
45
50
55
60
65
70
° 2θ Cu kα


Sample 30 – BANK EROSION RED CLAY
1.409 nm HIM/Sme
0.990 nm Mica
0.831 nm Isc
0.711 nm Kaol
0.647 nm
0.633 nm
0.494 nm
0.470 nm
0.424 nm Qz/Mic
0.364 nm Alb
0.356 nm Kaol
0.346 nm Alb
0.323 nm Rut/Alb/Mic
0.318 nm Ano/Alb
0.269 nm Hem
0.245 nm
0.227 nm Cal
0.215 nm Dol
0.212 nm Mag
0.199 nm
0.181 nm Qz/Dol
0.167 nm Rut/Hem
0.167 nm Rut/Hem
0.153 nm Qz/Dol
550° C K-sat
250° C K-sat
110° C K-sat
EG Ca-sat
AD Ca-sat
5
10
15
20
25
30
35
40
45
50
55
60
65
70
° 2θ Cu kα



Notes: Lake sediments: 1 (FWM), 3 (CB), 5 (SteC), 7 (WM), Input load sediments=17 (Pokegama River), 23 (Nemadji River), 26 (Duluth Harbor), 30 (LS Bank Erosion- red clay) and 32 (LS Bank Erosion-white clay). Minerals: HIM, hydroxy-Al interlayer mineral; Chl, chlorite; Sme, smectite; ISC, interstratified clay; Mica, mica; Mic, microcline; Kao, kaolinite; Qz, quartz; Alb, albite; Dol, dolomite; Cal, calcite; Hem, hematite; Rut, rutile; Ano, anorthite; Mag, magnesite; Aug, augite.

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