UNIVERSIDADE FEDERAL DE LAVRAS

GUILHERME LOPES

FITOTECNOLOGIA, DISTRIBUIÇÃO DE ELEMENTOS-TRAÇO E ESPECIAÇÃO DE Zn USANDO EXAFS: ESTUDOS EM ÁREAS DE MINERAÇÃO E METALURGIA

LAVRAS – MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Recursos Ambientais e Uso da Terra, para a obtenção do título de Doutor.

Orientador
Dr. Luiz Roberto Guimarães Guilherme

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APROVADA em 16 de agosto de 2013.

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LAVRAS – MG
2013

A Deus,por me dar forças
para vencer mais essa etapa,

DEDICO.

Aos meus pais, irmãos,
filha e esposa, pelo apoio,
incentivo e carinho,

OFEREÇO.

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RESUMO GERAL

Áreas de mineração contaminadas com elementos-traço (e.g., As, Zn, Cd e Pb) têm sido foco de estudos, visto os efeitos danosos que eles podem causar aos ecossistemas, caso suas concentrações – totais ou biodisponíveis – excedam os limites considerados seguros. Objetivou-se, com esse trabalho, i) avaliar o potencial de plantas (*Brachiaria decumbens*, *Crotalaria spectabilis* e *Stylosanthes* cv. Campo Grande) na fitorremediação, usando subprodutos industriais como amenizantes [lama vermelha (LV) e uma mistura de 75% de LV com 25% de fosfogesso (LVG)], em um solo contendo elevados teores de As, oriundo de uma área de mineração de ouro; ii) avaliar a mobilidade e a especiação de Zn, Pb e Cd, por meio de extrações simples e sequenciais em solos afetados por atividades de mineração e metalurgia de Zn e iii) investigar a dessorção e a especiação de Zn, buscando associar a formação de diferentes fases sólidas de Zn com a fração trocável desse elemento. Com relação ao estudo envolvendo fitorremediação, os amenizantes LV e LVG foram adicionados ao solo contaminado com As, visando elevar o seu pH para 6, tendo as plantas sido cultivadas por 60 dias. Por outro lado, estudos envolvendo extrações simples e sequenciais de Zn, Cd e Pb, bem como especiação de Zn usando espectroscopia de absorção de raios-X (XAS) foram realizados nos solos provenientes de áreas de mineração e metalurgia de Zn. Em geral, o uso de LV e LVG aumentou a produção de matéria seca (MS) e reduziu as concentrações de As na MS das plantas. As plantas de braquiária e crotalária foram consideradas tolerantes ao As, podendo ser empregadas na fitorremediação, especialmente com a utilização do amenizante LVG, devido à vantagem de conter nutrientes (Ca e S oriundos do fosfogesso). O Zn e o Cd foram, principalmente, associados a formas de carbonatos nos solos da área de mineração de Zn, o que não ocorreu no caso do Pb. Os óxidos de Fe e Mn, bem como a fração residual, também tiveram contribuições para o Zn e o Pb nesses solos. Para o solo oriundo da área de metalurgia de Zn, mais de 70% do Zn e do Cd foram associados à fração trocável, mostrando a maior mobilidade e disponibilidade desses metais neste local, comparado aos solos da área de mineração, o que foi comprovado pelos estudos de dessorção. Essa diferença de mobilidade foi explicada pelos resultados de XAS, os quais mostraram que o Zn nos solos da área de mineração ocorre, dentre outras espécies químicas, na forma de alguns precipitados, reduzindo a mobilidade do metal, ao passo que o Zn no solo da área de metalurgia encontra-se associado a materiais fracamente ligados à fase sólida do solo, e, portanto, com grande mobilidade.

Palavras-chave: Contaminação do solo. Subprodutos. Fitorremediação. Mobilidade. Espectroscopia de absorção de raios-X.

GENERAL ABSTRACT

Several mining areas contaminated with trace elements (e.g., As, Zn, Cd, Pb) have been the target of recent studies due to the negative effects that these elements may cause to ecosystems when their concentration – either total or bioavailable – exceed limits considered safe to human health and the environment. In this context, this study aimed to: i) evaluate the potential of three plant species (*Brachiaria decumbens*, *Crotalaria spectabilis*, and *Stylosanthes* cv. Campo Grande) for phytoremediation, using industrial by-products RM and RMG as amendments (red mud – RM – and a mixture of 75% of RM with 25% of phosphogypsum – RMG) in a soil containing high level of As from a gold mining area located in Paracatu, MG; ii) evaluate the mobility and speciation of Zn, Pb, and Cd using single and sequential extractions in soils affected by Zn mining and smelting activities; and, iii) investigate the desorption kinetics and the solid phase speciation of Zn in soils affected by Zn mining and smelting activities, in order to find out which solid phases govern Zn availability and mobility in such soils. In the first study involving the use of a phytotechnology in a gold mining area, the amendments RM and RMG were added to an As-contaminated soil in order to raise its pH to 6. After the incubation time, the tested plants were exposed to As during 60 days. Studies involving single and sequential extractions of Zn, Cd, and Pb as well as Zn speciation using X-ray absorption spectroscopy (XAS) were conducted with soils from a Zn mine, which were contrasted with a tailing sample collected in a Zn smelting site. The use of RM and RMG resulted in increases in the dry matter production and in decreases in As concentrations in the plants. Brachiaria and Crotalaria could be considered as tolerant to As toxicity and thus likely to be employed for phytoremediation purposes, especially with the use of RMG due to its advantage in terms of nutrient supply (Ca and S from phosphogypsum). Zinc and Cd were mainly associated with carbonate forms in the soils from the mining area. The fraction associated with Fe-Mn oxides as well as the residual fraction had also important contributions for retaining Zn and Pb in those soils. For the tailing from the smelting area, more than 70% of Zn and Cd were found in the exchangeable fraction, showing a much higher mobility and availability at this site compared with the soils from the mining area, which was proved with the desorption results. This difference regarding Zn mobility was explained with the XAS results, which showed that Zn in soils from the mining area occurs mainly as Zn-precipitate forms, whereas in the tailing from the smelting area such metal was found in a weakly bound form, being, as a result, quite mobile.

Keywords: Soil contamination. By-products. Phytoremediation. Mobility. X-ray absorption spectroscopy.

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PRIMEIRA PARTE

1 INTRODUÇÃO

Nos últimos anos, o termo sustentabilidade tem recebido grande enfoque, devido, dentre outros aspectos, à preocupação com a qualidade de vida da população, visando garantir essa qualidade para as gerações futuras. Assim, a contaminação ambiental tem gerado preocupações, visto seus efeitos maléficos causados ao meio e, consequentemente, às pessoas que nele se encontram. Nesse contexto, dentre os contaminantes que oferecem riscos ao meio, alguns elementos-traço apresentam alta toxicidade, além de efeitos carcinogênicos e, portanto, recebem atenção especial.

Esses elementos-traço podem ser adicionados ao meio de forma natural ou antropogênica, sendo essa última de elevada relevância em áreas de mineração e metalurgia de metais. Isso é devido ao próprio processo de extração de alguns metais, pois são expostos à superfície do solo materiais de rochas contendo As, Cd, Pb, Zn e outros elementos, os quais contaminam o meio, gerando áreas com solos e corpos d'água contaminados, o que acarreta diversos efeitos danosos.

Em função da contaminação do meio por elementos-traço, especialmente em áreas de mineração (ALLOWAY, 1990), existe, hoje, necessidade de se adequarem tecnologias visando à amenização desse passivo ambiental. Nesse contexto, uma alternativa promissora que vem sendo estudada para a remediação dessas áreas de mineração é a utilização de amenizantes, visando à estabilização para a posterior revegetação da área, ou seja, a fitorremediação (ACCIOLY; SIQUEIRA, 2000) que, quando é acompanhada do uso de amenizantes, pode ser denominada de fitotecnologia.

Tendo em vista a localização de cidades próximo a áreas de mineração, a fitorremediação e/ou fitotecnologia torna-se de grande relevância, visto que a cobertura vegetal propicia uma diminuição no transporte de partículas sólidas via água (chuva-erosão) e ar (vento), além de propiciar também uma redução do fluxo descendente de água no solo, reduzindo riscos de contaminação de lençol freático.

Sabe-se que uma etapa crucial para o estabelecimento de uma eficiente estratégia para a recuperação de áreas contaminadas é o conhecimento inicial da área a ser avaliada, especialmente no que diz respeito aos contaminantes presentes. Nesse contexto, além da determinação dos teores totais desses contaminantes, estudos envolvendo extrações sequenciais são úteis para o conhecimento dos compartimentos sólidos do solo, aos quais os contaminantes estão associados (FILGUEIRAS; LAVILLA; BENDICHO, 2002). Além disso, esses estudos também fornecem informações sobre a mobilidade e a biodisponibilidade do elemento avaliado (HEJABI; BASAVARAJAPPA, 2013).

Além de procedimentos de extrações sequenciais, com a espectroscopia de absorção de raios-X (XAS) aplicada a solos também se pode realizar a especiação química de contaminantes na fase sólida (NACHTEGAAL et al., 2005; ROBERTS; SCHEINOST; SPARKS, 2002). Além disso, XAS fornece informações detalhadas impossíveis de serem obtidas por extrações sequenciais, as quais têm algumas desvantagens (CALMANO; MANGOLD; WELTER, 2001) que são contornadas com o uso de XAS. Por fim, ressalta-se que a caracterização detalhada de solos contaminados por metais, por meio de XAS, é de suma importância para dar suporte ao entendimento da ocorrência de uma maior ou menor mobilidade do metal nessas áreas.

De acordo com o exposto, o presente trabalho foi realizado com os seguintes objetivos: i) avaliar o potencial de espécies de plantas para o emprego da fitotecnologia, usando subprodutos industriais como amenizantes, em um solo contaminado com As, oriundo de uma área de mineração de ouro (trabalho apresentado no artigo 1); ii) avaliar a mobilidade e a especiação de Zn, Pb e Cd por meio de extrações simples e sequenciais em solos afetados por atividades de mineração e metalurgia de Zn (trabalho apresentado no artigo 2) e iii) investigar a cinética de dessorção e especiação de Zn, usando um sistema de agitação com fluxo (*stirred-flow*) e a técnica de XAS, respectivamente (trabalho apresentado no artigo 3). O foco principal é procurar entender como o uso de diferentes amenizantes ou a formação de diferentes fases sólidas de elementos-traço de relevância em área de mineração e metalurgia pode afetar a disponibilidade e a mobilidade desses elementos nos ecossistemas, no intuito de torná-los mais aptos ao desenvolvimento de plantas e seja possível revegetar essas áreas.

2 REFERECIAL TEÓRICO

2.1 Contaminação do solo e técnicas de remediação

A contaminação do meio, em especial a do solo, vem sendo cada vez mais estudada, pois pode apresentar sérios riscos à saúde humana e à qualidade do ambiente (GUILHERME, 1999). Nesse contexto, vários são os poluentes que podem ser encontrados no solo, destacando-se, dentre eles, os elementos-traço. Muitos desses elementos são considerados essenciais para plantas e animais. Contudo, mesmo elementos considerados essenciais, como o Zn, podem, dependendo das condições, ser encarados como poluentes por causarem toxidez quando em elevadas concentrações.

De acordo com Sparks (2003), o termo elementos-traço tem sido utilizado para definir metais catiônicos e oxiânions que ocorrem em concentrações normalmente menores que 1 g kg^{-1}. As fontes de elementos-traço para os solos podem ser tanto naturais como antropogênicas. Dentre as naturais, destacam-se o intemperismo de rochas e minerais e as emissões vulcânicas, ao passo que as principais fontes antropogênicas são os aterros sanitários; as adições de corretivos, fertilizantes, pesticidas e as atividades de mineração e metalurgia de metais.

Sabe-se que a atividade mineradora tem importância crucial para a obtenção de materiais necessários à fabricação de bens indispensáveis ao homem, além de aumentar significativamente a geração de empregos. Entretanto, tais atividades contribuem de forma expressiva para a incorporação de elementos tóxicos em elevadas concentrações no ambiente. É por essa razão que altos teores de elementos-traço são frequentemente encontrados em solos afetados por áreas de mineração e metalurgia de metais, o que resulta em considerável contaminação do solo (ALLOWAY, 1990).

De acordo com o exposto e tendo em vista o elevado risco que os elementos-traço oferecem à população, o desenvolvimento de tecnologias visando à remediação de áreas contaminadas por elementos-traço, em especial as afetadas por atividades de mineração e metalurgia de metais, é de suma importância para a redução dos danos advindos dessa contaminação. Nesse contexto, buscando manter o desenvolvimento das tecnologias geradas pela atividade mineradora e, paralelamente, diminuindo os efeitos negativos gerados por essas atividades, é que são desenvolvidas estratégias para remediar tais áreas contaminadas.

Várias estratégias ou técnicas de remediação podem ser empregadas, a exemplo da lavagem do solo, eletrocinética, vitrificação, solidificação, escavação, fitorremediação e biorremediação. Contudo, dentre essas estratégias, a estabilização da área usando amenizantes, seguida pelo uso de plantas tolerantes ou hiperacumuladoras (fitotecnologia), é considerada uma técnica bastante promissora (ACCIOLY; SIQUEIRA, 2000). Assim, diversos materiais têm sido testados como amenizantes para a imobilização de elementos-traço em solos. Exemplos desses materiais incluem calcário (MENCH et al., 1994), zeólitas (OSTE; LEXMOND; RIEMSDIJK, 2002), óxidos de ferro e manganês (MENCH et al., 1994) e lama vermelha (COSTA et al., 2008).

No caso específico da lama vermelha, um resíduo gerado em grandes quantidades na extração do alumínio a partir da bauxita, tem sido demonstrada, em estudos, a elevada capacidade desse material, o qual é alcalino e rico em óxidos de Fe e Al, em adsorver os mais variados tipos de elementos-traço (GUPTA; SHARMA, 2002), além de sua aplicabilidade como amenizante para a remediação em áreas contaminadas (CICCU et al., 2003; COSTA et al., 2008).

Resultados de experimentos de campo indicaram que a adição de calcário e 3% ou a 5% de lama vermelha aumentou o pH do solo e, ao mesmo tempo, diminuiu a solubilidade e a disponibilidade de metais pesados (e.g., Zn, Pb, Ni, Cd e Cu), reduzindo a absorção pelas plantas e permitindo a revegetação quase que completa de um solo contaminado (GRAY et al., 2006). Os autores ressaltam que monitoramentos futuros precisam ser realizados, para avaliar a longevidade do tratamento com lama vermelha comparado ao calcário.

Em estudos conduzidos por Costa et al. (2008), avaliando o potencial da lama vermelha em reter Cd e Pb, constatou-se que o uso desse material em solos contaminados apresenta-se como uma técnica não somente eficiente para reduzir a lixiviação desses elementos-traço em solos, mas também para possibilitar um melhor crescimento de plantas.

Em diversos trabalhos também há relatos do potencial da lama vermelha em adsorver As (ALTUNDOGAN et al., 2002; GENÇ et al., 2003). Entre esses estudos, Lopes et al. (2012), avaliando a retenção de As pela lama vermelha pura ou misturada com diferentes proporções de gesso, constataram aumentos significativos na adsorção, à medida que aumentaram as porcentagens de gesso na mistura , tendo o adsorvente composto por 75% de lama vermelha com 25% de gesso sido o mais eficiente na retenção do elemento em questão. Tendo em vista esse resultado, os autores indicaram essa mistura com 25% de gesso como um bom amenizante para ser testado em estudos envolvendo a fitorremediação de áreas contaminadas com As.

2.2 Especiação e dessorção de elementos-traço em solos

O solo é um sistema complexo e heterogêneo, possuindo uma mistura de componentes orgânicos e inorgânicos, além da água e do ar que nele também se encontram. A composição do solo é extremamente diversa, sendo governada por vários fatores, a exemplo das condições climáticas e do material de origem. Dentre os diferentes compartimentos do solo, a fase sólida, constituída por minerais e matéria orgânica, desempenha papel fundamental, visto que é nela que os elementos essenciais ou tóxicos (e.g., elementos-traço) são retidos/adsorvidos. Entretanto, vale salientar que essa fase do solo encontra-se em equilíbrio dinâmico com os demais compartimentos, o que governa a dinâmica dos elementos-traço na interface solo-solução (Figura 1).

De acordo com o exposto e tendo em vista a elevada preocupação com a contaminação dos solos em áreas afetadas por atividades de mineração (ALLOWAY, 1990), estudos visando avaliar a interação dos elementos-traço com as diferentes fases sólidas do solo assumem grande relevância. Nesse contexto, sabe-se que o risco associado à presença de elementos tóxicos (e.g., Cd, As, Zn em elevadas concentrações) no ambiente é influenciado pela quantidade total do elemento presente no ambiente, sua toxicidade e biodisponibilidade.

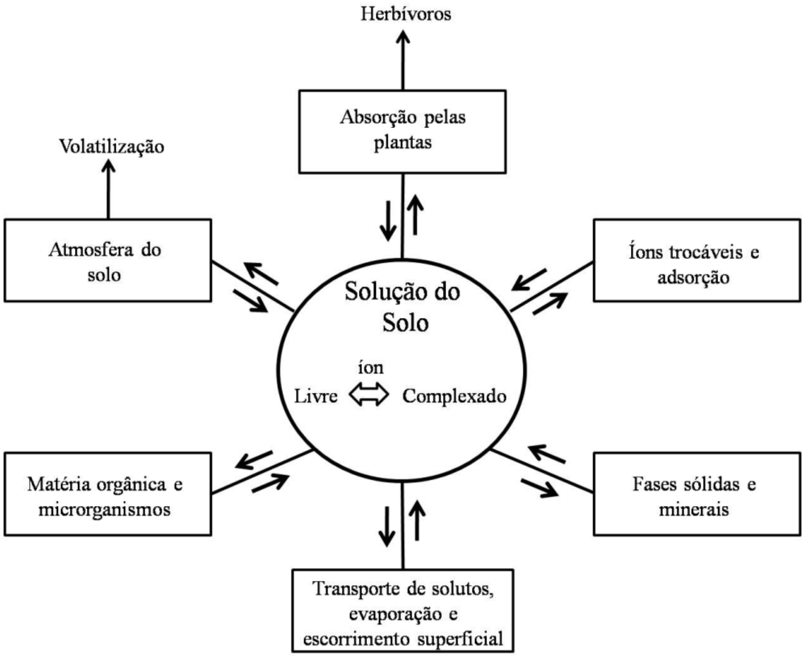

Figura 1 Dinâmica dos elementos-traço na interface solo/solução
Fonte: Adaptado de Lindsay (1979)

A determinação de teores totais de elementos-traço usando ácidos fortes é importante para uma primeira estimativa de risco em áreas contaminadas. Porém, tais determinações, quando aplicadas de forma isolada, não fornecem informações a respeito da mobilidade e da biodisponibilidade dos elementos envolvidos (HO et al., 2013). Assim, visando obter informações dessa magnitude, estudos envolvendo a especiação de contaminantes têm sido realizados (RODRÍGUEZ et al., 2009).

A especiação é um processo de identificação e quantificação das diferentes espécies, formas e fases químicas às quais o elemento de investigação está associado. Como o solo é um material heterogêneo com diferentes substâncias orgânicas, minerais de argila, óxidos de Fe, Al e Mn e outros componentes, além de uma diversidade de substâncias solúveis, existem vários mecanismos de ligação de elementos-traço em solos, os quais variam com a composição e as propriedades do solo (KABATA-PENDIAS; PENDIAS, 2011).

Assim, visando avaliar a especiação ou as formas de ligação dos elementos-traço nos solos, diferentes procedimentos analíticos têm sido desenvolvidos, destacando-se os métodos de extrações sequenciais (HAN et al., 2003; TESSIER; CAMPBELL; BISSON, 1979). Esses métodos são úteis por fornecerem informações sobre os componentes sólidos do solo aos quais os elementos avaliados estão associados (SPARKS, 2003). Isso é possível, pois, quando se aplica um procedimento de extração sequencial, os metais (elementos de interesse) ligados a uma fase sólida específica (e.g., carbonatos, óxidos, matéria orgânica e outros) são convertidos em formas solúveis com o uso de um reagente químico. Assim, o fracionamento do elemento avaliado é obtido, visto que os reagentes químicos são aplicados sequencialmente (FILGUEIRAS; LAVILLA; BENDICHO, 2002).

A maioria dos procedimentos de extrações sequenciais conhecidos divide o solo entre três a nove frações sólidas, envolvendo, geralmente, a separação química das seguintes fases: solúvel em água, trocável, associada a carbonatos, redutível ou associado a óxidos de Fe e Mn, oxidável ou associado a matéria orgânica e enxofre e residual ou associado com silicatos. Nesse contexto, as frações solúveis em água e trocáveis referem-se às quantidades do elemento analisado disponíveis para as plantas e podem facilmente ser mobilizadas, ao passo que a fração ligada a carbonatos pode se tornar móvel com a redução do pH. Além disso, as frações ligadas aos óxidos de Fe e Mn e à matéria orgânica podem ser mobilizadas pelo aumento das condições de redução e oxidação no ambiente e, por fim, os elementos associados à fração residual são de pouca mobilidade, podendo ser liberados somente com a ação do inteperismo por longo período (FILGUEIRAS; LAVILLA; BENDICHO, 2002).

Em todos os procedimentos de extrações sequenciais, os reagentes químicos utilizados são aplicados, visando aumentar a reatividade. Sendo assim, as primeiras frações, as quais são atacadas com reagentes mais fracos, extraem os elementos de interesse em uma forma com maior mobilidade, ao passo que as frações superiores removem os elementos quando em menor mobilidade ou fortemente retidos. Contudo, tais procedimentos fornecem informações sobre a mobilidade dos elementos avaliados, o que é de suma importância para a avaliação do real risco de uma área contaminada.

Apesar da aplicabilidade dos procedimentos de extrações sequenciais visando avaliar, dentre outros parâmetros, a mobilidade dos elementos-traço, ressalta-se que tais procedimentos também apresentam alguns inconvenientes. As principais limitações referentes ao uso da extração sequencial são: a dissolução incompleta da fase alvo, a extração de espécies não almejadas, a incompleta remoção de uma espécie dissolvida devido à readsorção ou reprecipitação e mudanças da valência de elementos sensíveis a alterações no potencial redox (CALMANO; MANGOLD; WELTER, 2001).

A mobilidade de contaminantes em solos também pode ser avaliada por meio de estudos de dessorção, os quais podem extrair os elementos usando diferentes soluções. Nesse contexto, uma alternativa para avaliar a dessorção é colocar o solo em contato com a solução escolhida para a dessorção/extração, sendo os elementos, após determinado período de agitação, analisados no sobrenadante. Esse procedimento é conhecido na literatura como método *batch* e tem sido amplamente utilizado devido à sua facilidade de aplicação e rapidez. Entretanto, esse método apresenta desvantagens e uma das principais é a readsorção dos elementos previamente dessorvidos, devido ao fato de o sistema ser fechado e à ocorrência de aumentos na concentração do elemento avaliado na solução (SHI, 2006).

Outra forma disponível para o estudo de dessorção de elementos em solos é utilizar o procedimento de fluxo agitado (*stirred-flow*), o qual é preferido por alguns autores (STRAWN; SPARKS, 2000). Na Figura 2 apresenta-se, de forma simplificada, o funcionamento dessa técnica de dessorção. Assim, verifica-se que a solução escolhida para a dessorção é succionada por uma bomba, passando pela câmara de reação, onde se localiza o solo em contínua agitação, chegando aos frascos coletores. Esses frascos coletores são regulados para mudarem de posição, sendo possível a coleta de alíquotas em diferentes tempos, o que é importante para avaliar a cinética de dessorção.

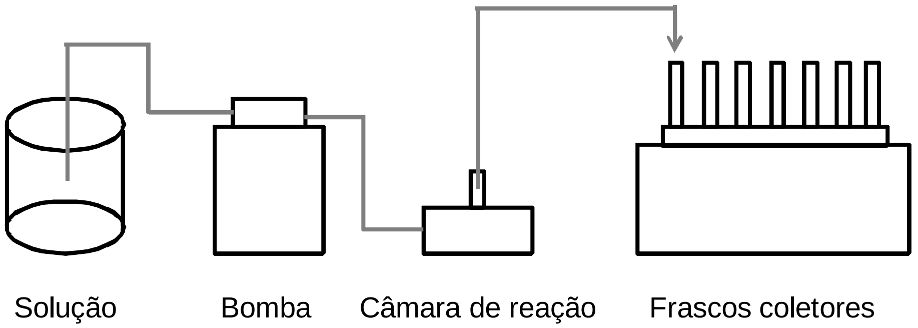

Figura 2 Esquema ilustrativo do funcionamento da técnica de fluxo agitado (*stirred-flow*), utilizada para a dessorção de elementos em solos

Por se tratar de um sistema aberto, no qual os elementos dessorvidos são liberados da câmara de reação para serem coletados visando à posterior análise, a utilização da técnica de fluxo agitado para a dessorção de elementos em solos reduz significativamente o processo de readsorção, aproximando-se mais das condições reais de campo (SHI, 2006). Ressalta-se que essa é uma grande vantagem em relação ao método *bacth*, principalmente em se tratando do estudo de áreas contaminadas, as quais apresentam elevadas concentrações de contaminantes e, portanto, com maiores possibilidades de ocorrência da readsorção. Além disso, com o método *bacth*, o sistema solo-solução entra em equilíbrio rapidamente, sendo, por essa razão, a quantidade dessorvida subestimada em algumas situações.

2.3 Espectroscopia de absorção de raios-X aplicada a solos

A espectroscopia de absorção de raios-X (XAS) é uma importante técnica amplamente utilizada baseada em radiação síncrotron. Ela pode ser aplicada para o estudo de diversos elementos químicos em sólidos cristalinos e não cristalinos, bem como em estado líquido ou gasoso e em plantas (SPARKS, 2013). As informações estruturais obtidas a partir dessa análise são úteis para a identificação das espécies químicas do elemento em interesse.

Basicamente, a XAS mede o coeficiente de absorção dos raios-X em função da energia da radiação incidente. Nesse contexto, quando a energia incidente é superior à energia de ligação do elemento de interesse (energia necessária para extrair os elétrons localizados nos níveis mais internos do átomo), ocorre um aumento drástico na absorção, observando-se um salto no espectro, conhecido como borda de absorção (RIBEIRO et al., 2003). Esse espectro, conforme ilustrado na Figura 3, é, geralmente, dividido em duas regiões, conhecidas como *X-ray absorption near edge spectroscopy (*XANES) e *extended X-ray absorption fine structure spectroscopy* (EXAFS). A região XANES (-50 a 200 eV em relação à borda de absorção) é fortemente influenciada pelo estado de oxidação do átomo absorvedor dos raios-X (elemento de interesse), enquanto a interpretação da região EXAFS (50 a 1000 eV acima da borda de absorção) pode fornecer informações detalhadas sobre a distância interatômica, o número de coordenação, além da identificação dos elementos vizinhos ao átomo absorvedor (KELLY; HESTERBERG; RAVEL, 2008).

O fato de a região XANES fornecer informações a respeito do estado de oxidação do átomo absorvedor dos raios X é atribuído à energia de ligação, visto que essa energia varia de acordo com a configuração dos elétrons no átomo. Nesse contexto, quando ocorre a remoção de elétrons de um átomo, ou seja, uma oxidação, os elétrons remanescentes ficam mais pertos do núcleo positivamente carregado. Sendo assim, a energia de ligação é aumentada, sendo necessárias maiores energias para arrancar esses elétrons, ocorrendo, consequentemente, um pequeno deslocamento da borda de absorção para valores maiores de energia (FENDORF; SPARKS, 1996).

Enquanto a região XANES fornece, essencialmente, informações sobre o estado de oxidação do átomo de interesse, a de EXAFS alcança informações ao redor do átomo absorvedor, as quais são de suma importância para o melhor entendimento das espécies químicas presentes em um solo contaminado por exemplo. De forma simples, pode-se considerar que o espectro EXAFS constitui-se de oscilações oriundas de interferências no átomo absorvedor causadas por sua vizinhança, ou seja, por seus átomos vizinhos. Nesse contexto, cada oscilação é dependente do número (número de coordenação) e do tipo de átomo vizinho (RIBEIRO et al., 2003), fazendo com que uma oscilação seja característica para determinada espécie química envolvendo o elemento de interesse.

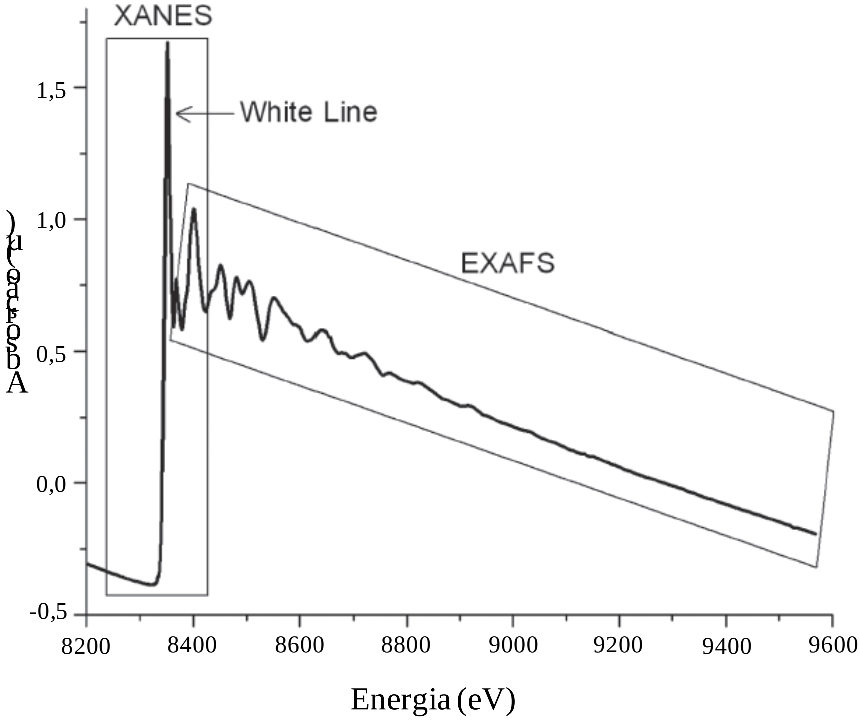

Figura 3 Espectro de XAS de NiO, mostrando as regiões XANES e EXAFS, bem como a borda de absorção (*white line*)
Fonte: Adaptado de Kelly, Hesterberg e Ravel (2008)

A identificação dos elementos vizinhos ao átomo absorvedor, determinando quantos eles são e qual a distância interatômica entre eles, é bastante complexa, e, para isso, tem-se uma equação levando em consideração todos esses parâmetros, conhecida como fórmula EXAFS. Como mencionado anteriormente, esse processo de interpretação não é simples, sendo discutido em maiores detalhes em outros trabalhos (FENDORF; SPARKS, 1996; KELLY; HESTERBERG; RAVEL, 2008). Contudo, ressalta-se que o conhecimento desses parâmetros, a exemplo da distância interatômica, é muito importante para um melhor entendimento em estudos envolvendo, por exemplo, a adsorção de metais. Nesse contexto, estudos diferenciam adsorção de esfera interna e externa de Pb, tendo como base esses parâmetros (STRAWN; SPARKS, 1999).

Essa análise do espectro EXAFS, determinando a distância interatômica, o número de coordenação e os átomos vizinhos do elemento de interesse, tem maior aplicabilidade para substâncias mais puras. Isso se deve ao fato de que, em substâncias heterogêneas, ocorrem interferências de vários elementos ao átomo absorvedor, tornando essa análise (ajuste), a qual é realizada por diferentes softwares, mais complicada. Nesse contexto, para sistemas complexos, a exemplo de solos, a interpretação do espectro EXAFS tem sido realizada utilizando-se a técnica conhecida como *linear combination fitting* (LCF), que também é realizada por programas de computador.

A análise de LCF consta de uma modelagem matemática da amostra desconhecida usando espectros de diferentes amostras representativas de materiais com as espécies químicas conhecidas ou padrões (KELLY; HESTERBERG; RAVEL, 2008). Cada amostra, seja de composição química conhecida ou não, gera oscilações na região de EXAFS, devido à interferência dos elementos vizinhos ao átomo analisado. Assim, quando se têm vários espectros coletados em amostras padrões (com a especiação química conhecida), pode-se, por meio de LCF, combinar todos esses espectros com o espectro da amostra a ser avaliada, encontrando quais as amostras padrões e porcentagens de cada uma que contribuem para a obtenção do melhor ajuste da amostra desconhecida. Essa análise de LCF é realizada em programas de análise de dados envolvendo XAS, a exemplo do Athena (RAVEL; NEWVILLE, 2005).

De acordo com o exposto, aplicando-se a análise de LCF em espectros oriundos de solos contaminados, pode-se realizar uma detalhada especiação química desses contaminantes. Contudo, é de suma importância, para isso, a coleta de dados em várias amostras padrões, as quais são possíveis candidatas de ocorrência na área. Nesse contexto, em estudos conduzidos em solo contaminado com Zn, devido à atividade de mineração e metalurgia do metal, constatou-se, por meio de LCF no espectro EXAFS, a presença de 66% de $ZnFe_2O_4$ e de 34% de ZnS na camada superficial do solo (ROBERTS; SCHEINOST; SPARKS, 2002).

Tendo em vista que os dois minerais encontrados no estudo mencionado anteriormente ($ZnFe_2O_4$ e ZnS) têm estrutura cristalina, eles poderiam, dependendo das concentrações, ser detectados com o uso da técnica de difratometria de raios-X (DRX), a qual é mais simples, rápida e barata, comparada ao uso de XAS. Entretanto, o uso da técnica de XAS pode contribuir de forma significativa para o conhecimento das espécies químicas de uma área. Isso porque, além de essa técnica permitir o reconhecimento de minerais em proporções bem menores que a técnica de DRX (SPARKS, 2013), ela ainda pode identificar materiais precipitados que, na maioria dos casos, são amorfos ou mal cristalizados e, portanto, impossíveis de serem detectados por DRX.

Nesse contexto, diversos trabalhos avaliando a especiação de metais em solos contaminados usando a técnica de XAS foram desenvolvidos. Dentre eles, Nachtegaal et al. (2005) investigaram a especiação de Zn em solos oriundos de áreas de mineração/metalurgia e constataram significativa porcentagem do Zn associado a formas de precipitados. Os autores ressaltaram que tais precipitados levaram a uma drástica redução da fração trocável/biodisponível de Zn, o que reduziu significativamente a mobilidade desse elemento. Em outros estudos utilizando a técnica de XAS também tem sido verificada a presença dessas formas de precipitados em solos contaminados com Zn (KHAOKAEW et al., 2012).

3 CONSIDERAÇÕES FINAIS

Com os estudos da presente tese foi possível constatar a eficiência de diferentes espécies de plantas, especialmente braquiária e crotalária, para a revegetação de uma área de mineração de ouro com altos teores de As. Essas plantas se mostraram promissoras para a utilização na fitorremediação da área avaliada, sendo consideradas tolerantes ao As. Além disso, verificou-se a eficiência de utilização de subprodutos industriais (lama vermelha pura ou misturada com 25% de fosfogesso) como amenizantes para o emprego da fitotecnologia nessa área, tendo o amenizante com 75% de lama vermelha com 25% de fosfogesso sido mais eficiente que a lama vermelha pura, apresentando, ainda, a vantagem potencial em termos de suprimento de nutrientes (Ca e S oriundos do fosfogesso).

Além disso, os estudos envolvendo extrações sequenciais de Zn, Pb e Cd em áreas de mineração e metalurgia de Zn proporcionaram informações importantes a respeito da mobilidade desses elementos nos dois diferentes ambientes, sendo essa mobilidade maior na área de metalurgia, comparada com a área de mineração, para todos os contaminantes avaliados, especialmente para o Zn e o Cd.

Essa diferença de mobilidade verificada nos dois locais também foi constatada para o Zn, por meio de testes de dessorção usando o procedimento de agitação com fluxo (*stirred-flow*). Esses resultados divergentes, em termos de mobilidade do Zn, nas duas diferentes áreas, foram explicados realizando-se uma especiação desse elemento por espectroscopia de absorção de raios-X (XAS). Nesse contexto, a baixa mobilidade do Zn encontrada nos solos oriundos da área de mineração do metal foi atribuída à formação de alguns precipitados de Zn, os quais reduzem significantemente a mobilidade do elemento. Por outro lado, a elevada mobilidade desse metal observada na área de metalurgia foi atribuída, também de acordo com os resultados de XAS, ao fato de grande quantidade do Zn nessa área estar associado a materiais fracamente ligados à fase sólida do solo e, consequentemente, de elevada mobilidade.

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SEGUNDA PARTE

ARTIGO 1

Industry by-products as amendments for phytoremediation of as-rich soils of a gold mining in Brazil

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Industry by-products as amendments for phytoremediation of as-rich soils of a gold mining in Brazil

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Abstract

Arsenic release into soils is a well-known problem nearby gold mining areas. We investigated two industry by-products – red mud (RM) and its mixture with phosphogypsum (RMG), as amendments in an As-contaminated soil from a gold mining area in Brazil in order to grow three plant species: *Brachiaria decumbens, Crotalaria spectabilis*, and *Stylosanthes* cv. Campo Grande. These amendments were applied to reach a soil pH of 6.0. Using RM and RMG increased SDM and RDM of most plants, with RMG being more effective. Adding RMG increased the SDM of *Brachiaria* and *Crotalaria* by 18 and 25% and the RDM by 25 and 12%, respectively. *Stylosanthes* was sensitive to As toxicity and grew poorly in all treatments. Arsenic concentration in shoots of *Brachiaria* and *Crotalaria* decreased by 26% with the use of RMG while As in roots reduced by 11 and 30%, respectively. Also, the activities of the plant oxidative stress enzymes varied following treatments with the by-products. *Brachiaria* and *Crotalaria* could be considered as tolerant to As toxicity and thus liable to be employed for phytoremediation purposes, especially with the use of RMG due to its potential advantage in terms of nutrient supply (Ca^{2+} and SO_4^{2-} from phosphogypsum).

Index terms: contamination, phytotechnology, red mud, phosphogypsum

1. Introduction

Metal and metalloid concentrations exceeding permissible limits set by local legislations have been documented in many places around the world, which may pose a threat to human health and/or ecological systems. Arsenic – a known human carcinogenic – is one of such elements and much attention has been given lately to this metalloid due to increasing records of environmental contamination as a result of human activities [1]. The major anthropogenic sources of As are associated with mining and smelting activities [2]. Arsenic has been ranked first in the priority list of harmful substances to human health by the Agency for Toxic Substances and Disease Registry since 1997 [3]. Because of that, studies involving the remediation of As-contaminated soils have become of great importance, particularly those concerning the use of phytoremediation (phytotechnologies) [4].

Among the various phytotechnologies used for remediation of contaminated areas, stabilization (with soil amendments) followed by the use of tolerant or (hyper) accumulator species has been considered as a promising technique [5]. Yet, the choice of an appropriate amendment is very important for the success of the phytoremediation process. In this context and taking into account that Fe and Al oxides have been identified as primary sinks for As in soils [2], several studies have been conducted in order to evaluate the use of red mud (RM), an alkaline and oxide-rich material, as a soil amendment [6,7].

Red mud is an aluminum industry by-product generated in large amounts worldwide. Considering that the production of 1 ton of alumina generates 1-1.5 tons of RM [8], the production of RM in Brazil was estimated at 16.52 million tons in 2005 [9]. This by-product is considered to be a good adsorvent for As due to its high concentrations of Fe and Al oxides [7,10].

Although pure RM could be considered a good sorbent for As, recent studies have pointed out that a mixture containing 75% of RM + 25% of phosphogypsum (hereafter called RMG) could be a promising material due to its higher As adsorption capacity when compared with RM alone [10], which indicates RMG as a good amendment to be tested in experiments involving phytoremediation of As-contaminated sites.

Considering that phosphogypsum (a phosphate fertilizer industry by-product) is also produced in large amounts around the world, including Brazil [11,12], the utilization of RMG as an amendment of As-contaminated soils has a dual advantage because besides acting as an amendment, the RMG may also decrease the great amounts of RM and phosphogypsum stored in the industries, thus eliminating an environmental liability.

Many batch and pot experiments involving phytoremediation of As-contaminated soils from mining areas have been conducted all over the world. In Brazil, these studies mostly refer to soils artificially contaminated with As [13,14]. Nevertheless, phytoremediation studies using As-rich soils occurring in natural environments, such as in mining areas, are still required. Furthermore, no previous studies have evaluated the use of RMG as an amendment in As-contaminated areas. Therefore, this study aims to investigate the efficiency of a phytotechnology employing red mud (RM), as well as its mixture with phosphogypsum (RMG), as amendments for decreasing As phytoavailability in order to grow three plant species in an As-rich soil from an important Brazilian gold mining area. The effectiveness of the soil amendments and the plant species was assessed through analyses of As-related soil and plant traits, including the activities of plant oxidative stress enzymes.

2. Materials and Methods

2.1. Site description and sampling

Soil samples were randomly collected at the 0–20 cm depth in a gold mining area located in Paracatu and were supplied by KINROSS Brazil. In this area two different soils were collected, which are hereafter called B1 and PNR (Private Natural Reserve). The soil B1 is known to have high arsenic levels while the PNR came from a native Brazilian savannah (Cerrado biome) area, being considered an uncontaminated soil and used in this study as a control.

The red mud (RM) sample was collected at the 0-20 cm depth in a reservoir located in Poços de Caldas and was supplied by ALCOA Brazil while the phosphogypsum (G) sample came from Uberaba and was supplied by FOSFÉRTIL. Paracatu, Poços de Caldas, and Uberaba cities are all located in Minas Gerais State, Brazil, being 864, 256, and 496 kilometers away from São Paulo city, respectively. The soils and by-products (RM and G) were air-dried at room temperature and then passed through sieves of 4 and 2 mm, respectively, for further tests.

2.2. By-products characterization and soil incubation

The by-products tested as amendments in this present work were red mud (RM) and a mixture containing 75% RM + 25% of gypsum (RMG). The RM used has maghemite, gibbsite, goethite, hematite, and quartz while the G has gypsum and anhydrite (anhydrous calcium sulfate) as the main mineralogical components based on previous X-ray diffraction analyses [10]. The RM is a material rich in oxides, presenting as major oxides Al (26% of Al_2O_3), Si (19% of SiO_2), and Fe (20% of Fe_2O_3). Additional details regarding the characterization of these by-products can be found at Lopes et al. [10].

Due to the alkaline reaction of both RM and RMG, a pre-test was conducted prior to the definitive soil incubation (by-product application preceding plant growth) in order to determine the rate of each by-product to be applied to the soil as well as the time required for complete reaction of each by-product in the soil. Under such circumstances, the goal was to add both amendments RM and RMG to raise the soil pH to approximately 6, which is a situation that represents a worst case scenario for As phytoavailability, since As availability increases with increasing soil pH. Incubation curves were constructed adding the by-products (RM and RMG) to soil B1 in the following proportions (% by weight): 0, 0.10, 0.20, and 0.40. For that, both materials were homogenized and incubated up to 30 days with a soil moisture close to field capacity and final pH values were recorded to adjust the incubation curve. The final amendment doses required to increase soil B1 pH to 6 were 0.05% for RM and 0.13% for RMG (Fig. 1), which are equivalent to 1.0 and 2.6 tons per hectare of RM and RMG, respectively.

Following this pre-test and knowing the incubation time (30 days) and the percentages of each by-product required to increase the soil B1 pH to 6, these doses were added to soil B1. These materials along with soils B1 and PNR without amendments were placed into plastic bags and kept moist close to field capacity for 30 days. Samples were then taken from each plastic bag for soil fertility analyses, as well as for measuring soil As concentrations using the Mehlich-1 (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4) procedure [15].

It was also determined arsenic semi-total concentrations following soil digestion in a microwave oven, using HNO_3, according to the 3051A method

[16]. Semi-total concentration of As was also determined using certified soil standards (Montana soil, NIST 2710a; National Institute of Standards and Technology) to ensure adequate quality control of the analyses.

After soil incubation and prior to cultivation, soil samples were removed from the plastic bags and placed into pots assembled with 2-L bottles of polyethylene terephthalate (PET), which have been cutted approximately in half in order to be used as pots, but with the advantage of being able to collect soil leachates. Deionized water was then added in excess to each pot in order to force leaching. Soil leachates were analyzed for pH and EC (electrolytical conductivity), as well as for As (using graphite furnace atomic absorption spectrometry), and Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} (using ionic chromatography).

2.3. Greenhouse experiment

The plant species *Brachiaria decumbens*, a high biomass production grass, and *Crotalaria spectabilis*, and *Stylosanthes* cv. Campo Grande, two perennial legumes were selected for this study. All plants were sown in the PET pots and after germination six homogeneous plants were kept per pot. During the experiment, which was conducted with 5 replicates, the pots were maintained with a soil moisture close to field capacity by weighing and daily irrigation with deionized water. Plant nutrients were applied to pots as follow (mg dm^{-3}): 300 of N, 200 of P, 300 of K, 75 of Ca, 30 of Mg, 50 of S, 0.5 of B, 1.5 of Cu, 5 of Fe, 10 of Mn, and 0.1 of Mo. Except for N and K, which were split in three applications, all other nutrients were applied at planting.

After 60 days of exposure to each treatment, all plants were collected individually and separated into shoots and roots. Shoots were washed with deionized water while the roots were washed with tap water until completely clean, followed by a 0.1 mol L^{-1} HCl solution wash and deionized water wash.

After that, they were then oven-dried with a forced-air circulation system at 60 °C. The shoot dry matter (SDM) and the root dry matter (RDM) weights were recorded and then these materials were ground and subjected to HNO_3 digestion in a microwave oven with a soil:acid ratio of 1:10 [16] to determine the As concentrations present in the extracts. Arsenic analyses were performed using an atomic absorption spectrometer (PerkinElmer AAnalyst 800®) with either flame (measurements in the range of mg L^{-1}) or graphite furnace atomization (measurements in the range of µg L^{-1}). Similarly to soils, a certified reference material (Plankton, BCR 414; Institute for Reference Materials and Measurements) was used to check the accuracy of As determinations, which was found satisfactory, i.e., less than 6% of variation.

The phytoextraction ability of the plants with respect to As was evaluated using both the translocation factor (TF) and the bioaccumulation factor (BF). The translocation factor was calculated dividing the As concentration in the shoot by the As concentration in the root and, the bioaccumulation factor, was calculated as the ratio of the As concentration in the shoot divided by the As concentration in the soil [17,18].

The oxidative stress due to 60 days of exposure to different As-stressing conditions in plant shoots was also assessed by determining the activities of the plant oxidative stress enzymes. The apex of the third fully expanded trifoliate leaf was removed for enzymatic analysis, kept in liquid nitrogen during collection, and stored at -80°C. About 0.1-0.3 mg of fresh leaf tissue was homogenized in 1 mL of extraction buffer (100 mmol L^{-1} phosphate buffer, pH 7.0, 0.1 mmol L^{-1} EDTA; 10 mmol L^{-1} ascorbic acid) in a pre-chilled mortar and pestle with liquid nitrogen. The homogenate was centrifuged at 12,000 g for 30 minutes at 4°C, and the supernatant was collected for enzymatic activity analysis, being the enzymes as follow: superoxide dismutase (SOD) [19], ascorbate peroxidase (APX) [20], catalase (CAT) [21], and glutathione reductase (GR) [22].

The results of dry matter production and concentration of As in shoots and roots were subjected to an analysis of variance using the statistical analysis system SISVAR [23]. Under these circumstances, the means of the treatments that correspond to each plant species were compared by the Scott-Knott test ($p < 0.05$).

3. Results and Discussion

3.1. Soil characterization and leachate analysis

The soil fertility parameters for each treatment (after incubation with by-products and in control soils) are shown in Table 1. First at all, it is possible to note that the pH values of soil B1 treated with by-products increased to around 6 as expected from the pre-incubation test (Fig. 1). It is noteworthy that both control soils (PNR and B1) had a natural pH close to 5 (Table 1), which hiddens As availability, because the lower the pH the higher is the soil affinity for As. As pointed out earlier, by increasing soil pH to 6, we expect As availability to increase, which creates worse conditions for plant growth. This would be the best situation for each by-product to express its effectiveness.

The concentrations of Na increased with the application of both by-products (Table 1). This fact may be attributed to the high alkalinity of RM due to its elevated Na levels that came from the Bayer Process [24]. In general, as can be seen in Table 1, the soil B1 presents general limitations to the plant development, as in the studies conducted by Silva et al. [25].

Soil arsenic concentrations (semi-total and Mehlich-1 extractable) following the incubation with by-products are shown in Table 2. As can be seen, it was confirmed that the control soil PNR is considered uncontaminated taking into account that its As semi-total concentration was smaller than the value established by the Brazilian legislation as a warming value for soils (35 mg kg^{-1}) [26]. On the other hand, the soil B1 has a high As concentration (Table 2), which probably came from the gold mining process, particularly from the minerals that the gold is associated with (e.g., arsenopyrite).

The As concentrations that were extracted by Mehlich-1 presented a slightly decrease following the treatment with RM or RMG (Table 2). These results indicate the positive effect of these by-products for diminishing As availability. Such results corroborate previous findings pointing out red mud as a good adsorbent for As removal [27,28], as well as the adjuvant effect of phosphogypsum (G), i.e. G acts as a helping agent to increase the As sorption capacity of RM [10].

The pH of soil leachates from soil B1 increased with the utilization of both by-products RM and RMG (Table 3). Costa et al. [9] evaluating the use of red mud as an amendment in contaminated soils reported similar results. Moreover, the electrolytical conductivity (EC) as well as the Na concentrations were greater when the by-products were used, especially the RMG. This fact can be explained due to the fact that both by-products add more ions to the soil (as can be seen, in general, in Table 3 for Ca^{2+}, Na^{+}, Cl^{-}, NO_3^{-}, PO_4^{3-}, and SO_4^{2-}), thus increasing EC. Leite et al. [29] mentioned that adding gypsum to soils contributes to an increase in EC due to two different reasons. The first is the increase of soluble Ca in solution due to gypsum solubilization and the second is the displacement of Na by Ca from the soil exchangeable complex to soil solution.

Arsenic concentrations in the leachates were slightly higher following the treatment of the soil B1 with RM and RMG (Table 3). This fact is linked to the greater pH values found when soil B1 was treated with the by-products, taking into account that high pH values favor As desorption from red mud [30].

Furthermore, studies checking the effect of pH upon As concentration in solution as determined by the TCLP test (Toxicity characteristic leaching procedure) showed that the fraction of As leached can be 3 to 4 fold higher when the pH is increased by a unit [31]. It has to be mentioned that besides the As concentrations in the leachates were slightly higher when the soil was treated with the by-products, this parameter was very small in all treatments.

3.2. Plant growth assessment

The dry matter production of shoots (SDM) and roots (RDM) of the evaluated plants are shown in Fig. 2. Initially, the dry matter production (shoots and roots) was lower for the *Stylosanthes* compared with the other two plant species. Also, the dry matter production was even lower when *Stylosanthes* was cultivated in treatments involving the contaminated soil in comparison with the uncontaminated one. Thus, *Stylosanthes* was found to be more sensitive to As toxicity than other plants and grew weakly in all treatments.

The RMG application resulted in increases in the production of SDM of the *Brachiaria* and *Crotalaria* (Fig. 2). Positive effects of the by-products on the dry matter production were also verified for the roots, and a higher production of RDM was observed with the use of RM and RMG for *Brachiaria* and with RM for *Crotalaria*. The effectiveness of red mud for the remediation of contaminated areas with trace elements has been documented in several works [32]. Costa et al. [9] evaluated the growth of *Brachiaria* in Cd- and Pb-contaminated soils and showed dry matter production increases when the soil was amended with red mud. These authors mentioned that red mud reduced trace metals availability and consequently improved the conditions for plant development, which was reflected on their dry matter productions.

Fig. 3 shows As concentrations (mg kg^{-1}) in the SDM and RDM as well as the quantity of arsenic in each pot (µg pot^{-1}). The concentration of As in the

SDM reduced with the use of the amendment RMG for *Brachiaria* and *Crotalaria*, whereas an increase of these concentrations can be noted for the *Stylosanthes* (Fig. 3A). Moreover, with respect to the utilization of RM, no significant effects were observed in As concentration in the SDM for *Braquiaria*, while greater and smaller As concentrations where observed for *Crotalaria* and *Stylosanthes*, respectively when compared with the unamended control.

The amounts of As (mg kg^{-1}), in the SDM and RDM for the *Stylosanthes* were relatively in the same order of magnitude, being comparable with the values observed for the *Braquiaria* and *Crotalaria* (Fig. 3A and 3C). However, this fact can be attributed to the concentration effect, taking into account that the development of the *Stylosanthes* was smaller (Fig. 2). This concentration effect was reflected on the low quantity of As, in µg pot^{-1}, accumulated in each pot for *Stylosanthes* (Fig. 3B and 3D).

Following treatments with RM and RMG, As concentration in the RDM decreased, except for *Brachiaria,* which presented no significant alterations (Fig. 3C). Studies under field conditions involving the use of red mud and lime as amendments to remediate contaminated soils with trace metals have showed improvement in the growth of *Festuca rubra* with the utilization of these materials as stabilizers of the contamination [33].

The alterations due to the RM and RMG utilization in the production of SDM and RDM as well as in As concentration in SDM and RDM are shown in Table 4 as percentages in comparison with the unamended control (soil B1). It is noteworthy that the by-products utilization resulted in increases in the production of SDM and RDM and in decreases in As concentration in SDM (As-SDM) and RDM (As-RDM) for *Brachiaria* and *Crotalaria*, except for the As-SDM of *Crotalaria* when RM was used, which increased 14%. As can be seen, in general, this effect in raising or reducing the SDM and RDM or the As-SDM and As-RDM was higher with the utilization of RMG compared with RM, respectively. In this context, following the treatment of soil B1 with RMG, there was an increase of 18% in the SDM and of 23% in RDM of *Brachiaria* and of 25 and 12% in *Crotalaria*, respectively. On the other hand, considering the application of RMG for *Brachiaria* and *Crotalaria*, the As-SDM had a decrease of approximately 26% (±0.67%), while reductions of 11%, 30%, and 53% were verified in As-RDM in *Brachiaria*, *Crotalaria*, and *Stylosanthes*, respectively (Table 4).

The bioaccumulation (BF) and translocation factors (TF) are shown in Table 5. Both factors were lower than 1.0 for all treatments and plant species. Taking into account that hyperaccumulator plants have to present BF greater than 1.0 [34], these results show that all tested plant species are not As hyperaccumulator, yet could be considered As tolerant. *Brachiaria* has been reported as a tolerant plant when cultivated in different soils contaminated with As elsewhere [13]. According to Fitz & Wenzel [34], tolerant plants tend to restrict As translocation from the soil to plants and from the root to shoots, while the hyperaccumulator plants strongly absorb and translocate As.

Tolerant plants present BF lower than 1.0. Thus, a good example to show this trend is to compare the BF from a tolerant plant *Agrostis catellana* Boiss cultivated in a soil containing 17,000 mg kg^{-1} of As [35] with a hyperaccumulator plant *Pterris Vittata* L., which grew in a soil with 97 mg kg^{-1} of As [36]. The tolerant plant (*A. catellana*) presented 170 and 1,000 mg kg^{-1} of As in the shoots and roots, respectively (BF = 0.01), whereas that the *P. vittata* had 7,234 mg kg^{-1} of As in the shoots and 303 mg kg^{-1} of As in the roots (BF = 74.6).

Arsenic tends to present low translocation from roots to shoots [37], corroborating the results obtained in the present work, in which As translocation was small (TF lower than 1.0). As can be seen in Table 5, higher TF values were found for *Stylosanthes*. However, this trend can be attributed again to the concentration effect, taking into account that the development of the *Stylosanthes* was smaller (Fig. 2).

Plant exposure to As may increase the production of oxygen reactive species such as O_2^-, H_2O_2, and OH^-, which are continuously produced by the plants [38]. In this context, the plants have several biochemical protective mechanisms against oxidant agents, including enzymatic, which involve the simultaneously activities of SOD, CAT, APX, and GR and non-enzymatic mechanisms such as the increase of the thiol (phytochelatin) production [39]. In general, as can be seen in Table 6, following treatments with the by-products, the CAT and APX activities in plant shoots decreased compared with the unamended control. Taking into consideration only the enzymatic aspect, this fact indicates that the oxidant agents decreased when the soil was amended with RM and RMG, which resulted, in general, in decreases in the As concentrations in the SDM, as reported in Table 4.

The GR activities did not present significant differences with or without the application of by-products for all plants evaluated (Table 6). However, the activity of this enzyme was higher in plants cultivated in the As-contaminated soil than in the uncontaminated soil control. Ultimately, the SOD activities tend to increase or decrease followed by treatments with by-products for *Brachiaria* and *Crotalaria* or *Stylosanthes*, respectively. Studies involving the exposure of *Crotalaria spectabilis* to As revealed that the SOD activity increased upon increasing As contamination [40].

4. Conclusions

The plant species tested in the present study exhibited differences in sensitivity and response to As toxicity and to the application of the by-products, with *Stylosanthes* being more sensitive than *Brachiaria* and *Crotalaria*.

The by-product RMG was more efficient than RM as an amendment for alleviating As, presenting also a potential advantage in terms of nutrient supply (Ca^{2+} and SO_4^{2-} from phosphogypsum).

Brachiaria and *Crotalaria* were not regarded as hyperaccumulators, but tolerant to As toxicity, yet they could still be used for phytoremediation purposes in As-contaminated soils.

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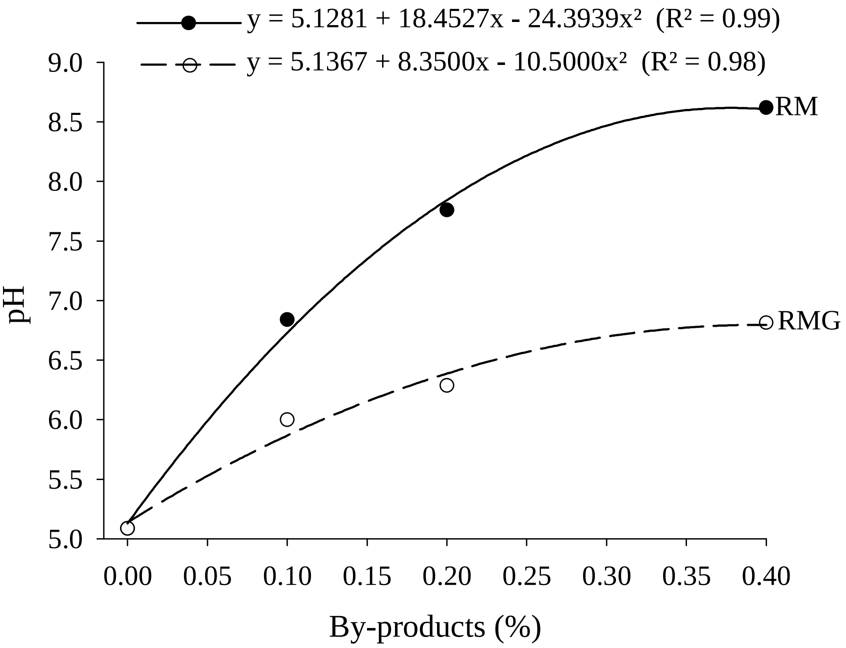

Fig. 1. Incubations curves for the soil B1. RM, red mud, and RMG, 75% of RM mixed with 25% of phophogypsum.

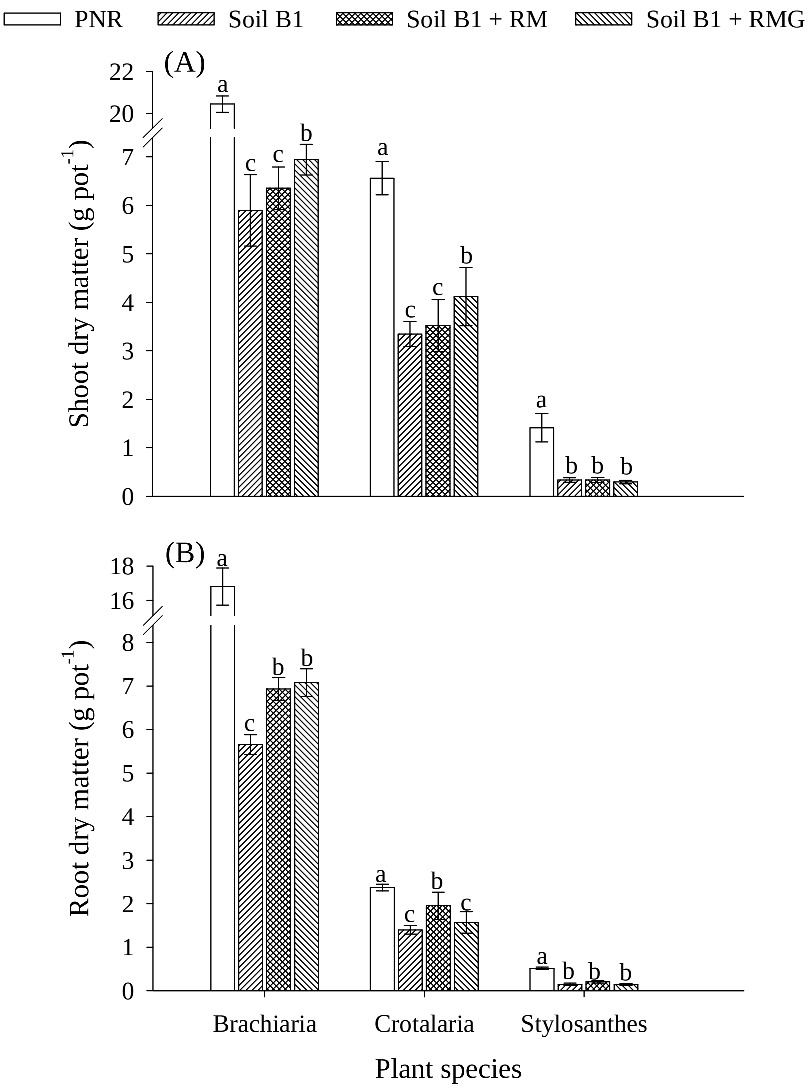

Fig. 2. Shoots (A) and roots (B) dry matter productions (g pot^{-1}) of the evaluated plants. The columns that correspond to each plant species followed by same letters do not differ by Scott–Knott test at 95% probability. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

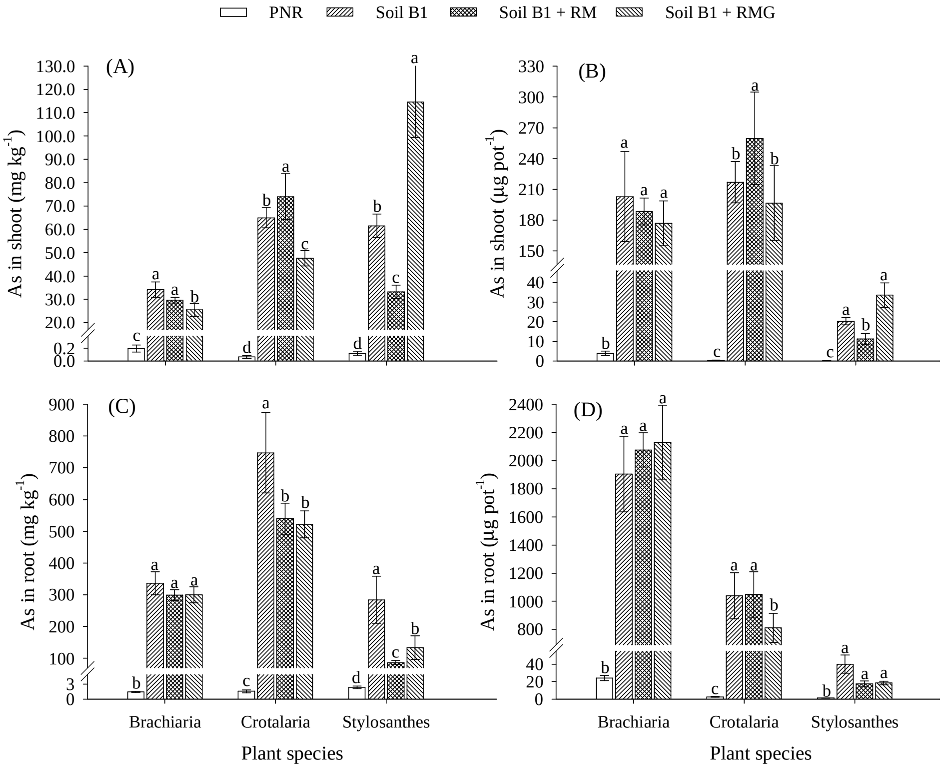

Fig. 3. As concentrations (mg kg^{-1}) in the SDM (A) and RDM (C) and quantities of As accumulated (B and D) in each pot (µg pot^{-1}) of the evaluated plants. The columns that correspond to each plant species followed by same letters do not differ by Scott–Knott test at 95% probability. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

Table 1

Soil fertility parameters following the incubation with by-products.

Attributes (1)	PNR	B1	B1 + RM	B1 + RMG
pH (H_2O)	4.87	5.12	5.77	5.96
P (mg dm^{-3})	2.30	3.10	3.70	4.30
K^+ (mg dm^{-3})	144	22.0	23.0	22.0
Na^+ (mg dm^{-3})	6.40	8.30	34.0	51.5
Ca^{2+} ($cmol_c$ dm^{-3})	0.30	0.10	0.10	0.30
Mg^{2+} ($cmol_c$ dm^{-3})	0.60	0.20	0.20	0.20
Al^{3+} ($cmol_c$ dm^{-3})	0.80	0.10	0.10	0.10
H^+ + Al^{3+} ($cmol_c$ dm^{-3})	5.00	1.10	0.90	0.90
SB ($cmol_c$ dm^{-3})	1.30	0.40	0.40	0.60
Effective CEC ($cmol_c$ dm^{-3})	2.10	0.50	0.50	0.70
pH 7.0 CEC ($cmol_c$ dm^{-3})	6.30	1.40	1.20	1.40
V (%)	20.1	25.0	29.7	39.5
m (%)	38.7	21.9	21.7	15.2
SOM (g kg^{-1})	38.0	6.00	6.00	4.00
P-rem (mg L^{-1})	26.0	48.8	43.5	44.8
Zn (mg dm^{-3})	0.80	0.50	0.40	0.40
Fe (mg dm^{-3})	97.4	20.9	22.2	19.4
Mn (mg dm^{-3})	12.4	2.00	1.80	1.60
Cu (mg dm^{-3})	1.70	0.60	0.70	0.60
B (mg dm^{-3})	0.10	0.00	0.00	0.00
S (mg dm^{-3})	372.2	413.8	28.5	59.4

(1) Determined according to Embrapa [15]. SB, sum of bases; effective CEC, cation exchange capacity (CEC) in the natural soil pH; pH 7.0 CEC, CEC in the pH 7.0; V, saturation of bases; m, saturation of Al; SOM, soil organic matter; PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

Table 2

Semi-total and Mehlich-1 extractable arsenic in the soils following the incubation with by-products

Treatments	As (mg kg^{-1})	As Mehlich-1 (mg kg^{-1})
PNR	10.3 (0.87)	0.71 (0.04)
B1	600 (37.7)	85.5 (1.69)
B1 + RM	551 (26.3)	75.4 (6.68)
B1 + RMG	526 (28.3)	77.0 (2.01)
Reference soil (NIST 2710a) (1)	1348 (285)	-

(1) The As recovery concentration value in the reference soil was close to 90%. The values represent the averages (n=4) with their standard deviations in parentheses. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

Table 3

Chemical characterizations of soil leachates following the incubation with by-products

Treatments	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	As	EC
	---------------------- mg L^{-1} ----------------------					- µg L^{-1} -	- dS m^{-1} -
PNR	11.4 (0.21)	78.0 (5.46)	74.6 (4.65)	22.7 (1.62)	26.2 (0.64)	-	1.23 (0.23)
B1	53.4 (1.35)	-	32.2 (1.33)	30.1 (2.69)	8.41 (0.08)	6.59 (0.97)	0.86 (0.07)
B1 + RM	134 (12.7)	-	-	11.6 (1.32)	9.64 (1.12)	9.07 (2.38)	0.92 (0.16)
B1 + RMG	366 (6.09)	-	-	8.43 (1.14)	31.5 (3.25)	10.2 (2.27)	2.59 (0.17)

	pH	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
		----------------------- mg L^{-1} -----------------------				
PNR	4.67 (0.13)	0.02 (0.01)	12.9 (1.45)	603 (34.3)	2.60 (0.20)	0.71 (0.10)
B1	5.44 (0.43)	0.06 (0.02)	3.10 (0.55)	7.49 (0.96)	0.66 (0.05)	8.17 (0.58)
B1 + RM	6.67 (0.14)	0.08 (0.01)	6.30 (3.27)	6.72 (1.08)	0.63 (0.04)	12.6 (1.17)
B1 + RMG	6.60 (0.09)	0.15 (0.03)	16.3 (1.72)	15.2 (1.01)	1.19 (0.02)	82.9 (4.71)

The values represent the averages (n=4) with their standard deviations in parentheses. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

Table 4

Percentages of increase (+) or decrease (-) due to the RM and RMG utilization in the production of SDM and RDM (g pot^{-1}) as well as in As concentration in SDM and RDM (mg kg^{-1}).

Attributes	Plant species					
	Brachiaria		*Crotalaria*		*Stylosanthes*	
	RM	RMG	RM	RMG	RM	RMG
SDM	+7.76	+17.8	+5.39	+23.2	+0.75	-12.0
RDM	+22.7	+25.3	+39.5	+12.0	+40.4	0.00
As-SDM	-13.2	-25.4	+13.9	-26.7	-46.0	+86.4
As-RDM	-10.9	-10.7	-27.8	-30.1	-69.5	-53.0

+ or – before the numbers means increases and decreases, respectively.

Table 5

Bioaccumulation (BF) and translocation (TF) factors of As of the evaluated plants after 60 days of exposure to different As-stressing conditions following the incubation with by-products

Treatments	Plant species					
	Brachiaria		*Crotalaria*		*Stylosanthes*	
	BF	TF	BF	TF	BF	TF
PNR	0.019 (0.005)	0.132 (0.031)	0.006 (0.002)	0.038 (0.008)	0.011 (0.003)	0.049 (0.008)
B1	0.057 (0.005)	0.102 (0.012)	0.108 (0.007)	0.088 (0.011)	0.103 (0.008)	0.223 (0.033)
B1 + RM	0.054 (0.002)	0.099 (0.006)	0.134 (0.018)	0.139 (0.030)	0.060 (0.005)	0.385 (0.047)
B1 + RMG	0.048 (0.005)	0.085 (0.013)	0.091 (0.006)	0.092 (0.011)	0.218 (0.029)	0.887 (0.160)

The values represent the averages (n=4) with their standard deviations in parentheses. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

Table 6

Catalase (CAT), ascorbate peroxidase (APX), glutathione reductase (GR), and superoxide dismutase (SOD) activities in the shoots of the evaluated plants after 60 days of exposure to different As-stressing conditions following the incubation with by-products

Plant species	PNR	B1	B1 + RM	B1 + RMG
	--------------- CAT (µmol H_2O_2 g^{-1} MF min^{-1}) ---------------			
Brachiaria	197 (8.14)	163 (26.4)	97.2 (59.7)	114 (19.8)
Crotalaria	246 (12.5)	201 (30.8)	304 (22.3)	35.4 (1.73)
Stylosanthes	536 (39.1)	1079 (99.0)	613 (173)	713 (156)
	------------ APX (µmol Ascorbate g^{-1} MF min^{-1}) ------------			
Brachiaria	3281 (103)	4022 (431)	2138 (442)	2405 (465)
Crotalaria	761 (125)	906 (159)	305 (63.8)	1042 (148)
Stylosanthes	1072 (222)	1604 (393)	1372 (293)	1761 (67.1)
	-------------- GR (µmol NADPH g^{-1} MF min^{-1}) --------------			
Brachiaria	1.96 (0.03)	3.90 (0.07)	4.05 (2.01)	4.93 (1.02)
Crotalaria	0.00	1.12 (0.31)	1.57 (0.58)	1.59 (0.01)
Stylosanthes	3.40 (0.34)	4.30 (0.77)	4.34 (0.70)	5.55 (1.94)
	------------------------ SOD (U g^{-1} MF) ------------------------			
Brachiaria	2.32 (0.12)	1.70 (0.34)	1.90 (0.38)	2.43 (0.37)
Crotalaria	1.35 (0.09)	0.36 (0.11)	2.29 (0.22)	0.85 (0.13)
Stylosanthes	2.22 (0.38)	2.42 (0.40)	1.07 (0.55)	1.35 (0.90)

The values represent the averages with their standard deviations in parentheses. PNR, Private Natural Reserve (soil uncontaminated); Soil B1, As-contaminated soil; RM, red mud; and RMG, 75% of RM mixed with 25% of phosphogypsum.

ARTIGO 2

Binding intensity and metal partitioning in soils affected by mining and smelting activities in Minas Gerais, Brazil

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Binding intensity and metal partitioning in soils affected by mining and smelting activities in Minas Gerais, Brazil

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Abstract

This study investigated single and sequential extractions of Zn, Pb, and Cd in Brazilian soils affected by mining and smelting activities. Soils from a Zn mining area and a tailing from a smelting area were collected in Brazil. The risk assessment code (RAC), the redistribution index (Uts), and the reduced partition index (I_R) have been applied to the data. Zinc and Cd, in soil samples from the mining area, were found mainly associated with carbonate forms, which did not occur for Pb. For the tailing, more than 70% of Zn and Cd were released in the exchangeable fraction, showing a much higher mobility of these metals at this site, which was also supported by results of RAC and I_R. These differences in terms of mobility might be due to different chemical forms of the metals in the two sites, which are attributable to natural occurrence as well as ore processing.

Index terms: extractions, speciation, mobility

1. Introduction

Heavy metal contamination of soils is an environmental problem that has increased in the past few decades. Heavy metals can enter ecosystems through both natural and anthropogenic processes. Mining and smelting activities are very important for societal development, yet these activities are known to have a potential of generating heavy metal contamination (He et al., 2005).

High metal contents are commonly found in soils affected by mining and smelting activities, which can result in considerable soil contamination (Alloway, 1990). Although there are several Zn mining areas containing sulfide zinc as their deposits, the Zn mining area of Vazante, located in Minas Gerais State (MG), Brazil is one of the major known silicate zinc deposits in the world (Hitzman et al., 2003). This deposit is responsible for a substantial portion of Zn production in Brazil (Monteiro et al., 2006), which has been increasing in recent years (MME, 2010). High Zn concentrations were previously reported in soils from Vazante (Júnior et al., 2008). Besides Zn, other heavy metals such as Pb and Cd can also be present at high concentration in the area, which is relevant for human health risk assessments, due to the high toxicity of Pb and Cd to humans.

Measuring total metal contents in contaminated soils using strong acids may be valuable for a first estimate of risk assessment in these areas. However, such determinations do not provide information on the mobility and bioavailability of heavy metals (Pagnanelli et al., 2004). The mobility and availability of heavy metals are controlled by many processes such as precipitation-dissolution, adsorption-desorption, complexation-dissociation, and oxidation-reduction (Sparks, 2003). Such reactions affect the chemical form as well as the soil-metal interaction, which can be inferred by sequential extraction techniques (Hejabi and Basavarajappa, 2013). These techniques provide useful information on metal quantities that could be associated with different phases (Sparks, 2003).

There are several sequential extraction methods for partitioning of heavy metals in soils and sediments (Tessier et al., 1979; Ahnstrom and Parker, 1999; Han et al., 2003). These procedures are all based on the general principle of reacting a soil sample with chemical solutions characterized by increasing strength. Using results from sequential extraction procedures, Han et al. (2003) developed an approach to study metal redistribution in soils. The authors mentioned the definitions and applications of two parameters, the redistribution index (U_{ts}) and the reduced partitioning parameter (I_R). These parameters provide useful information in quantifying redistribution processes and binding intensity of heavy metals in contaminated soils. Thus, U_{ts} and I_R may assist data interpretation as well as comparison among different soil samples.

Several studies evaluating contaminated soils or sediments worldwide through sequential extraction procedures can be found in the literature. In Brazil, these studies mostly refer to river sediments (Fernandes, 1997; Perin et al., 1997; Silva et al., 2002), with a few ones concerning contaminated soils/sediments from mining areas (Ribeiro Filho et al., 1999; Soares et al., 2001). Júnior et al. (2008) used sequential extraction procedures to evaluate Zn distribution in soils of Vazante (MG) as well as to verify if Zn contamination could expand from mining areas to the soils in the municipality. However, they did not evaluate the effect of the smelting process on the mobility and availability of Zn, as well as other metals (e.g., Cd and Pb) that can also be present at high concentrations in soils and sediments. Therefore, no studies comparing soils/sediments derived from mining and smelting activities with respect to the heavy metals distribution among the different solid-phase components have been carried out in the area. Additionally, no previous studies in Brazil have applied the approach of estimating mobility/availability, as well as risk using the redistribution index (U_{ts}) and the reduced partitioning parameter (I_R).

This study aims to investigate single (using Mehlich-1 solution) and sequential extractions of Zn, Pb, and Cd in soils affected by mining and smelting activities in Brazil. For that, both parameters – U_{ts} and the I_R – were applied to the data to improve the understanding as well as to enable a better comparison among the samples, especially the contrast between the soil samples from the mining area with a sample of tailing from a smelting site.

2. Materials and Methods

2.1. Area of study and soil sampling

Soil samples were taken from a Zn mining area located in Vazante, Minas Gerais State, Brazil (Fig. 1). A total of six soil samples were collected at 0-20 cm depth from six different locations in the site, which were divided due to their differences in properties (i.e., total concentration of heavy metals). For heavy metals fractionation analyses, in addition to the six soil samples, a tailing sample was also collected (0-10 cm) nearby a smelting plant located in Três Marias, Minas Gerais State, Brazil (close to geographic coordinates 18°11’16” S, 45°14’20” W). Such tailing is a result of smelting Zn ore from two different locations (Vazante – where the soil samples were taken– and the region of Morro Agudo, which is mostly a Zn sulfide ore body). The samples (soils and the tailing) were air-dried at room temperature and then passed through a 2 mm sieve for further analyses.

2.2. Characterization

The properties of the soil samples (< 2 mm fraction), such as pH in water, cation exchange capacity (CEC), and particle-size distribution were characterized according to Embrapa (1999). Single extractions were carried out on the soil samples using Mehlich-1 solution (Embrapa, 1999). For that, 10 g of soil were suspended in 100 mL of Mehlich-1 solution (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4), stirred for 5 minutes, resting overnight, being the supernatant then analyzed for Zn, Pb, and Cd using an atomic absorption spectrometry (Perkin Elmer AAnalyst 800®).

The mineralogical study of the soil samples was carried out by XRD analysis, according to the methodology recommended by Jackson (1979). The scanning interval used was 4–60° 2θ in a Philips PW 1830/40 equipment, using cobalt Kα radiation with a nickel filter.

2.3. Methodology of heavy metal fractionation

The sequential extraction procedure was applied (in duplicate) to assess heavy metal (Zn, Pb, and Cd) fractionation in different mineral phases of the soil samples as well as in the tailing sample. This procedure was a slightly modified version of the protocol developed by Han et al. (2003). Fig. 2 illustrates the procedure used for heavy metal fractionation. It should be mentioned that the only difference between the procedure used in the present study and the one applied by Han et al. (2003) was in the last step (residual fraction). Instead of using a 4 mol L^{-1} HNO_3 solution, for this fraction, we have digested the soil in a microwave oven according to the 3051A USEPA protocol (USEPA, 1998) with a soil:acid ratio of 1:10.

After each step, the samples were centrifuged for 15 min at 2000 rpm and then filtered through a 0.45 μm filter. The analyses of Zn, Pb, and Cd were performed using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). The quality of the soil digestion applied to obtain the residual fraction was determined using a standard reference material (NIST 2586; National Institute of Standards and Technology). Recoveries of Zn, Pb, and Cd were 91, 102, and 98%, respectively. The total concentrations of the metals were calculated from the sum of all fractions.

The fractional redistribution index (U_{tf}) of the soil samples was used to describe the ratio of a heavy metal bound to a solid phase in a contaminated soil related to the control soil (Han et al., 2003; Miretzky et al., 2011). The U_{tf} was calculated using the following equation:

$$U_{tf} = F_a / F_c \quad [1]$$

where, F_a is the percentage of the total metal (Zn, Pb, and Cd) bound to a given component in a metal-contaminated soil, and F_c is the percentage of the total of metal bound to the same component in the control soil.

This index, U_{tf}, compares the amount of metal between the contaminated and uncontaminated soils for the same solid components. The whole-soil redistribution index (U_{ts}) for a given metal is defined as the sum, for i = 1,…,k components (number of soil fractions) of the products of the total metal percentage bound to a given component by its U_{tf} (Han & Banin, 1999; Han et al., 2003), according to the equation below:

$$U_{ts} = \sum_{i=1}^{k} \left(F_i \times U_{tfi} \right) \quad [2]$$

where, F_i is the percentage of the total metal bound to a fraction *i* in a contaminated soil, and U_{tfi} is the U_{tf} function value of a given solid-phase component.

For convention, U_{ts} is equal to 1 for non-amended or non-contaminated (control) soils. This index for a contaminated soil is usually higher than 1 and tends to slowly converge towards one over time (Han et al., 2003). Higher U_{ts} values for contaminated soils mean that there are more differences in the heavy metal distribution among the different solid-phase components compared with the control soil.

In addition to these indexes, which were calculated for the soils from Vazante, it was also determined the reduced partition index (I_R) for all samples (soils and tailing). This index is used to describe quantitatively the relative binding intensity of a metal to a soil, allowing for the comparison of the binding intensity of a metal to different soils, as well as the comparison of the binding intensity of different metals to the same soil (Han et al., 2003). Prior to the calculation of the I_R, we calculated the partition index (I), according to the following equations (Miretzky et al., 2011):

$$I = \sum_{i=1}^{k} (F_i \times (i)^n)/100 \quad [3]$$

$$I_R = I/k^n \quad [4]$$

where, (*i*) is the extraction step number (1 for the least aggressive and k for the most aggressive); *n* is an integer, usually 1 or 2, and F_i is the percentage of the total metal bound to the component *i*. In this study, k=6, and n=2, the latter, arbitrarily chosen. It has to be considered that there is a maximum and a minimum value for I_R. Under such circumstances, the maximum I_R value is 1, which is obtained when the metal percentage in the residual fraction (F_6) is 100%. On the other hand, the minimum I_R value is 0.028 and is obtained when the metal percentage in the exchangeable fraction (F_1) is 100%. Therefore, I_R

measures the binding intensity of heavy metals in soils, where higher and lower I_R values refer to smaller and greater mobility and availability, respectively.

The risk of environmental contamination by the release of Zn, Pb, and Cd in the soil samples as well as in the tailing was evaluated through the risk assessment code (RAC). This code has been applied elsewhere (Jain et al., 2004; Singh et al., 2005; Rodríguez et al., 2009) and correlates the amount of metal in the exchangeable and carbonate fractions with environmental risk (Jainet et al., 2008), thru a classification scale ranging from no risk to very high risk for the environment.

3. Results and Discussion

3.1. Soil characterization

Physicochemical properties of the soil samples from the Vazante mine area are presented in Table 1. In general, the soils were alkaline. This can be attributed to the presence of calcareous minerals, as reported in the XRD results (Fig. 3). Percentages of organic matter were low, with the highest value found in the control soil. The presence of vegetation in the area where the control soil was collected could explain its higher OM content compared with the other soil samples. Also, a higher CEC was verified for the control soil, which can be explained due to its greater OM content. Soil texture of the soil samples, as per the USDA classification, varied from sandy-loam to clay.

High total concentrations of Zn, Pb, and Cd were found in the soil samples, especially Zn (Table 2). In general, the major contaminants were Zn and Pb. Even in the control soil, which was collected in an area of native vegetation located next to the pit mining (Fig. 1), the total concentrations of these metals are not considered low compared with the normal range found in agricultural soils. However, studies have shown that the heavy metal concentration ranges in the region of Vazante are normally elevated (Júnior et al., 2008).

Single metal extraction results using Mehlich-1 solution are also shown in Table 2. The amount of the metals released using Mehlich-1 was different among the soils. Comparing such soils with respect to their Mehlich-1 extractable metal content is problematic, taking into account that the soils do not have the same total metal contents. In this context, the numbers in parentheses in Table 2 represent the percentage of the total metal concentration that was released with Mehlich-1 solution. A small fraction of the total content of Pb was desorbed by this single extraction. On the other hand, for Zn and Cd, the percentages removed using the same solution were higher, with Cd showing greater values when compared with Zn. Similar results were also reported by Maiz et al. (2000). However, it should be noted that the Zn total concentration, as well as its amount removed with the Mehlich-1 solution were significantly higher than Cd.

Mineralogical analysis (XRD) of the soil samples showed, in most cases, the presence of the following minerals: chlorite, quartz, mica, kaolinite, hematite, dolomite, fayalite, ankerite, and siderite (Fig. 3). According to Rigobello et al. (1988), the region of Vazante is composed predominantly of dolomitic minerals. In addition to these basic minerals, XRD analysis of soil E also revealed the presence of willemite and hemimorphite, which are Zn minerals associated with silicate. These minerals have been identified just in the Soil E because, among all samples studied, only this had a Zn concentration high enough to be detected by XRD (detection limit ~ 5%).

The Vazante zinc deposit is one of the major known non-sulfide Zn deposits in the world, sharing characteristics with a relatively small number of the other deposits, such as Beltana (Australia), Berg Aukus/Abenab (Namibia), and Kabwe (Zambia) (Hitzman et al., 2003; Monteiro et al., 2006). Moreover, the ores in Vazante are characterized by the predominance of hemimorphite or willemite (Monteiro et al., 2007).

3.2. Heavy metal fractionation

The targeted components (soil phase) in each fraction obtained from the sequential extraction procedure were operationally defined as: exchangeable (F_1), bound to carbonate (F_2), bound to easily reducible oxides (F_3), bound to organic matter (F_4), bound to reducible oxides (F_5), and residual fraction (F_6). Fractions F_3 and F_5 refer to metals bound to non-crystalline and crystalline manganese and iron oxides, respectively. Moreover, the residual fraction (F_6) contains naturally occurring minerals that may hold trace metals within their crystalline matrix (Jain et al., 2008). The metal in this fraction is assumed to be bound to silicates and can only be mobilized as a result of weathering, which can only be released in the long-term. A good description concerning the details of each fraction usually removed from sequential extraction procedures can be found in Filgueiras et al. (2002).

The concentrations of Zn, Pb, and Cd (mg kg^{-1}) within each fraction of the sequential extraction analysis are given in Table 3. As can be seen, each heavy metal and soil evaluated showed different distribution patterns. However, it should be mentioned again that the different soils studied do not have the same total metal concentrations (Table 2) and, as a result, the comparison among these concentrations in each fraction, in mg kg^{-1}, should be done with caution. Therefore, a large difference that is possible to note is the greater metal concentration in the initial fractions, especially in the first one, for the tailing (smelting) when compared with the soil samples from Vazante.

The fractionation profiles (as a % of the total) of Zn, Pb, and Cd in the soil samples from Vazante (Fig. 4a) as well as in the tailing from Três Marias (Fig. 4b) are shown in Fig. 4. In the soil samples from the Vazante mining area

Zn showed different fractionation profiles (Fig. 4a). For soil D, more than 90% of the Zn was associated with the residual fraction indicating its low risk of mobilization. For the other soil samples from Vazante, Zn was mainly associated with the carbonate and residual fractions, except for soil B, where the metal bound to non-crystalline Fe-Mn oxides had a significant contribution instead of the carbonate phase. The exchangeable fraction of Zn in these soil samples (Vazante mine are) was very low, which agrees with results found elsewhere (Li and Thornton, 2001).

The large contribution of the Zn fraction bound to carbonate can be explained due to the presence of carbonates in the area, based on XRD results (Fig. 3). Several studies involving sequential extraction procedures have shown that Zn tends to occur mainly associated with the residual and Fe-Mn oxides fractions (Lu et al., 2003; Jalali and Khanboluki, 2008; Miretzky et al., 2011). It should be stated that several extraction procedures have been developed to separate metal fractions and may differ among studies. In this context, the Tessier's procedure (divided into five fractions) do not separate the non-crystalline from the crystalline Fe-Mn oxides fractions (Tessier et al., 1979), as we did in this present work. Thus, considering these two fractions together (F_3 + F_5), Fe-Mn oxides made a significant contribution to the retention of Zn.

The fractionation profile of Pb in the soil samples from the mine area in Vazante showed a low association with the carbonate fraction, except for soil A, in which approximately 22% of the Pb found was bound to this solid-phase component (Fig. 4a). In general, the major component for Pb was the residual fractions, ranging from 34% for soil D to 66% for the control soil. In addition to this major solid phase, Pb also was significantly associated with the Fe-Mn oxides fraction. Similar results were reported by Miretzky et al. (2011). Approximately 30% and 50% of Pb were found in the organic matter fraction (F_4) for the soils B and D, respectively. Taking into consideration that these soils have low OM contents, this fact can be attributed to the reagent used in this step, which can also remove metal bound to sulfides (Filgueiras et al., 2002).

The fractionation profile of Cd in the soil samples from the mine area in Vazante is also shown in Fig. 4a. Except for soil D, Cd in the soils was strongly associated with the carbonate fraction (30-53%). Cadmium release from the exchangeable fraction was higher than for Zn and Pb. This result agrees with studies reported by Maiz et al. (2000), who found that among several metals, the most labile metal (exchangeable plus bounds to carbonate) was Cd followed by Zn. High Cd in carbonate forms can be attributed due to the similarity of the ionic radius of Cd^{2+} (0.97Å) when compared with Ca^{2+} (0.99Å). In this context, several studies have shown that Cd^{2+} and Ca^{2+} can substitute for each other in minerals, (e.g. phosphate and carbonate minerals), due to this similar ionic radius (Pickering, 1983; Garin et al., 2003; Korfali and Jurdi, 2010).

Fig. 4b shows the fractionation profile of Zn, Pb, and Cd in the tailing (smelting). More than 70% of the total concentration of Zn and Cd in the tailing (smelting area) was bound to the exchangeable fraction, which was much higher than the amount found for the soils from the mining area of Vazante. These results indicate greater Zn and Cd mobility and bioavailability in the tailing compared with the material from the Vazante mining area (soil samples). Another study evaluating the chemical partitioning of trace metals in soils contaminated by mining and smelting activities in Derbyshire, England also showed higher mobility and availability of trace metals (Zn, Cd, and Pb) at smelting sites compared with mining areas (Li and Thornton, 2001). The larger mobility in the tailing compared with the soil samples can be due to the process used to extract Zn, which the materials are treated, perhaps, with chemical products.

Lead in the tailing was associated with the carbonate phase (~30%), non-crystalline Fe-Mn oxides (~25%) and, at higher proportions, with the residual fractions (~40%) (Fig. 4b). The high contribution of Pb in the residual fraction has been observed previously (Li and Thornton, 2001; Miretzkyet al., 2011). This indicates that the large percentage of Pb is in primary minerals, such as galena (PbS) and/or the Pb in silicates. The sum of Pb in the exchangeable and carbonate fractions, which are considered to be potentially mobile, was higher for the tailing (32%) compared with the soil samples (0.2-22%) (Fig. 4). This suggests that the mobility and availability of Pb also have showed to be greater in the tailing compared with the areas in Vazante, which agrees with previous results described for Zn and Cd.

In order to evaluate the risks, the samples were classified according to the Risk Assessment Code (RAC), which has been used by several authors for assessing heavy metal pollution in soils and sediments (Jain et al., 2004; Jain et al., 2008; Singh et al., 2005; Rodríguez et al., 2009). This code is assigned by taking into account the percentages of metal associated with the soil in the exchangeable and carbonate fractions. Under such circumstances, there is no risk when F_1+ F_2 is lower than 1%, a low risk for a range of 1–10%, a medium risk for a range of 11–30%, a high risk from 31 to 50%, and a very high risk for higher F_1+ F_2 percentages (> 50%).

In this context, Table 4 shows the classification of the samples according to the RAC. It can be seen that the RAC ranged from no risk to very high risk for Zn, from no risk to high risk for Pb, and from low risk to very high risk for Cd. The classifications of very high risk and high risk observed for Zn and Pb, respectively occurred only in the tailing, which demonstrates the greater release of these metals (percentage of the total) from this sample compared with the soil samples from Vazante. Cadmium was classified as high and very high risk in all soils, except for soil D, in which it was classified as low risk. A higher Cd percentage in the fractions F_1+ F_2 was found in the tailing (~86%), showing its higher mobility compared with the other samples.

Miretzky et al. (2011), applying the RAC for different metals in a soil sample, found that Cu was considered highly dangerous, Cd and Cr pose a medium risk, and Co, Ni, Zn, and Pb a low risk. According to the authors, Cd in the exchangeable and carbonate fractions was more released compared with Zn and Pb, which agrees with results from this study. In general, Pb represents lower risk than Zn (Table 4). Similar results have been shown by Rodríguez at al. (2009). Studies evaluating the adsorption of Cd and Pb on soils (oxisols) have showed lower Cd retention, being this metal more available in solution (Pierangeli et al., 2004; Pierangeli et al., 2007), agreeing also with our results, which showed higher Cd mobility compared with other elements.

3.3. Redistribution and partition indexes

The fractional (Utf) and in-the-whole-soil (Uts) redistribution indexes of the soil samples from Vazante are presented in Table 5. First at all, it has to be stated that these indexes were not calculated for the tailing, because they are dependent of the metal redistribution in the control soil. As detailed in the Materials and Methods section, Zn ores from two different locations are usually transported to where the tailing sample was collected. Thus, the control soil collected in Vazante (Fig. 1) was not considered as a natural soil for the tailing generated after the Zn extraction in the smelting plant located in Três Marias.

It can be seen that U_{ts} values for the metals were > 1 and ranged from 1.17 to 2.80 for Zn and from 1.21 to 2.00 for Cd, with values close to 1 (lower values) indicating a distribution pattern more similar to the one verified in the control soil. In case of Pb, U_{ts} was not calculated because the Pb concentration was below the detection limit in the F_1 fraction for the control soil.

The I_R of Zn, Pb, and Cd in the soil samples from Vazante as well as in the tailing from Três Marias are shown in Fig. 5. The I_R values in general were lower for Cd compared with Zn and Pb, demonstrating the higher mobility and availability of Cd, compared for the other metals. Studies evaluating heavy metal concentrations in the exchangeable fraction (mobile fraction) of soils near a Pb/Zn mining and smelting area located in Upper Silesia, Poland showed that the quantity of exchangeable metals were generally low for Pb, moderate for Zn, and high for Cd (Ullrich et al., 1999), which also demonstrates the greater Cd mobility.

I_R values showed the differences among the soils and metals for the soil samples from Vazante and, mainly, the lower binding intensity in the tailing compared with the other soil samples (Fig. 5), which strengthens the higher metal mobility verified for materials after the smelting process.

Fig. 5d compares I_R values determined for the tailing (smelting site) with the mean of the values for the soil samples from Vazante (mining site). As can be seen, the I_R values for the metals were lower in the tailing compared with the soil samples, especially for Zn and Cd. Therefore, the sample from the smelting site contains metals in a more mobile and bioavailable form, which potentially might cause more severe environmental problems than those in the mining area.

4. Conclusions

The soils from the mining area (Vazante, MG) had a different distribution pattern obtained by sequential extraction, which depend on both, soil properties and chemical characteristics of the metal evaluated.

The marked differences in the partitioning patterns between the soils from Vazante (mining area) and the tailing from Três Marias (smelting area) were the higher percentages of Zn and Cd in the exchangeable fraction in the tailing, indicating its greater heavy metal mobility and availability, which can be associated with different chemical forms of these metals in this site (smelting site).

The application of reduced partition index (I_R) to the data obtained from the sequential extraction has shown to be a good tool, assisting on the interpretation and understanding of the results. This index takes into accounts the behavior for all sequential extraction steps and, as a result, it is useful for comparing the binding intensity of metal in soils.

Acknowledgements

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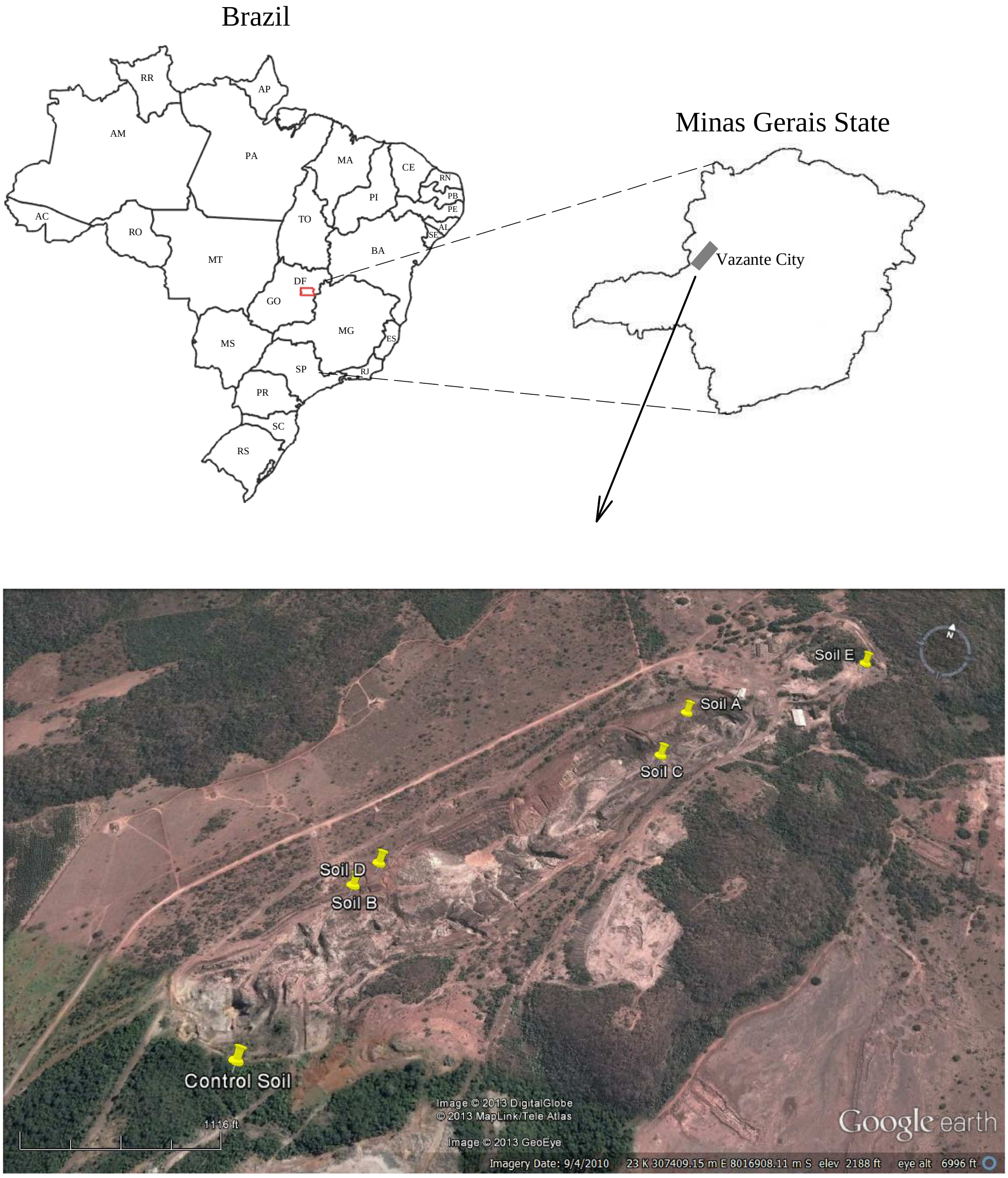

Fig. 1 Location of the soil samples collected from the mine area of Vazante, Minas Gerais State, Brazil.

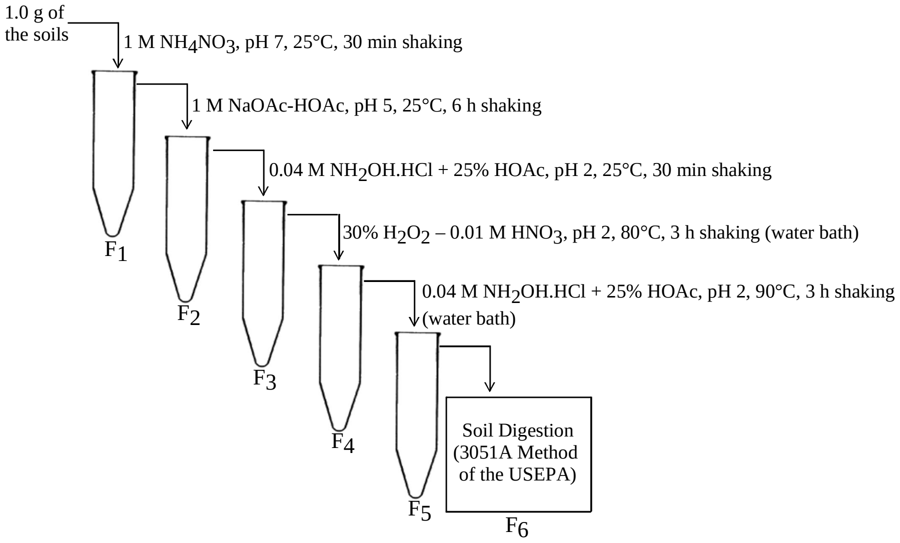

Fig. 2 Protocol used for the selective sequential dissolution procedure (heavy metal fractionation). The solution:soil ratio was 25:1 in all steps. The targeted components (soil phase) in each fraction were considered: F_1, exchangeable; F_2, carbonate; F_3, easily reducible oxides; F_4, organic matter; F_5, reducible oxides; and F_6, residual fraction.

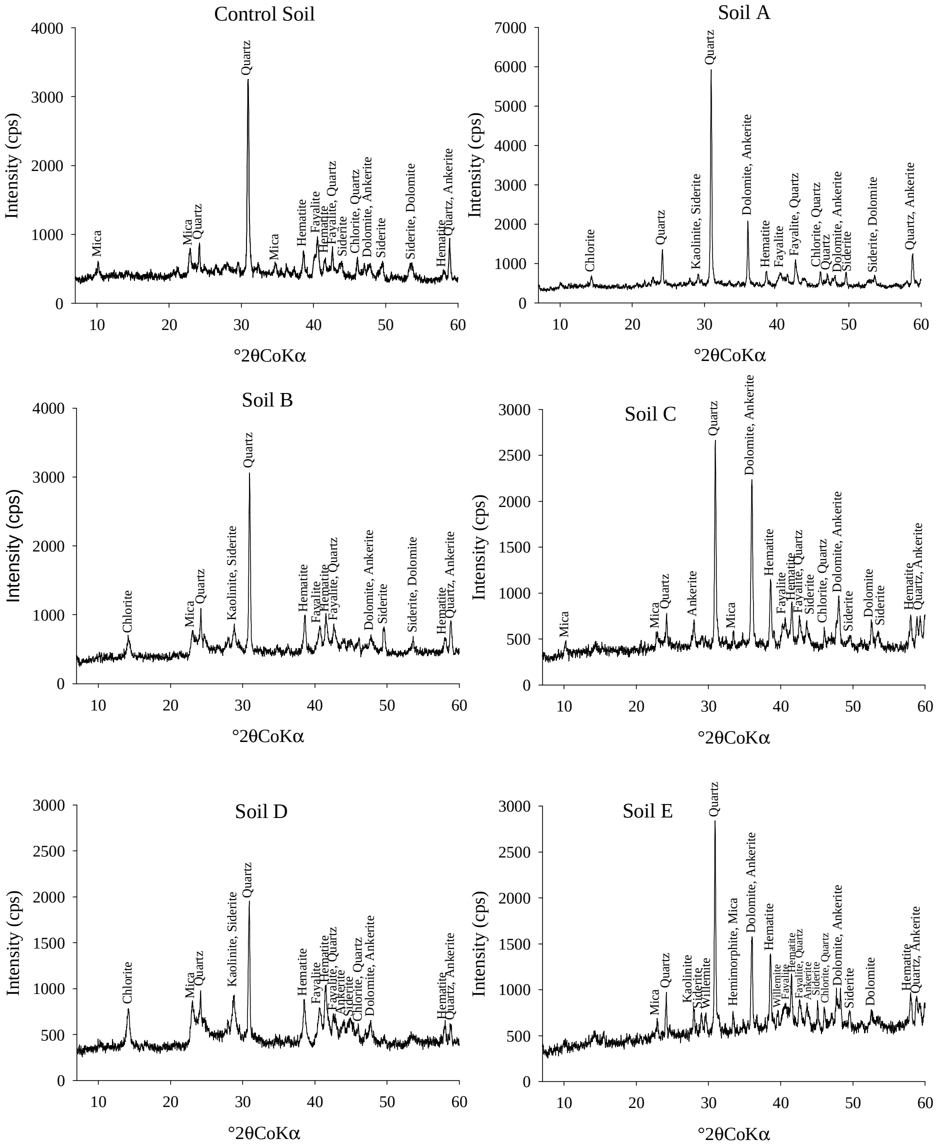

Fig. 3 X-ray diffractogram (XRD) of the soil samples from the Vazante mine area.

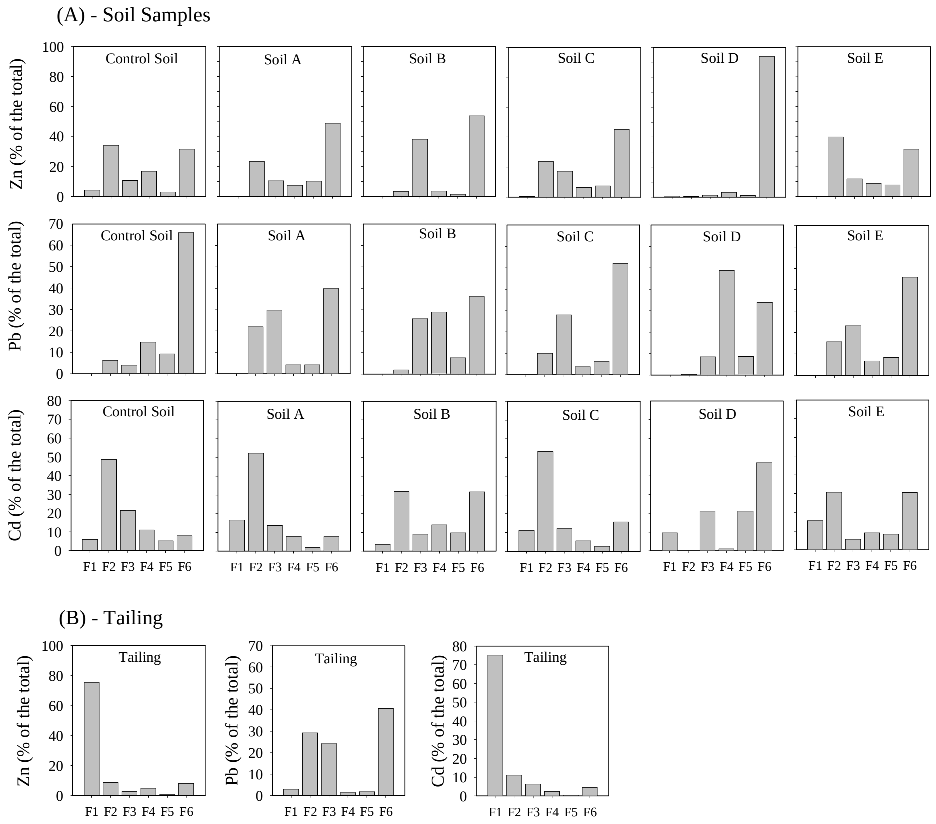

Fig. 4 Percentages of the total of Zn, Pb, and Cd in different mineral phases for soils from the Vazante mine area and a mine tailing from Três Marias (F_1, exchangeable; F_2, carbonate; F_3, easily reducible oxides; F_4, organic matter; F_5, reducible oxides; and F_6, residual fraction).

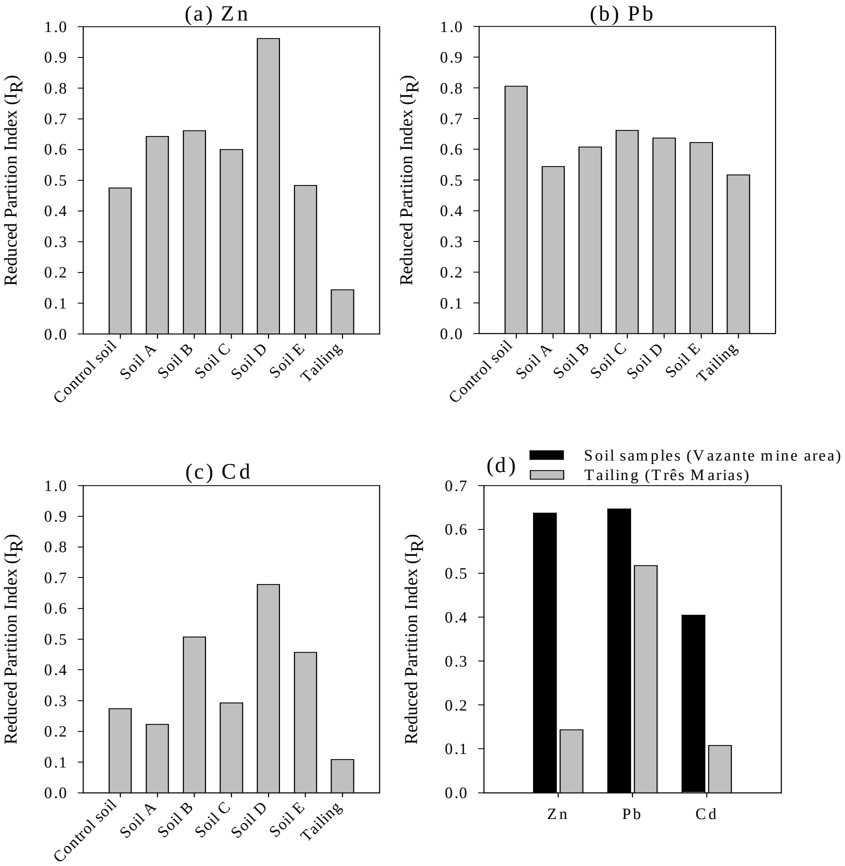

Fig. 5 Reduced partitioning parameters of Zn, Pb, and Cd for soils from the Vazante mine area as well as for a mine tailing.

Table 1 Physicochemical properties of the soil samples from the Vazante mine area.

Soil	pH	CEC	OM	Clay	Silt	Sand	USDA texture class
		$cmol_c\ dm^{-3}$	------------ g kg^{-1} ------------				
Control	5.6	21.7	19.5	255	440	305	Loamy
Soil A	7.4	5.2	5.8	145	430	425	Loamy
Soil B	7.6	5.1	3.1	525	225	250	Clay
Soil C	7.4	5.7	4.1	125	495	380	Loamy
Soil D	5.9	3.8	0.6	560	295	145	Clay
Soil E	7.3	4.6	1.4	105	315	580	Sandy-loam

Table 2 Total metal concentrations (mg kg^{-1}) and single metal extraction using Mehlich I solution (mg dm^{-3}) in soil samples from the Vazante mine area

Soil	Total (mg kg^{-1})			Mehlich I (mg dm^{-3})[1]		
	Zn	Pb	Cd	Zn	Pb	Cd
Control	865±56.0	230±16.4	4.39±0.38	555±29.0 (64%)	5.31±0.08 (2%)	2.91±0.17 (66%)
Soil A	19375±652	5637±379	83.8±6.79	4162±21.4 (21%)	56.3±7.22 (1%)	51.3±0.19 (61%)
Soil B	2299±169	6440±597	5.39±0.45	425±0.92 (18%)	107±15.1 (2%)	4.00±1.75 (74%)
Soil C	14407±1731	4083±745	140±25.0	1919±140 (13%)	3.90±0.96 (0.1%)	59.3±1.95 (42%)
Soil D	680±82.8	3059±283	1.74±0.06	144±36.8 (21%)	33.5±4.48 (1%)	0.53±0.15 (30%)
Soil E	84646±5839	3263±396	346±22.4	10489±180 (12%)	48.1±0.84 (1%)	158±2.25 (46%)

[1] Number in parentheses represents the percent fraction that Mehlich I values represent with respect to the total values

Table 3 Zn, Pb, and Cd concentrations (mg kg^{-1}) in different mineral phases of soils from the Vazante mine area and a mine tailing from Três Marias (F_1, exchangeable; F_2, carbonate; F_3, easily reducible oxides; F_4, organic matter; F_5, reducible oxides; and F_6, residual fraction).

Soil	F_1	F_2	F_3	F_4	F_5	F_6
Zn (mg kg^{-1})						
Control	36.0±1.56	295±17.9	91.6±2.47	144±2.76	25.2±3.81	273±24.6
Soil A	29.1±0.11	4499±502	2004±41.4	1431±13.8	1977±83.4	9434±134
Soil B	1.97±0.17	74.8±3.13	875±69.7	81.9±2.09	30.4±3.75	1235±108
Soil C	56.7±2.95	3407±1171	2479±351	909±13.6	1064±110	6491±424
Soil D	3.91±0.00	2.26±0.14	8.75±0.92	21.3±2.70	6.53±2.52	638±31.4
Soil E	226±0.18	33591±4453	9951±189	7495±841	6635±336	26747±2638
Tailing	24667±384	2812±142	857±11.7	1595±25.5	171±3.08	2659±188
Pb (mg kg^{-1})						
Control	0.00	14.2±3.09	9.01±0.00	33.9±0.28	21.2±2.12	151±4.64
Soil A	1.40±0.20	1239±171	1679±12.9	240±3.32	235±1.47	2243±381
Soil B	0.07±0.02	118±1.08	1657±335	1858±195	485±20.5	2322±244
Soil C	0.17±0.09	407±96.1	1141±410	152±25.1	256±6.89	2126±266
Soil D	0.25±0.08	6.54±0.02	260±19.2	1494±25.8	262±5.83	1036±359
Soil E	1.92±0.17	514±150	757±59.2	221±16.0	272±18.4	1496±151
Tailing	239±3.20	2333±420	1922±52.5	97.8±18.6	143±18.6	3234±598
Cd (mg kg^{-1})						
Control	0.26±0.01	2.13±0.14	0.94±0.03	0.48±0.01	0.23±0.01	0.35±0.06
Soil A	13.9±0.17	43.8±10.0	11.4±0.42	6.57±0.69	1.60±0.11	6.47±0.20
Soil B	0.19±0.01	1.72±0.09	0.49±0.12	0.76±0.08	0.53±0.02	1.71±0.08
Soil C	15.4±1.18	74.5±7.67	16.8±0.06	7.65±0.63	3.73±1.33	22.0±10.1
Soil D	0.17±0.01	0.00	0.37±0.01	0.03±0.00	0.37±0.01	0.82±0.04
Soil E	53.6±3.25	107±1.26	19.8±2.71	31.2±0.04	28.8±1.17	106±14.5
Tailing	412±6.01	60.6±3.25	35.0±1.48	12.9±0.12	2.20±0.07	24.7±0.83

Table 4 Risk of assessment code for Zn, Pb, and Cd in soils from the Vazante mine area as well as for a mine tailing

Soil	Risk assessment code (RAC[a])		
	Zn	Pb	Cd
Control	38% (high risk)	6.2% (low risk)	54% (very high risk)
Soil A	23% (medium risk)	22% (medium risk)	69% (very high risk)
Soil B	3.3% (low risk)	1.8% (low risk)	35% (high risk)
Soil C	24% (medium risk)	10% (low risk)	64% (very high risk)
Soil D	0.9% (no risk)	0.2% (no risk)	9.6% (low risk)
Soil E	40% (high risk)	16% (medium risk)	46% (high risk)
Tailing	84% (very high risk)	32% (high risk)	86% (very high risk)

[a] RAC, based on $F_1 + F_2$ percentages: % (F_1+ F_2) < 1, no risk; % (F_1+ F_2) = 1-10, low risk; % (F_1+ F_2) = 11-30, medium risk; % (F_1+ F_2) = 31-50, high risk; % (F_1+ F_2) > 50, very high risk (Jain et al., 2008).

Table 5 Redistribution indexes of Zn and Cd for soils from the Vazante mine area.

Soil	Fractional Redistribution Index (U_{tf})						Uts^1
	F_1	F_2	F_3	F_4	F_5	F_6	
				Zn			
Soil A	0.04	0.68	0.98	0.44	3.51	1.54	1.40
Soil B	0.02	0.10	3.59	0.21	0.45	1.70	2.30
Soil C	0.09	0.69	1.63	0.38	2.54	1.43	1.30
Soil D	0.14	0.01	0.12	0.19	0.33	2.97	2.80
Soil E	0.06	1.16	1.11	0.53	2.69	1.00	1.17
				Pb			
Soil A	-	3.56	7.59	0.29	0.45	0.60	-
Soil B	-	0.30	6.56	1.96	0.82	0.55	-
Soil C	-	1.62	7.12	0.25	0.68	0.79	-
Soil D	-	0.03	2.17	3.31	0.93	0.51	-
Soil E	-	2.55	5.91	0.46	0.90	0.70	-
				Cd			
Soil A	2.82	1.08	0.63	0.72	0.36	0.97	1.26
Soil B	0.60	0.66	0.42	1.29	1.87	3.98	1.90
Soil C	1.86	1.10	0.56	0.50	0.51	1.97	1.21
Soil D	1.62	-	0.99	0.10	4.05	5.89	-
Soil E	2.63	0.64	0.27	0.82	1.59	3.84	2.00

[1] Uts is the redistribution index considering all fractions of the sequential extraction procedure.

ARTIGO 3

Zinc desorption and speciation using x-ray absorption spectroscopy in soils affected by mining and smelting activities in Minas Gerais, Brazil

Zinc desorption and speciation using x-ray absorption spectroscopy in soils affected by mining and smelting activities in Minas Gerais, Brazil

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Abstract

Zinc contents exceeding regulatory levels have been documented in several areas in Brazil and elsewhere, especially in sites surrounding mining and smelting activities. Zinc is essential for plants and humans, but its excess in the soil can impair the development of most plant species. Although the determination of total Zn contents may be of environmental relevance, studies involving Zn release and speciation are key to assess the mobility and bioavailability and thus the potential ecological risk of such important element. This study evaluated Zn desorption and speciation from soils affected by mining (soils M1, M2, and M3 from a mine area located in Vazante) and smelting (tailing nearby a smelting plant located in Três Marias) activities in Brazil using a stirred-flow approach and a synchrotron based technique, in order to better assess Zn availability and mobility in such environments. The exchangeable fraction represented only a small (< 1%) portion of the Zn desorbed from soils of the mining site, while accounting for ~ 80% of the Zn released from tailings of the smelting site. In the mine area (Vazante), X-ray absorption fine structure (XAFS) showed that Zn was associated with hemimorphite, Zn-ferrihydrite, Zn-phyllosilicates (Zn-kerolite), and Zn-layered double hydroxides (Zn-LDH). This could explain the small desorption of Zn from these soils taking into consideration that those secondary forms (Zn-ferrihydrite, Zn-kerolite, and Zn-LDH) can lead to a significant decrease of the exchangeable/mobilefraction of

Zn in soils. On the other hand, the higher Zn percentage desorbed from the tailing material located in the smelting site (Três Marias) could be attributed to the predominance of weakly bound forms of Zn, comparable to $Zn(NO_3)_2$ (~ 70%), which is an aqueous form of Zn.

Keywords: Zinc release, Mobility, Bioavailability, Chemical species.

Introduction

Zn-mining and smelting activities are very important for societal development, yet these activities can lead to significant amounts of Cd, Pb, and Zn in the soils (ROBERTS; SCHEINOST; SPARKS, 2002). The Zn mining area of Vazante, located in Minas Gerais state (MG), Brazil is responsible for a substantial portion of the Zn production in Brazil (MONTEIRO et al., 2006), which has been increasing in recent years (BRASIL, 2010). As a result of this mining operation, high levels of Zn have been documented in the neighboring region, with the higher contents concentrated in mining pits (BORGES JÚNIOR et al., 2008).

Although Zn is an essential element for plants and humans, its excess may hinder the adequate development of several plant species. Thus, a better understanding of Zn mobility and bioavailability is useful to find the best remediation strategy so as to attenuate the potential toxicity caused by this element. The fate of trace metals in the environment is affected by precipitation-dissolution, adsorption-desorption, complexation-dissociation, and oxidation-reduction reactions (SPARKS, 2003), which in turn alter Zn speciation and hence its toxicity, mobility, and bioavailability in the environment.

One of the most widely used synchrotron-based spectroscopic techniques to speciate contaminants in soils is X-ray absorption spectroscopy

(XAS) (SPARKS, 2013). This technique can be used to study crystalline and non-crystalline solids as well as liquid or gaseous states (KELLY; HESTERBERG; RAVEL, 2008). X-ray absorption spectroscopy has a great advantage to characterize metal-contaminated samples when compared with X-ray diffraction (XRD), because the last technique can only be applied to crystalline solids, yet in some cases the metal of interest might be present in amorphous forms of precipitates. However, it has to be mentioned that the XRD technique is very importante for characterize minerals in soils, being these two techniques (XAS and XRD) considered complementary.

Several studies using XAS to characterize different Zn species in contaminated soils from mining and smelting sites have been developed worldwide (KHAOKAEW et al., 2012; MANCEAU et al., 2000; NACHTEGAAL et al., 2005). However, none of them have been carried out in Brazilian soils. Most studies regarding solid speciation of metals in Brazil have been conducted with sequential extraction procedures (PERIN et al., 1997; SILVA et al., 2002; SOARES et al., 2001), which are important to provide a first approximation on metal behavior in the environment. However, the use of a molecular scale technique such as XAS leads to significant advances on understanding metal species, thus providing a better knowledge concerning metal availability and mobility.

Desorption experiments can be used to determine the metal mobility, including bacth and stirred-flow methods. Taking into considerations the ocorrence of continuous mixing in the reaction chamber and continuously removing products from the solution in the stirred-flow method, this desorption technique decreases diffusion and re-adsorption effects, being preferred by several researchers to study trace metal desorption from soils (SHI, 2006).

This study evaluated Zn desorption and speciation from soils affected by mining and smelting activities in Brazil using a stirred-flow approach and a synchrotron-based technique aiming to associate Zn speciation to Zn mobility and to show the role of different Zn species upon Zn mobility and availability in such environments. Our ultimate goal is to better understand the behavior of Zn on such sites in order to propose adequate management techniques to alleviate any potential Zn toxicity that could impair plant development, thus allowing future revegetation strategies.

Materials and Methods

Studied sites and soil characterization

Soil samples were taken in a Zn mining area located in Vazante, Minas Gerais State, Brazil (close to geographic coordinates 17°55’35” S, 46°49’03” W). In this area, a total of three soil samples were collected at the 0-20 cm depth, with two samples collected inside the pit mining (M1 and M2) and another one in an adjacent area (M3). For comparison in terms of mobility as well as the chemical species occurring in those areas, a sample of a tailing was also collected (0-10 cm) nearby a smelting plant located in Três Marias, Minas Gerais State, Brazil (close togeographic coordinates 18°11’16” S, 45°14’20” W). Such tailing is a result of smelting Zn ore from two different locations (Vazante – where the soil samples were taken– and the region of Morro Agudo, which is mostly a Zn sulfide ore body). The samples (soils and the tailing) were air-dried at room temperature and then passed through a 2-mm sieve for further analyses.

The pH of the samples was determined in deionized water using a soil:water ratio of 1:2.5 (EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA, 1999). The organic matter content was determined according to the Walkley-Black method (WALKLEY; BLACK, 1934). For elemental analyses, soil samples were first subjected to a microwave-furnace digestion according to the 3051A method of the United State Environmental Protection Agency - USEPA (1998). Then, the elements Al, As, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, S, and Zn were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The quality control was performed using a reference soil sample from the National Institute of Standard and Technology (NIST 2586) to check for the accuracy of the determinations, which were found to be satisfactory, i.e., having less than 20% of variation from certified values.

Desorption Experiments

Desorption experiments were conducted in all soil samples from both sites Vazante and Três Marias using a stirred-flow technique. The experimental set up was similar to the one used in Strawn and Sparks (2000). Briefly, a stirred-flow reaction chamber was connected to a pump at the inlet and to a fraction collector at the outlet. The chamber was covered with a 0.45-µm filter to separate the solids from the solution. The chamber volume of 12 mL contained a suspension of 0.6 g of soil, which was stirred using a magnetic stir bar. The solution used as a desorption agent to assess the exchangeable Zn fraction was 0.1 mol L^{-1} $CaCl_2$ adjusted to the respective soil pH. The experiments were run, in duplicate, for 200 minutes at a flow rate of 0.95 mL min^{-1} and the Zn concentrations were measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Zinc speciation using bulk XAFS spectroscopy

Reference Zinc Standards

Natural and synthetic Zn minerals were used to assist in the spectral analysis of the unknown soil spectra. Zinc standards considered in XAS analyses were: hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$), sphalerite (ZnS from XLS Ruby sphalerite, Joplin, MO), smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), zincite (ZnO), willemite (Zn_2SiO_4), ZnOH, Zn-hydrotalcite,ZnFeO, ZnAl – layered double hydroxide (ZnAl-LDH), Zn-kerolite, Zn-ferrihydrite, and a solution of 1 mM Zn^{2+}. Willemite, hemimorphite, Zn-kerolite, Zn-LDH, and Zn-ferrihydrite were synthesized in previous studies (NACHTEGAAL; SPARKS, 2004; ROBERTS; FORD; SPARKS, 2003; ROBERTS; SCHEINOST; SPARKS, 2002; SCHEINOST et al., 2002). All standards spectra are the same reported in Khaokaew et al. (2012).

Zn K-edge spectra of the reference compounds were collected at beamline X-11A at the National Synchrotron Light Source (NSLS), Brokhaven National Laboratory, Upton NY. The double crystal Si(111) monochromator was detuned by reducing I_0 by 30%. The beam energy was calibrated to the first inflection point of the first derivative of the Zn absorption edge (9659 eV) of a Zn metal foil XANES spectrum. Bulk-XAFS spectra were collected at room temperature, from 150 eV below the absorption edge energy, to k values of 12.5 $Å^{-1}$. Depending on the Zn concentration, multiple scans were collected using both fluorescence and transmission modes until satisfactory signal-to-noise ratios were achieved.

Soil Samples

Soil samples (three from the mining site – Vazante – and one from the smelting site – Três Marias) were analyzed by bulk-XAFS at beamline 4-1 at the Stanford Synchrotron Radiation Light Source (SSRL). Similarly as described for the reference compounds, both fluorescence and transmission modes were used. At least four scans were recorded per sample in order to improve the signal-to-noise ratio.

EXAFS data reduction was performed following standard procedures (EICK; FENDORF, 1998; NACHTEGAAL; SPARKS, 2003). Bulk-XAFS spectra from reference standards as well as from soil samples were normalized to obtain extended X-ray absorption fine structure (EXAFS) function using the Athena software (RAVEL; NEWVILLE, 2005). In order to identify and quantify the Zn species prevailing in the soil samples, a linear combination fitting (LCF) was also performed using the Athena software. For that, firstly the energy axis (eV) was converted to photoelectronwave vector units ($Å^{-1}$) by assigning the origin, E_0, to the first inflexion point of the absorption edge. The resulting $\chi(k)$ functions were weighted with k^3 (k is the photoelectron wavenumber) to compensate for the dampening of the XAFS amplitude with increasing k. The LCF analyses were performed using the EXAFS function, which was k^3 weighted, with k values between 2 and 10 $Å^{-1}$.

Results and discussion

Soil characterizations

Bulk soil parameters of the soil samples are presented in table 1. Soil pH is a major factor differentiating the samples of the mining area (neutral to alkaline) from that of the smelting site, which presented an acidic pH of 5.3. The organic matter contents were low in all soil samples, particularly in soil M3. High Zn concentrations were found in all soil samples ranging from approximately 2 to 8% (table 1), which agrees with other studies reporting high Zn concentration in soils of the Vazanteregion (BORGES JÚNIOR et al., 2008).

Table 1 Soil pH, organic matter content, and concentration of different elements ($mg\ kg^{-1}$) in samples collected in mining and smelting areas of Minas GeraisState, Brazil

Parameters	Soilsamples			
	M1 (A)	M2 (C)	M3 (E)	Tailing
pH	7.4	7.4	7.3	5.3
OM ($g\ kg^{-1}$)	5.8	4.1	1.4	5.1
Al ($mg\ kg^{-1}$)	19431	21675	15332	9037
As ($mg\ kg^{-1}$)	15.54	21.43	21.82	61.63
B ($mg\ kg^{-1}$)	4.087	7.992	4.062	6.600
Ca ($mg\ kg^{-1}$)	22709	47433	29086	26664
Cd ($mg\ kg^{-1}$)	103.4	208.3	328.9	612.4
Cr ($mg\ kg^{-1}$)	19.47	27.41	0	9.712
Cu ($mg\ kg^{-1}$)	100.4	91.14	77.19	1054
Fe ($mg\ kg^{-1}$)	52990	57891	44124	31455
K ($mg\ kg^{-1}$)	1328	3489	2037	1751
Mg ($mg\ kg^{-1}$)	28331	32000	22688	2620
Mn ($mg\ kg^{-1}$)	2512	2750	1677	19939
Na ($mg\ kg^{-1}$)	25.20	51.00	48.56	94.13
P ($mg\ kg^{-1}$)	698.7	1143	857.1	201.5
Pb ($mg\ kg^{-1}$)	4394	2485	2353	4729
S ($mg\ kg^{-1}$)	29.75	34.63	45.40	39539
Zn ($mg\ kg^{-1}$)	22132	18272	82457	32827

In addition to Zn, other metals were also detected at relatively high levels, especially Cd and Pb, which occurred in concentrations far exceeding the regulatory levels set for the State of Minas Gerais as well as for Brazil, even for industrial sites, i.e. 2.000 mg kg^{-1}for Zn, 900 mg kg^{-1} for Pb, and 20 mg kg^{-1} for Cd, respectively (BRASIL, 2009).

Stirred-flow desorption experiments

The Zn concentrations released from the studied soil samples using a 0.1 mol L^{-1} $CaCl_2$ solution and stirred-flow approach are shown in figure 1. Previous studies have suggested the use of 0.1 M $CaCl_2$ as a desorbing agent because this must release only the exchangeable fraction of Zn from soils (NACHTEGAAL et al., 2005). It is noteworthy that the exchangeable fractions of Zn desorbed after 200 minutes of reaction of the desorbing agent with the soils from Vazante (M1, M2, and M3) were all very low (< 0.5% of the total).

On the other hand, an opposite behavior in terms of Zn release was observed for the tailing, with approximately 20% of the Zn being rapidly released in the first 4 minutes of desorption, reaching a plateau corresponding to ~80% release within 50 minutes. This result shows the much higher Zn mobility in the tailing compared with the material from the Vazante mining area (soils M1, M2, and M3). Li and Thornton (2001), evaluating the chemical partitioning of trace metals in soils contaminated by mining and smelting activities in Derbyshire, England also have found larger mobilities and availabilities of trace metals (Zn, Cd, and Pb) at the smelting sites compared with the mining area.

Nachtegaal et al. (2005), working in a Zn contaminated soil, found a maximum of 8% of total Zn desorbed also using the stirred-flow approach and a 0.1 mol L^{-1} $CaCl_2$ solution as desorbing agent. Such value of 8% is higher than the amount reported in our study for soil samples from the mining area (Vazante) but a lot smaller than the percentage of Zn desorbed from the tailing sample of the smelting area (Três Marias). Ultimately, the marked difference on Zn desorbed percentages between the mining samples (M1, M2, and M3) and the smelting sample (tailing) found in this study can be associated with different chemical forms of Zn from those two sites. The smaller release of Zn from the soil samples from the mining site could be due to a possible transformation of Zn mineral phases in these soils into more stable Zn species (VOEGELIN et al., 2002), which does not occur in the tailing, where most Zn species would be associated to weakly bound or more soluble forms of Zn derived from the smelting procedure. This is further discussed by the use of XAS in the next section.

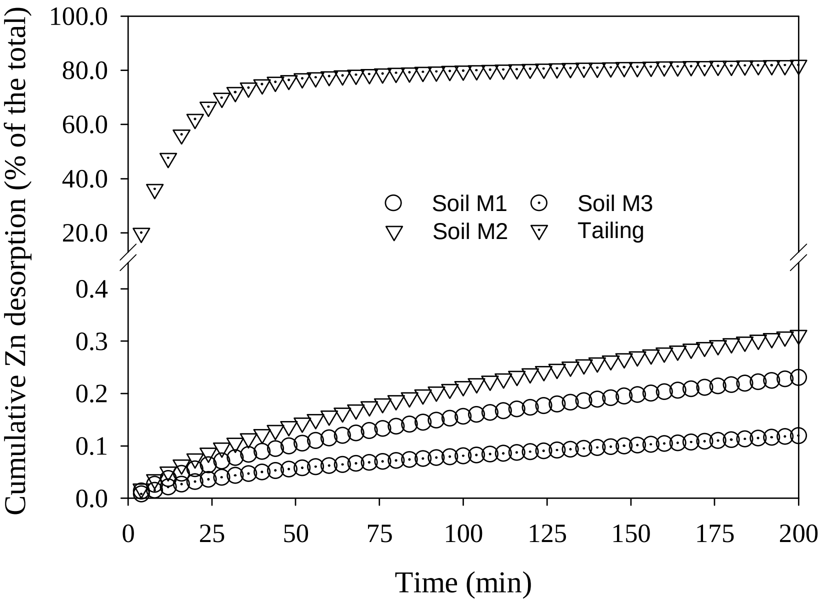

Figure 1 Cumulative Zn desorption from samples collected in mining and smelting areas of Minas Gerais State, Brazil (as % of the total) using a 0.1 mol L^{-1} $CaCl_2$ solution as desorption agent

Zinc speciation using EXAFS analysis

The chi(k) x k^3 EXAFS data for the reference compound are presented in Figure 2. All these standards were included on the linear combination fitting (LCF) to identify and quantify the predominant species in the studied soil samples (unknown samples). Basically, the linear combination fitting models the spectrum from a sample of unknown speciation with a linear combination of spectra from known reference compounds (standards) (KELLY; HESTERBERG; RAVEL, 2008).

The EXAFS data (k^3 weighted) of the soil samples (solid lines) showing the best fits using LCF approach (dotted lines) are shown in Figure 3. First at all, it should be noted that soils M1 and M2 presented EXAFS data with exactly the same frequency and amplitude. Also, the EXAFS data for the soil M3 was similar until a k $(Å)^{-1}$ value of 6 when compared to data reported for soils M1 and M2, presenting differences afterwards. Such behavior seems reasonable as all three soils came from the same Zn mining area. Soils M1 and M2, which showed the same EXAFS data, were collected inside the pit mining, while soil M3, in which changes in the EXAFS data were observed in higher K values, was taken in an area outside of the pit mining, but next to that.

The spectrum for the tailing was perceptively different from all spectra of the soil samples from the mining area, which can be attributed to the occurrence of distinct chemical species to which Zn is associated in both situations (smelting *versus* mining sites). The soil samples M1 and M2 were well fitted by LCF with Zn-LDH, Zn-kerolite, and hemimorphite, with Zn-kerolite being considered the main Zn phase (representing ~ 45%) in both soils. Khaokaew et al. (2012), working with XAS in Zn-contaminated paddy soils, revealed that Zn-layered double hydroxide (Zn-LDH) and Zn-phyllosilicate (Zn-kerolite) were the most important Zn species in those soils.

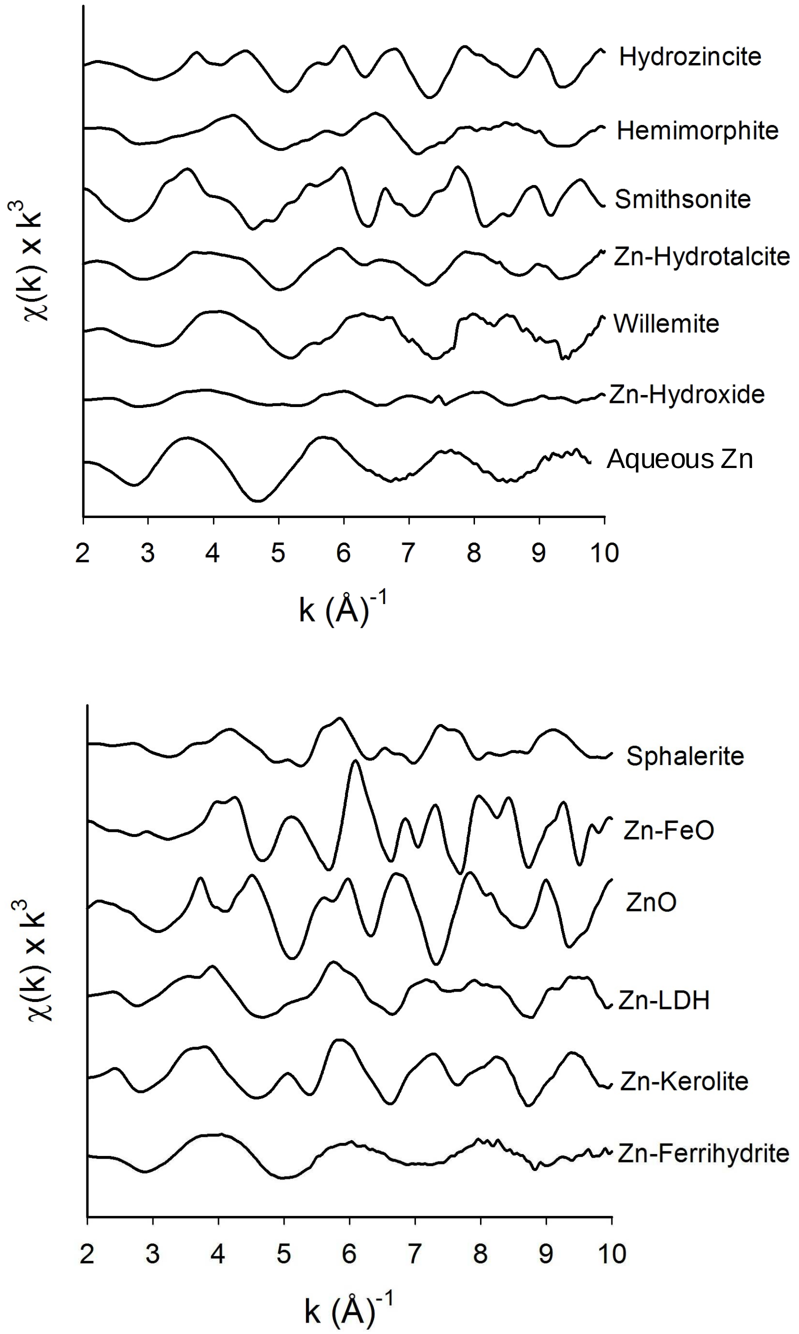

Figure 2 Zn-K edge k^3 weighted χ-spectra of the Zn reference compounds

The fact that hemimorphite provides also relatively significant contributions to the fit for soils M1 and M2 makes sense, because the Vazante zinc deposit is one of the major non-sulfide Zn deposit in the world (HITZMAN et al., 2003; MONTEIRO et al., 2006), with hemimorphite and willemite being previously reported in this region (MONTEIRO et al., 2007).

The spectrum for soil M3 was also fitted with the same species mentioned for soils M1 and M2, except for the absence of Zn-LDH (Figure 3). As can be seen, Zn-LDH did not contribute to the fit for the soil M3, with Zn-ferrihydrite being detected instead. Roberts, Scheinost and Sparks (2002) evaluated Zn speciation in a smelter-contaminated soil using a synchrotron-based technique and revealed also that Zn-ferrihydrite is an important component for the soil investigated.

Only approximately 30% of primary minerals (i.e., hemimorphite) were described in the soil samples from the Vazante mine area (M1, M2, and M3), with the remainder Zn being incorporated into neoformed precipitates (Zn-LDH, Zn-kerolite, and Zn-ferrihydrite).The formation of these Zn-containing precipitates can greatly decrease Zn bioavailability in contaminated soils (JUILLOT et al., 2003). It has to be mentioned that these neoformed precipitates, especially Zn-LDH and Zn-kerolite, occur mainly under high pH conditions (FORD; SPARKS, 2000; NACHTEGAAL et al., 2005; SCHLEGEL et al., 2001), and these phases are more stable than hydrozincite, $Zn(OH)_2$, and $ZnCO_3$ (JUILLOT et al., 2003). This could explain the low percentages of Zn desorbed from the soil samples M1, M2, and M3 of the Vazante mine area by means of the stirred-flow approach (Figure 1). A critical point that needs to be made here is that these precipitates formed in the soil samples from the Vazante mine area are poorlycrystalline and thus could not be picked up using X-ray diffraction (XRD).

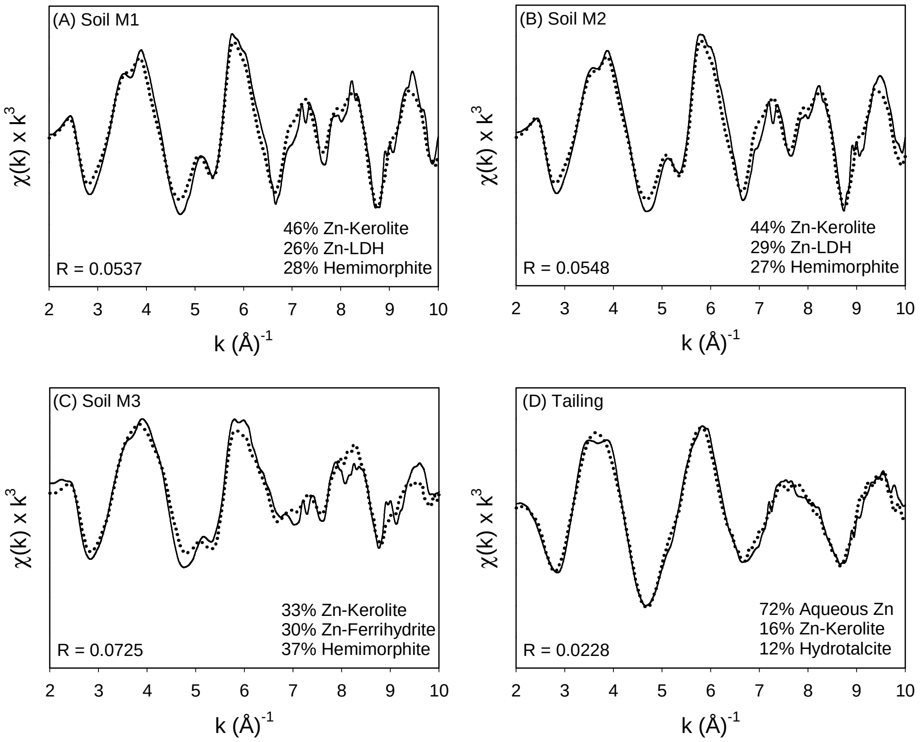

Figure 3 EXAFS spectra of samples collected in mining and smelting areas of Minas Gerais state, Brazil. The solid lines represent the raw $k^3\chi(k)$ data and the dotted lines indicate the best fits obtained by the LCF approach

Finally, it is noteworthy yet again that figure 1 showed a higher percentage of Zn released from the tailing when compared with the other soil samples from the mine. As can be seen in figure 3, the EXAFS spectrum of the tailing was well fitted by LCF with approximately 70% of the zinc as soluble Zn (Zn^{2+}). This standard is a reference for a material weakly bound to the solid, presenting Zn in a more mobile and bioavailable form. This clearly corroborates the results showing that ~ 80% of the Zn was desorbed from the tailing (Figure

1). Therefore, this study elucidated the marked difference in terms of Zn mobility in the two sites (mining and smelting) studied. The use of XAS showed in addition that the incorporation of Zn into newly formed precipitates found in the mining site leads to a considerably reduction of the exchangeable Zn fraction, which, in turns allows for a more successful approach for revegetating the area since Zn phytotoxicity is expected to be smaller in the mining area, when compared with the smelting area.

Conclusion

The soil samples from the Vazante mine area have much lower percentages of Zn in the exchangeable fraction compared with the tailing from the smelting site, in which approximately 80% of the Zn was desorbed using the stirred-flow technique.

The small quantities of Zn released from the soils M1, M2, and M3 were linked to the formation of neoformed Zn precipitates, which are poorly crystalline and deeply reduce Zn mobility.

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