UNIVERSIDADE FEDERAL DE LAVRAS

FÁBIO BENEDITO ONO

BIOACESSIBILIDADE DE Cd E Pb EM ÁREAS DE BENEFICIAMENTO DE METAIS E ESPECIAÇÃO DE As POR XANES EM ÁREAS DE MINERAÇÃO

LAVRAS - MG

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Orientador
Dr. Luiz Roberto Guimarães Guilherme

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Ficha Catalográfica Elaborada pela Coordenadoria de Produtos e Serviços da Biblioteca Universitária da UFLA

Ono, Fábio Benedito.
Bioacessibilidade de Cd e Pb em áreas de beneficiamento de metais e especiação de As por xanes em áreas de mineração / Fábio Benedito Ono. – Lavras : UFLA, 2013.
106 p. : il.

Tese (doutorado) – Universidade Federal de Lavras, 2013.
Orientador: Luiz Roberto Guimarães Guilherme.
Bibliografia.

1. Elementos-traço. 2. XAS. 3. Especiação de metais. 4. Rejeitos de mina. 5. Contaminação ambiental. 6. Particulados de poeira. I. Universidade Federal de Lavras. II. Título.

CDD – 549.13

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APROVADA em 28 de junho de 2013.

Dr. Leônidas Carrijo Azevedo Melo	UFV
Dr. Mário César Guerreiro	UFLA
Dr. João José Marques	UFLA
Dr. Nilton Curi	UFLA

Dr. Luiz Roberto Guimarães Guilherme
Orientador

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Aos meus pais, ***Norio*** *e* ***Creusa****, pela fé, amor e confiança;*
Aos meus irmãos, ***Fer, Tati, Laine, Júnior, Vivi e Etelvina,***
pela amizade, apoio e carinho;
A ***Karine Lopes****, pelo incentivo, paciência, companheirismo*
e por torcer pelo meu sucesso,

DEDICO

AGRADECIMENTOS

Agradeço a Deus, por sua fidelidade, amor e sabedoria concedida;

À Universidade Federal de Lavras, em especial ao Programa de Pós-Graduação em Ciência do Solo, pela oportunidade de realizar o doutorado;

Ao Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq, pela concessão da bolsa de estudo, e à Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES, pela bolsa de doutorado Sanduíche;

À FAPEMIG, CNPq e CAPES, pelos recursos para a execução do projeto de pesquisa;

Ao Laboratório Nacional de Luz Síncrotron, por permitir a execução da análise de XAS (projeto 11781, financiado por LNLS/ABTLuS/MCT);

Ao National Synchrotron Light Source - NSLS, Brookhaven National Laboratory - BNL, financiado pelo U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, por permitir a execução das análises de µ-XRF e µ-XANES;

À Universidade de Delaware, em especial ao Delaware Environmental Institute e ao grupo de pesquisa em Química do Solo Ambiental, especialmente: Donald Sparks, Matt Siebecker, Ryan Tappero, Cecily Moyer e Jerry Hendricks, pelo apoio dado para a realização da pequisa;

Ao professor Luiz Roberto Guimarães Guilherme, pelos valiosos ensinamentos, orientação, dedicação, incentivo, enorme confiança que sempre demonstrou ao longo desses anos e, em especial, pela amizade, sinceramente muito obrigado;

Aos membros da banca examinadora, Dr. Leônidas Carrijo Azevedo Melo, Dr. Mário César Guerreiro, Dr. João José Marques e Dr. Nilton Curi, pelas importantes sugestões para esta tese;

A Karine Lopes, pela valiosa contribuição na revisão do texto da tese;

Aos funcionários do DCS: Dirce, João Gualberto, Roberto, Pezão, Gilson, Humberto, Carlinhos, Adalberto e Maria Alice, pela amizade e pelo auxílio imprescindível nas atividades do cotidiano;

A todos os meus amigos do DCS, especialmente: Geila, Nise, Guilherme bombástico, Guilherme bombinha, Guilherme Amaral, Dani, Satoshi, Caconde, Veri, Rômulo, Ana Paula, Viviane, Henrique, Nilma, Gabriel, Carla, pela agradável convivência e pela valiosa ajuda para a concretização deste trabalho;

Aos amigos da república: Glauco, Coiote, Eugênio, Calouro e Walmes, pela agradável convivência, e à Dona Cidinha pela dedicação em manter a organização da república;

Enfim, a todos aqueles que, direta ou indiretamente, contribuíram para a realização deste trabalho.

Muito Obrigado!

RESUMO GERAL

Atividades de mineração e beneficiamento de metais geram resíduos que podem conter quantidades significativas de elementos-traço (TE). A disposição desses resíduos no ambiente pode fazer com que os elementos neles presentes sejam liberados e entrem na cadeia trófica. Investigar e monitorar os metais no ambiente é de suma importância, tornando os estudos com enfoque nesse problema cada vez mais relevantes nos contextos social e ambiental. Estudos quantificando a fração disponível dos elementos (e.g., testes de bioacessibilidade) e investigando suas espécies minerais e formas (e.g., absorção de raios-X) em solos/rejeitos são de grande relevância, pois uma caracterização detalhada do material é essencial para mensurar os riscos oferecidos pelos mesmos. Nesse contexto, dois estudos foram conduzidos para investigar TE em rejeitos de áreas de mineração e/ou beneficiamento de metais. Objetivou-se, no primeiro estudo, avaliar a bioacessibilidade e a cinética de dessorção de Cd e Pb em rejeitos de uma área de beneficiamento de zinco, situada próximo à cidade de Três Marias-MG; no segundo, visou-se avaliar os teores de As nos particulados de poeira e investigar, via análises de espectroscopia baseada na radiação síncrotron, a especiação de As em rejeitos de mina e em particulados de poeira de uma área de mineração de ouro situada próximo à cidade de Paracatu-MG. O primeiro estudo indicou altas concentrações de Cd e Pb nas amostras, indicando a importância de um adequado planejamento para a disposição final desses rejeitos. A bioacessibilidade de Cd e a de Pb na fase intestinal foram menores que 47 e 4%, respectivamente, o que demonstra que uma significante fração dos elementos não está disponível para absorção. Entretanto, esse material precisa ser monitorado, pois a bioacessibilidade dos metais pode aumentar em uma eventual mudança físico-química do ambiente, levando a disponibilização de Cd e Pb. Os experimentos de cinética de dessorção indicaram que a fração de Pb nas amostras é menos lábil e a de Cd mais lábil, concordando com o resultado de bioacessibilidade. O segundo estudo apontou que o As estava presente nas amostras na forma de arsenopirita e em seus produtos do intemperismo, predominando sua forma pentavalente, como arsenato de Fe pouco cristalino. Isto confirma a baixa bioacessibilidade de As nas amostras e reforça a importância dos óxidos de Fe na imobilização do As no ambiente terrestre. Detectou-se presença de As nos particulados de poeira, sendo os maiores teores para as amostras coletadas mais próximo à área da mina. Os particulados de poeira apresentaram espécies de As similares àquelas encontradas nos rejeitos da mina.

Palavras-chave: Elementos-traço. Bioacessibilidade. XAS. Especiação de metais. Contaminação ambiental.

GENERAL ABSTRACT

Mining and smelting activities of metals generate wastes that may contain significant amounts of trace elements. The disposal of these wastes in the environment can cause release of trace elements, which may then enter the food chain. The importance of investigating and monitoring the metals in the environment makes the studies on this concern even more relevant in the social and the environmental contexts. Studies quantifying the available fraction of the elements (e.g. bioaccessibility tests) and investigating their mineral species and forms (e.g. X-ray absorption) in soils/tailings are of great importance, since a detailed characterization of the material is essential for a better risk assessment. Two studies were conducted to investigate trace elements in tailings from mining and/or smelting of metals. The aim of the first study was to evaluate the bioaccessibility and desorption kinetics of Cd and Pb in tailings from a zinc smelting area located near Três Marias-MG; the second study evaluated As contents in windblown dust and investigate, via analysis of spectroscopy based on synchrotron radiation, As speciation in mine tailings and windblown dust from a gold mining area located near Paracatu-MG. The first study showed high concentrations of Cd and Pb in the samples, indicating the importance of adequate planning for their final disposal. Cadmium and Pb bioaccessibility in the intestinal phase was less than 47 and 4%, respectively. This indicates that a considerably high fraction of the elements was not available for absorption. However, this material has to be monitored since its bioaccessibility may increase with eventual physicochemical changes, releasing Cd and Pb. Desorption kinetics experiments revealed that the Pb in the samples remained in less labile fractions whereas Cd was found in more labile fractions, which is in accordance with the bioaccessibility result. The second study showed that As was present in the samples as arsenopyrite and its weathering products, but mostly it was As pentavalent as poorly crystalline ferric arsenate. This supports the finding of low bioaccessible As in the samples and highlights the importance of Fe oxides in immobilizing As in the terrestrial environment. All air particulate samples had As-rich particles, with the highest values for the samples collected closest to the mine area. The air particulates showed solid-phase As species very similar to those found in the mine tailings.

Keywords: Trace elements. Bioaccessibility. XAS. Metals speciation. Environmental contamination.

SUMÁRIO

PRIMEIRA PARTE

PRIMEIRA PARTE

1 INTRODUÇÃO

Mineração e beneficiamento de metais são importantes atividades econômicas, pois contribuem para o desenvolvimento do país, gerando renda e emprego, além de produzir os metais que são utilizados em diversos contextos. Entretanto, as atuais técnicas de mineração de metais fragmentam e expõem à superfície terrestre substratos de rochas que contêm elementos-traço, tais como arsênio (As), cádmio (Cd) e chumbo (Pb). Esses substratos, após o beneficiamento do metal de interesse (e.g., ouro, zinco, níquel), geralmente permanecem na superfície terrestre como rejeitos e podem ser uma relevante fonte de contaminação ambiental por elementos-traço, já que são, muitas vezes, transferidos para a água, solos, plantas e outros meios, atingindo eventualmente os humanos e representando uma considerável ameaça à sua saúde.

O encerramento das atividades de exploração de metais pode deixar extensas áreas contaminadas, favorecendo o risco de contaminação da população, especialmente crianças, as quais são mais frágeis em um cenário de avaliação de risco. A exposição humana ao As é conhecida pelo seu efeito carcinogênico (WORLD HEALTH ORGANIZATION - WHO, 1999), enquanto o Cd pode causar disfunção renal, distúrbios esqueléticos e problemas respiratórios (JARUP, 2003). O Pb, por sua vez, é responsável por sérios danos ao sistema nervoso central, principalmente de crianças, com significativa redução da inteligência (HAN et al., 2012). Tais efeitos demonstram o grande risco da exposição a esses elementos e confirmam a relevância da questão em discussão.

Diversos estudos têm reportado elevados teores de elementos-traço em áreas de mineração e beneficiamento de metais e em suas proximidades, especialmente de As no entorno de áreas de mineração aurífera (BOSSY et al., 2010; BUNDSCHUH et al., 2012; CHOE et al., 2009; FILIPPI; DOUŠOVÁ; MACHOVIČ, 2007; JUHASZ et al., 2007; LEE et al., 2008; MATSCHULLAT et al., 2000; PAKTUNC; FOSTER; LAFLAMME, 2003) e de Pb e Cd em áreas de mineração e beneficiamento de Zn (BI et al., 2006; CHRASTNÝ et al., 2012; DIAS-JÚNIOR et al., 1998; LAMB et al., 2009; RIBEIRO-FILHO et al., 1999; SANTOS, 2010). Embora esses elementos estejam, geralmente, presentes em rochas e solos na forma mineral de baixa solubilidade, podem formar outras espécies minerais mais solúveis quando expostos a diferentes condições físico-químicas do ambiente.

Em casos de ingestão de materiais contaminados com As, Cd e Pb, a avaliação dos teores totais dos elementos em amostras de áreas de mineração, por si só, não permite uma estimativa correta da avaliação de risco. Isto é devido ao fato de, na maioria das vezes, apenas uma fração de todo elemento ingerido ser absorvida pelo organismo, ou seja, a biodisponibilidade é menor que 100%. Desse modo, Ruby et al. (1996, 1999) propuseram os testes de bioacessibilidade (*in vitro*), que mensuram a quantidade do contaminante que é passível de ser absorvido pelo sistema digestivo humano, para serem utilizados em estimativas de avaliação de risco e proporcionar valores mais fidedignos.

Dada a relevância da atividade de exploração de ouro em Minas Gerais, pesquisas avaliando a bioacessibilidade de elementos-traço em áreas impactadas por atividades de mineração e beneficiamento de metais adquirem relevante importância. Estudos dessa natureza podem dar um indicativo do risco de contaminação pela exposição dos habitantes próximos a essas áreas.

Além de mensurar os valores bioacessíveis de metais para as estimativas de avaliação de risco, métodos instrumentais, como a espectroscopia de absorção de raios-X (XAS), são relevantes na caracterização de espécies moleculares e minerais presentes nas amostras, auxiliando no entendimento dos resultados de bioacessibilidade dos metais. Uma caracterização detalhada do material contaminado (solo, rejeito, entre outros) é essencial para a escolha do seu destino final, levando em consideração a possível exposição humana aos mesmos.

Diante do exposto, os objetivos do presente trabalho foram (i) avaliar a bioacessibilidade e a cinética de dessorção de Cd e Pb em amostras de rejeitos de uma área de beneficiamento de zinco, situada próximo à cidade de Três Marias-MG e ao rio São Francisco; e (ii) avaliar os teores de As nos particulados de poeira e investigar, via análises de espectroscopia baseada na radiação síncrotron, a especiação de As em amostras de rejeitos de mina e em particulados de poeira de uma área de mineração de ouro situada próximo à cidade de Paracatu-MG.

2 REFERENCIAL TEÓRICO

2.1 Elementos-traço

O termo "elementos-traço" tem sido utilizado para definir elementos presentes em baixa concentração (<0,1%) em materiais naturais, tais como a litosfera; se suas concentrações são suficientemente altas, eles podem ser tóxicos para os organismos vivos (ADRIANO, 1986). Compreendem elementos-traço os metais-traço, metais pesados (elementos com densidade maior que 5 g cm^{-3}, e.g., Cd, Pb, Hg), metaloides (elementos tendo propriedades dos metais e dos ametais, e.g., As) e micronutrientes. As fontes de elementos-traço são os materiais de origem dos solos (rochas), fertilizantes comerciais, materiais corretivos (calcários), biossólidos, águas de irrigação, resíduos da combustão do carvão, atividades de mineração e beneficiamento de metais, emissões de automóveis, entre outros (SPARKS, 2003).

Cada elemento-traço tem comportamentos particulares no ambiente (água, solo, ar, organismos vivos) e diferentes formas de interagir e manifestar seus efeitos nos seres vivos. Elementos-traço no solo estão associados a componentes orgânicos e inorgânicos, sendo o seu comportamento controlado por diversos processos físico-químicos que regulam sua mobilidade, tais como precipitação-dissolução de solutos, oxidação-redução, complexação com ligantes orgânicos e inorgânicos e troca de íons por adsorção (MCBRIDE, 1994).

Elementos-traço, tais como As, Cd e Pb, têm sido investigados em vários meios (e.g., água, plantas, alimentos, solos, rejeitos) devido a seus potenciais efeitos tóxicos aos animais e humanos (BI et al., 2006; GROTEN; BLADEREN, 1994; LAMB et al., 2009; LEE et al., 2008; LU et al., 2011; PELFRÊNE et al., 2011; SCHAIDER et al., 2007). No ranking das 275 substâncias mais perigosas à saúde humana, estabelecido pela Agency for Toxic

Substances and Disease Registry - ATSDR (2011), As, Pb e Cd encontram-se na primeira, segunda e sétima posições, respectivamente. A classificação das substâncias é baseada na combinação de sua frequência, toxicidade e potencial de exposição humana aos locais contaminados.

2.1.1 Arsênio

Arsênio é um elemento de crescente preocupação ambiental devido à sua alta toxicidade e consequente risco à saúde humana e animal (SMITH; NAIDU; ALSTON, 1998). Ainda que em baixos níveis, os humanos são diariamente expostos ao As, por meio da ingestão de alimentos e água e pela inalação do ar (BASU et al., 2001). O elemento é fortemente associado a cânceres de pele, bexiga e pulmão em humanos (WHO, 1999). Sua presença em água potável, particularmente, tem sido associada à ocorrência de cânceres, diabetes e problemas cardiovasculares. Em geral, a contaminação de água potável por As, especificamente As inorgânico, decorre do intemperismo de minerais em rochas e solos (SPARKS, 2003).

Arsênio é amplamente distribuído no ambiente, sendo o vigésimo elemento mais abundante na crosta terrestre, com concentração média em torno de 0,5 e 2,5 mg kg^{-1} (KABATA-PENDIAS; MUKHERJEE, 2007). Trata-se de um metaloide de ocorrência natural em ambientes terrestres e aquáticos, e componente de mais de 245 formas minerais, das quais aproximadamente 60% são arsenatos (e.g., escorodita, $FeAsO_4 \bullet 2H_2O$), 20% sulfetos e sulfossais, e os restantes 20% incluem os arsenetos, arsenitos (e.g., orpimento, As_2S_3), óxidos, silicatos e As elementar. Entretanto, apenas algumas dessas formas são geralmente encontradas em quantidades significativas (MANDAL; SUZUKI, 2002). Seus minerais mais comuns são arsenopirita (FeAsS), orpimento (As_2S_3), realgar (As_4S_4) e arsenolita (As_2O_3). Arsenopirita pode ser facilmente oxidada por O_2 e Fe^{3+} e transformada em seus produtos secundários, gerando formas de As mais disponíveis e móveis no solo (KABATA-PENDIAS; MUKHERJEE, 2007).

Solos não contaminados geralmente contêm entre 1 e 40 mg As kg^{-1}. O elemento ocorre principalmente como espécies inorgânicas, mas também pode se ligar a materiais orgânicos nos solos. Sua ocorrência nos solos é, majoritariamente, nos estados de oxidação III e V, sendo aquela bem mais tóxica do que esta. Sua forma oxidada, denominada arsenato, ocorre em solos bem aerados, enquanto que em ambiente quimicamente reduzido predominam as espécies de arsenito (MANDAL; SUZUKI, 2002).

A disponibilidade de As em solos é controlada pelo processo de sorção com os óxidos de Fe, Al e Mn, matéria orgânica e os minerais de argila (WANG; MULLIGAN, 2006a). O As é adsorvido fracamente na matéria orgânica e em argilominerais, ao passo que, à semelhança do fósforo, é altamente adsorvido a óxidos/hidróxidos, especialmente em meio ácido (MCBRIDE, 1994). Complexos de As com P, Fe, Al, Ca e Mn têm um significante impacto em seu comportamento nos solos. Em solos ácidos, as formas dominantes são os compostos de Al-As e Fe-As, e em condições alcalinas predominam as espécies de Ca-As (KABATA-PENDIAS; MUKHERJEE, 2007).

Tanto o arsenito quanto o arsenato são tóxicos a humanos, plantas e microrganismos, porém a forma mais oxidada é menos tóxica (DATTA; MAKRIS; SARKAR, 2007). Portanto, a toxidez do elemento varia de acordo com sua forma química e seu estado de oxidação (MANDAL; SUZUKI, 2002). Embora o As elementar não seja tóxico, também oferece riscos à saúde, já que, quando ingerido, é rapidamente convertido em produtos tóxicos pelo organismo humano. Em geral, os compostos contendo As, independentemente de serem orgânicos ou inorgânicos, penta- ou trivalentes, são convertidos pelo organismo ao trióxido de As, o qual reage muito rapidamente com os grupos sulfidrilas (-SH) de proteínas, provocando a redução da ação enzimática e impedindo a respiração celular (TSALEV; ZAPRIANOV, 1985). Em ordem decrescente de toxicidade, as diversas espécies de As dispõem-se da seguinte forma: compostos de As^{3+} inorgânico>compostos de As^{5+} inorgânico>compostos de As^{3+} orgânico >compostos de As^{5+} orgânico (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY - USEPA, 2000).

No ar, As existe predominantemente em materiais particulados e é usualmente presente como uma mistura de arsenito e arsenato, com espécies orgânicas sendo de importância significante. A exposição humana ao As por meio do ar é geralmente muito baixa e a concentração do elemento nesse meio varia, normalmente, de 0,4 a 30 ng m^{-3}. Considerando que 20 m^3 de ar são inalados por dia, a quantidade de As inalado nesse período é em torno de 50 ng em áreas não poluídas (MANDAL; SUZUKI, 2002).

O uso do As tem se dado em diversos contextos, tais como a indústria, a metalurgia, a medicina, a agricultura (inseticidas e herbicidas), como aditivo de alimento animal e na conservação de madeira (MANDAL; SUZUKI, 2002). O arsenato de sódio, por exemplo, tem sido extensivamente utilizado como pesticida (e.g., desfolhante em algodão) em campos agrícolas, elevando as concentrações de As no solo (DATTA; MAKRIS; SARKAR, 2007).

Por conta da deposição atmosférica e da reciclagem da vegetação, o elemento tende a se concentrar nos horizontes superficiais dos solos (ALLOWAY, 1990), acentuando os riscos de contaminação de produtos agrícolas e, consequentemente, de ingestão de alimentos contaminados, o que resulta em um sério risco para a saúde humana. Além disso, devido a esse acúmulo na camada superficial do solo, o contato do elemento com a pele e a ingestão de solo resultam em importantes rotas de exposição a serem consideradas (ZAKHAROVA; TATANO; MENSHIKOV, 2002).

2.1.2 Cádmio

Cádmio é considerado um dos metais mais tóxicos, exibindo efeitos adversos em todos os processos biológicos de humanos, animais e plantas. O teor médio de Cd na crosta terrestre é de cerca de 0,1-0,2 mg kg^{-1} e sua ocorrência na natureza raramente se dá na forma pura. Seus minerais mais comuns são: greenockita (CdS), octavita ($CdCO_3$), e monteponita (CdO). Durante o processo de intemperismo, Cd forma simples compostos, tais como CdO, $Cd(OH)_2$, $CdCl_2$ e CdF_2, que são facilmente móveis (KABATA-PENDIAS; MUKHERJEE, 2007).

Cádmio e Zn têm semelhante configuração eletrônica e estado de valência e pertencem ao grupo dos calcofílicos – afinidade pelo S (KUMMEROVA et al., 2010). Embora ambos assemelhem-se nas propriedades geoquímicas, Zn é um importante nutriente para as plantas, animais e humanos, enquanto o Cd não tem função biológica (CHANEY, 2010).

O principal uso de Cd (aproximadamente 70%) é na produção de baterias de Ni-Cd e Ag-Cd. O Cd é produzido principalmente como um subproduto da mineração e refinamento de Zn. Assim, sua produção é mais dependente da produção de Zn do que da demanda de Cd (KABATA-PENDIAS; MUKHERJEE, 2007).

A concentração média de Cd nos solos do mundo é estimada entre 0,06 e 1,1 mg kg^{-1}. Na maioria deles, 99% do metal está associado aos coloides do solo em formas mais lábeis; portanto, grande proporção de Cd tem potencial de ser tranferido para a solução do solo (CHRISTENSEN; HAUNG, 1999), podendo variar de 0,2 a 300 µg L^{-1}. Cádmio pode ocorrer como espécies catiônicas: $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdHS^+$ e como espécies aniônicas: $CdCl_3^-$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, $Cd(HS)_4^{2-}$. Além disso, é altamente móvel em condições de oxidação tanto em baixo pH (<3), na presença de baixos teores de partículas ricas em Fe, quanto em maiores valores de pH (>5) (KABATA-PENDIAS; SADURSKI, 2004).

No último século, a quantidade de solos agrícolas contaminados com Cd no mundo aumentou, o que se atribui à intensificação das atividades industriais, incluindo operações de mineração e beneficiamento de Zn e aplicação de lodo de esgoto e fertilizantes fosfatados (ALLOWAY, 1995). Considerando todas as fontes de Cd em solos, as principais causadoras de poluição são as deposições atmosféricas e os fertilizantes fosfatados. Emissão industrial de Cd é recorrentemente documentada como significante fonte do metal em solos agrícolas de vários países (KABATA-PENDIAS; MUKHERJEE, 2007). A maior parte da poluição por Cd (90%), a partir de várias fontes, permanece na camada superficial dos solos, nos primeiros 15 cm de profundidade (ALLOWAY; STEINNES, 1999).

A média de Cd em água doce (rios) tem sido estimada em 0,08 µg L^{-1} (GAILLARDET; VIERS; DUPRÉ, 2003), sendo presente como Cd^{2+}, $Cd(OH)^+$ e $CdCO_3$, e também como compostos inorgânicos e complexos orgânicos. O Cd pode ser inserido no ambiente aquático por meio de várias fontes, das quais as principais são decorrentes de beneficiamentos de metais não ferrosos (KABATA-PENDIAS; MUKHERJEE, 2007).

A concentração mediana de Cd no ar em regiões remotas é de 0,2-0,4 ng m^{-3}, ao passo que em locais poluídos é de 20 ng m^{-3}, podendo o Cd existir na atmosfera como partículas em suspensão e também na forma de vapor (WILBER; SMITH; MALANCHUK, 1992). Os teores de Cd em plantas alimentícias variam de 5 a 400 µg kg^{-1}, sendo um pouco maior nos vegetais folhosos e raízes do que em outras partes das plantas. Geralmente, a concentração de Cd é mais elevada nas raízes, diminuindo na parte aérea das plantas (WELCH; NORVELL, 1999).

O teor médio de Cd nos tecidos humanos é de 0,17 mg kg^{-1}, variando de 0,03 (músculos) a 14 mg kg^{-1} (rins) (LI, 2000). Cádmio é um dos metais mais tóxicos aos humanos, principalmente devido à sua grande afinidade em se ligar aos grupos sulfidrilas e assim ocasionar distúrbios em várias enzimas desse grupo, provocando alterações nas proteínas (KABATA-PENDIAS; MUKHERJEE, 2007). A exposição humana ao Cd pode resultar em disfunção renal, distúrbios esqueléticos e problemas respiratórios (JARUP, 2003). O metal pode acumular-se no corpo humano durante um longo período de tempo, de modo que os efeitos negativos podem aparecer após um longo período de exposição crônica (POGGIO et al., 2009).

Na década de 1960, a doença Itai-Itai despertou uma maior atenção à poluição ambiental por Cd e a seus efeitos à saúde humana. A doença foi consequência da ingestão de arroz contaminado com Cd por um longo período no Japão. O excesso do elemento no organismo causou principalmente danos à estrutura esquelética, sendo sua recorrência maior em mulheres idosas (NOMIYAMA, 1980).

A contaminação por Cd em humanos ocorre, na maioria dos casos, por inalação ou ingestão de alimentos e água. Contudo, sua concentração na atmosfera não é suficientemente alta para ser considerada uma ameaça aos humanos, exceto para residentes de áreas próximas a locais onde se realizam atividades de beneficiamento de Zn e Pb (KABATA-PENDIAS; MUKHERJEE, 2007).

2.1.3 Chumbo

Chumbo é um metal de ocorrência natural, amplamente utilizado há milhares de anos pela sua maleabilidade e resistência à corrosão, embora não apresente essencialidade a qualquer organismo. É um dos contaminantes mais comuns do ambiente, sendo seus efeitos nocivos aos humanos já conhecidos há muito tempo, por afetarem praticamente todos os órgãos e sistemas do organismo (XIE et al., 1998). Os primeiros registros de reações adversas provenientes da exposição ao Pb foram observados durante o Império Romano, quando o elemento teve grande utilidade na fabricação de canos para passagem de água e de recipientes para bebidas (KABATA-PENDIAS; MUKHERJEE, 2007).

A contaminação por Pb provoca sérios danos ao corpo humano, principalmente ao sistema nervoso central de crianças, o qual é afetado com significativa redução de inteligência (HAN et al., 2012). Fortes dores abdominais, mau funcionamento dos rins e alteração do funcionamento do sistema nervoso central podem ser causados no caso de contaminação aguda por Pb (FIGUEIREDO, 2000). Em casos de contaminação crônica em crianças, a anemia e o déficit no aprendizado, além de outros danos cerebrais, são alguns dos sintomas observados. Já em adultos, o sintoma mais comumente atribuído à contaminação crônica por Pb são as disfunções renais e intestinais (MOREIRA; MOREIRA, 2004). Segundo Saryan e Zenz (1994), o Pb está presente no organismo de todos os seres humanos, como consequência da exposição às fontes exógenas.

A concentração média do elemento na crosta terrestre é de cerca de 17 mg kg^{-1} (WEDEPOHL, 1995); entretanto, altas concentrações têm sido encontradas em pequenas áreas, por contaminação antrópica, principalmente nos arredores de áreas de mineração e de beneficiamento de metais (BI et al., 2006; CHRASTNÝ et al., 2012; LAMB et al., 2009; PELFRÊNE et al., 2011; RIEUWERTS; FARAGO, 1996). O mais importante minério de Pb é a galena (PbS), cujos depósitos são a principal fonte de obtenção do elemento (KABATA-PENDIAS; MUKHERJEE, 2007). Outros comuns minerais são:

anglesita, $PbSO_4$; cerussita, $PbCO_3$; mínio, Pb_3O_4; piroformita, $Pb_5(PO_4)_3Cl$ e mimetesita, $Pb_5(AsO_4)_3Cl$.

O elemento possui dois estados de oxidação (2+ e 4+) ocorrendo no ambiente principalmente na valência 2+, e seus compostos são, na maioria, insolúveis em água. O valor geral médio de Pb para diferentes solos tem sido calculado como 25 mg kg^{-1}. O elemento não é distribuído uniformemente nos horizontes do solo e mostra uma forte associação com os óxidos/hidróxidos, principalmente com Fe e Al (KABATA-PENDIAS; PENDIAS, 2001).

Chumbo é geralmente acumulado próximo à superfície do solo e possui uma baixa mobilização, o que se deve principalmente à sua afinidade com a MOS e os argilominerais (CLAUDIO; GODWIN; MAGYAR, 2003). A mobilização do Pb é normalmente lenta, mas algumas condições dos solos, tais como aumento da acidez (diminuição do pH) e formação de complexos orgânicos, podem aumentar sua solubilidade (KABATA-PENDIAS; PENDIAS, 2001).

Por suas interações com as partículas do solo, a concentração de Pb na solução do mesmo é baixa (varia de <1 a 60 µg L^{-1}), promovendo reduzida disponibilidade às plantas. Observa-se, geralmente, acentuada contaminação por Pb em solos ao redor de áreas de mineração, industriais, urbanas e ao longo de autoestradas (KABATA-PENDIAS; MUKHERJEE, 2007). Em água doce (i.e., rios), a concentração desse metal é de 0,08 µg L^{-1} em média, estando a maior fração do elemento precipitada em sedimentos de fundo de rios (GAILLARDET; VIERS; DUPRÉ, 2003).

No ar, a concentração de Pb varia consideravelmente (1 a >10.000 ng m^{-3}), e seus maiores teores estão associados a áreas urbanas/industriais e a países que amplamente utilizaram esse metal na composição da gasolina. Em plantas, a entrada de Pb ocorre por meio do solo e da poluição atmosférica (deposição de Pb nas folhas) e os maiores teores são encontrados nas raízes, enquanto os menores estão em grãos e frutos. A biodisponibilidade do Pb no solo para planta é limitada, mas pode ser acentuada pela redução do pH do solo, do teor de MOS, dos coloides orgânicos, dos óxidos de Fe e da concentração de Fe (KABATA-PENDIAS; MUKHERJEE, 2007).

A distribuição do Pb no corpo humano varia entre 0,18 e 11 mg kg^{-1} (tecidos moles e ossos, respectivamente) (LI, 2000) e sua entrada no corpo se dá principalmente por inalação ou ingestão. Sua absorção ocorre principalmente nos tratos gastrointestinal e respiratório e, uma vez absorvido, é encontrado no sangue e em tecidos moles e mineralizados. Cerca de 90% do Pb corpóreo é armazenado nos ossos, tornando este o principal depósito do metal no corpo. Aproximadamente 5% do Pb presente no sangue encontra-se no plasma, compreendendo esta a fração lábil capaz de atravessar as membranas celulares e causar seus efeitos tóxicos. A excreção do Pb se dá principalmente por meio da urina e das fezes (MOREIRA; MOREIRA, 2004).

2.2 Mineração e beneficiamento de metais versus elementos-traço

Atividades de mineração e beneficiamento de metais são de importância inquestionável, uma vez que garantem a produção de matéria-prima para a fabricação de bens indispensáveis para o homem e proporcionam muitos outros benefícios para a sociedade e o desenvolvimento do país. Todavia, são grandes os danos ambientais por elas provocados, compreendendo, assim, uma séria ameaça para os ecossistemas e para a saúde humana. Tais atividades têm resultado na geração de grandes quantidades de rejeitos, que são importantes fontes de elementos-traço, tais como As, Cd, Pb e Zn, e provocado, consequentemente, uma substancial contaminação ambiental, principalmente de solos (ALLOWAY, 1990).

Esses metais/poluentes são transferidos para a água, solos, plantas e outros meios, podendo eventualmente entrar no corpo humano por meio das rotas de ingestão, inalação, ou dérmica, representando uma considerável ameaça a humanos (BI et al., 2006; PELFRÊNE; WATERLOT; DOUAY, 2011). Impactos ambientais adversos de áreas de mineração contaminadas incluem o risco à saúde humana, a fitotoxicidade, a contaminação da água e do solo e a ecotoxicidade (ANJU; BANERJEE, 2011).

Materiais sólidos (rejeitos) contaminados com metais são muitas vezes estocados em grandes pilhas que funcionam como permanentes fontes de metais tóxicos para os ecossistemas e áreas residenciais nos arredores, por meio de dispersão de partículas finas pelo vento e transporte de metais, tanto dissolvidos como em particulado pela água (SCHAIDER et al., 2007). De acordo com Carrizales et al. (2006), a concentração de metais em solos urbanos localizados próximos de áreas de mina e de processamento de metais é maior que os valores de *background* para metais em solos.

Inúmeras pesquisas têm relatado elevados teores de elementos-traço em áreas de mineração e beneficiamento de metais e em suas proximidades, especialmente de As no entorno de áreas de mineração aurífera (BORBA; FIGUEIREDO; MATSCHULLAT, 2003; BOSSY et al., 2010; BUNDSCHUH et al., 2012; CHOE et al., 2009; FILIPPI; DOUŠOVÁ; MACHOVIČ, 2007; FOSTER et al., 1998; JUHASZ et al., 2007; LEE et al., 2008; MATSCHULLAT et al., 2000; PAKTUNC; FOSTER; LAFLAMME, 2003) e de Pb, Cd e Zn em áreas de mineração e beneficiamento de Zn (BI et al., 2006; CHRASTNÝ et al., 2012; DIAS-JÚNIOR et al., 1998; LAMB et al., 2009; RIBEIRO-FILHO et al., 1999; SANTOS, 2010). Embora esses elementos estejam, geralmente, presentes em rochas e solos na forma mineral de baixa solubilidade, os mesmos podem formar outras espécies minerais mais solúveis quando expostos a diferentes condições físico-químicas.

Estudos têm indicado a associação de fontes naturais de As principalmente com depósitos de ouro contendo minerais de sulfetos (DESCHAMPS et al., 2002; DRAHOTA; FILIPPI, 2009; MELLO et al., 2006). Geralmente, As existe nesses materiais como minerais de sulfetos na forma reduzida (e.g., arsenopirita, FeAsS) (MEUNIER et al., 2010). As atividades de mineração proporcionam o intemperismo desses sulfetos, liberando As juntamente com sulfatos e hidróxidos de Fe e gerando, assim, seus produtos secundários, que são formas mais oxidadas de As (MURCIEGO et al., 2011). Em rejeitos de mina, As geralmente ocorre associado com minerais de sulfetos, tais como arsenopirita, arsenatos, e As ligado a oxi-hidróxidos de Fe (FOSTER et al., 1998; WANG; MULLIGAN, 2006b). Entretanto, em solos de áreas de mineração, As está principalmente associado com oxi-hidróxidos de Fe amorfos (FILIPPI; GOLIÁŠ; PERTOLD, 2004; MORIN; CALAS, 2006).

A presença de Cd é recorrente em áreas de mineração de Pb-Zn, devido à sua ocorrência como um contaminante geológico no minério de Pb, juntamente com o Zn. Portanto, Cd pode ocorrer como subproduto de processos de beneficiamento envolvendo minério de Pb-Zn (WAALKES; WAHBA; RODRIGUEZ, 1992). Minérios de Zn geralmente contêm entre 0,1 e 5% de Cd (NAN et al., 2002). Segundo Kabata-Pendias e Mukherjee (2007), o Cd é produzido principalmente como um subproduto da mineração e refinamento de Zn.

Vários estudos têm reportado a presença de altos teores Cd, Pb e Zn nas proximidades de áreas de mineração e beneficiamento de Pb ou Zn e, geralmente, os teores nos solos diminuem à medida que se distancia dessas áreas. Chrastný et al. (2012), analisando Pb, Zn e Cd em solos próximos a uma área de mineração e beneficiamento na Polônia, encontraram os seguintes valores máximos para os elementos: 25.000 mg Pb kg^{-1}, 20.000 mg Zn kg^{-1} e 200 mg Cd kg^{-1}. Lamb et al. (2009) investigaram Cu, Zn, Cd e Pb em solos ao redor de uma área de beneficiamento de Pb/Zn na Austrália e reportaram valores de teor total dos elementos de até 6841 mg Cu kg^{-1}, 39.000 mg Zn kg^{-1}, 302 mg Cd kg^{-1} e 12.000 mg Pb kg^{-1}. Apesar dos altos teores dos metais nos solos neste estudo, Zn, Cd e Pb não foram, no geral, encontrados em elevadas concentrações na solução do solo.

Um estudo conduzido por Rieuwerts e Farago (1996), avaliando poluição por metais pesados em solos das proximidades de uma área de mineração e beneficiamento na República Checa relatou altos teores de Pb (até 37.300 mg kg^{-1}) para os solos mais próximos da área de beneficiamento, sendo os valores mais baixos com o aumento da distância. Bi et al. (2006), investigando metais pesados (Cd, Cr, Cu, Pb e Zn) em amostras de rejeitos, solos, culturas e musgos coletadas em áreas de beneficiamento de Zn na China, reportaram que as amostras de solos da plantação de milho próxima das áreas tinham altos teores de Cd (até 74 mg kg^{-1}), Pb (14.000 mg kg^{-1}) e Zn (16.000 mg kg^{-1}). Além disso, elevados teores de metais foram encontrados nas plantas de milho e nos musgos.

2.3 Biodisponibilidade e bioacessibilidade

As legislações preconizam valores de referência de qualidade para elementos-traço em solos baseando-se em seus teores totais (i.e., extração por digestão ácida), podendo ser tomadas como exemplo as regulamentações do Conselho Estadual de Política Ambiental - COPAM (2011) e Conselho Nacional de Meio Ambiente - CONAMA (2009). Ambas categorizam os valores orientadores em valores de (i) referência de qualidade, (ii) prevenção e (iii) intervenção, sendo este estabelecido para solos agrícolas, residenciais e industriais.

Porém, sabe-se que o teor total do metal no solo não é o melhor estimador da quantidade do elemento que pode ser disponível e absorvido pelos humanos e animais, e tal análise tende a gerar, na maioria das vezes, uma superestimativa em uma avaliação de risco (DEMETRIADES et al., 2010; RODRIGUEZ et al., 1999; RUBY et al., 1996), fornecendo medidas equivocadas de remediação da área e gerando, consequentemente, um custo desnecessário para a indústria e o governo (LAMB et al., 2009). Assim sendo, a fração do elemento disponível aos humanos não pode ser arbitrariamente assumida como sendo o teor total do elemento, como reportado por diversos autores (JUHASZ et al., 2007; RODRIGUEZ et al., 1999; RUBY et al., 1996; SARKAR; DATTA; SHARMA, 2005; YANG et al., 2002), pois ela é influenciada por vários parâmetros do solo (JUHASZ et al., 2007; PELFRÊNE et al., 2011) e, também, pelas características do indivíduo, como idade, condições nutricionais e habitacionais, entre outros (RUBY et al., 1999).

Assim, testes de biodisponibilidade (*in vivo*), que utilizam animais como cobaias, são sugeridos para se obter uma avaliação de risco mais fidedigna (KOCH et al., 2007; RODRIGUEZ et al., 1999; RUBY et al., 1993, 1996, 1999). A biodisponibilidade do elemento é definida como a fração da dose administrada que atinge a circulação sanguínea a partir do trato gastrintestinal (RUBY et al., 1999). Tais testes são os únicos capazes de medir a biodisponibilidade de contaminantes presentes em matrizes naturais (FREEMAN et al., 1992), sendo considerados uma ferramenta para promover tomadas de decisão mais acertadas em avaliações de risco e propostas de remediação (HARMSEN; NAIDU, 2013).

A realização dos testes de biodisponibilidade tem se dado em solos e rejeitos de áreas de mineração de metais por meio de experimentos com animais. Para a seleção do tipo de animal a ser testado para estimar a biodisponibilidade de metais em crianças, consideram-se as semelhanças de idade e de características anatômicas e fisiológicas. Os suínos são frequentemente utilizados por assemelharem-se aos humanos em diversos aspectos – trato digestivo, necessidades nutricionais, desenvolvimento ósseo e metabolismo mineral (DODDS, 1982).

Os testes *in vivo* são os únicos testes padronizados para a quantificação da biodisponibilidade de elementos tóxicos em solos e rejeitos e por conta disto são considerados os mais confiáveis (FREEMAN et al., 1992). No entanto, são de alto custo, consomem tempo, requerem especialistas no manejo dos animais e exigem uma infraestrutura adequada para a sua execução (HETTIARACHCHI; PIERZYNSKI, 2004).

Considerando essas dificuldades, Ruby et al. (1993, 1996, 1999) sugerem como alternativa os testes de bioacessibilidade (*in vitro*), que consistem em ensaios simulando as condições do trato gastrintestinal de humanos por meio do uso de soluções contendo enzimas (e.g., pepsina, pancreatina, sais de bile) similares às reais, sendo também considerada a temperatura e o tempo de residência do solo nos órgãos do sistema digestivo, permitindo avaliar a solubilidade dos metais, caso o material seja ingerido por crianças.

A ingestão acidental de partículas de solos/rejeitos por crianças via contato com o solo (*hand-to-mouth activity*) é considerada a principal via de exposição a elementos-traço, tais como As, Cd e Pb, oferecendo riscos à saúde humana (HEMOND; SOLO-GABRIELE, 2004; KWON et al., 2004; RODRIGUEZ et al., 1999). De acordo com estudos realizados pela USEPA (2002), a média de ingestão de partículas de solos por crianças na faixa etária de 1 a 6 anos é de 100 mg por dia. Outras rotas de exposição, como a absorção dérmica e a inalação, são consideradas insignificantes comparadas à de ingestão (KWON et al., 2004; MIGUEL et al., 2007).

Com os testes de bioacessibilidade, pode-se determinar a fração solúvel de um contaminante que está disponível para absorção nas condições do trato gastrintestinal (DATTA; MAKRIS; SARKAR, 2007). Esse tipo de ensaio é considerado uma ferramenta simples, de rápida execução e baixo custo, em comparação aos testes *in vivo* (KOCH et al., 2007; OOMEN et al., 2002; RUBY et al., 1996, 1999).

Um protocolo de bioacessibilidade foi proposto por Ruby et al. (1993) para avaliar o Pb e, posteriormente (RUBY et al., 1996), o As em matriz sólida, sendo denominado "teste de extração baseado na fisiologia" (PBET, do inglês *physiologically based extration test*) e integrando parâmetros do trato gastrintestinal de humanos (incluindo pH, temperatura, tempo de residência do solo nos órgãos do sistema digestivo, substâncias químicas do estômago e intestino delgado, razão solo-solução e contração do estômago). O protocolo foi validado utilizando animais em um estudo paralelo. Os valores de Pb bioacessível foram linearmente correlacionados (r^2=0,93) com os resultados de biodisponibilidade, com utilização de ratos como cobaias. Os de As bioacessível superestimaram os resultados de As biodisponível utilizando coelhos e macacos (2 a 11% de diferença, respectivamente). Segundo os autores, o protocolo não foi desenvolvido para substituir os estudos de biodisponibilidade utilizando animais, mas sim para estimar a biodisponibilidade de As e Pb quando ensaios com animais forem inviáveis.

Rodriguez et al. (1999) propuseram outro protocolo de bioacessibilidade, IVG (*in vitro gastrointestinal*), o qual é amplamente utilizado para estimar a biodisponibilidade de As em solos e rejeitos. O protocolo foi validado por ensaio *in vivo* utilizando suínos. O experimento foi conduzido em condições anaeróbias com agitação e dividido em duas fases distintas: a gástrica, que envolveu a redução do pH, e a gastrintestinal, na qual o pH é aumentado com a adição de bicarbonato de sódio. Os valores de As bioacessível em ambas as fases foram linearmente correlacionados (r=0,83 e 0,82, respectivamente; p<0,01) com os resultados de As biodisponível (*in vivo*).

Análises de bioacessibilidade têm sido recorrentemente utilizadas em amostras de solos e rejeitos de áreas de mineração e de suas redondezas, possibilitando a obtenção de relevantes resultados na última década (LAMB et al., 2009; LU et al., 2011; MEUNIER et al., 2010; MURCIEGO et al., 2011; ONO et al., 2012; PELFRÊNE et al., 2011; TOUJAGUEZ et al., 2013). Schaider et al. (2007), avaliando a bioacessibilidade de Zn, Pb e Cd em rejeitos de mina em Oklahoma, reportaram bioacessibilidade de 60 a 80% para esses elementos, enquanto compostos de ZnS e PbS exibiram baixa bioacessibilidade. Os autores indicaram que de 50 a 65% do Zn, Pb e Cd estavam presentes na forma trocável e associados a carbonatos. Um estudo conduzido por Navarro et al. (2006), investigando a bioacessibilidade de Pb, Cd e As em uma mina abandonada na Espanha, indicou o Cd como o elemento mais bioacessível (média de 47 e 28% para a fase gástrica e a intestinal, respectivamente), seguido pelo Pb (25 e 12%). Análise de correlação apontou que o pH e a composição mineralógica foram os fatores mais importantes no controle da biodisponibilidade do metal a partir dos materiais estudados. Ono et al. (2012), avaliando a bioacessibilidade de As em substratos e rejeitos de uma área de mineração de ouro situada em Minas Gerais, Brasil, reportaram uma baixa bioacessibilidade de As (<4,4%), mesmo as amostras apresentando altos teores totais do elemento (até 2666 mg As kg^{-1}).

2.4 Análises utilizando a fonte de radiação síncrotron

Além da determinação da bioacessibilidade de elementos-traço para as estimativas de avaliação de risco, métodos instrumentais utilizando a fonte de luz síncrotron, como a espectroscopia de absorção de raios-X (XAS), são úteis e relevantes na caracterização de espécies moleculares e/ou minerais presentes nas amostras. Tais técnicas auxiliam na explicação do motivo pelo qual certos materiais (i.e., solos, sedimentos, rejeitos) possuem menores ou maiores percentagens de elementos-traço biodisponíveis. A utilização de técnicas de pequena escala (i.e., escala molecular ou menor) em pesquisas na área ambiental tem resultado em uma nova área de estudo multidisciplinar, a qual tem sido chamada de ciência molecular ambiental e tem interessado aos cientistas da química do solo ambiental (SPARKS, 2003).

Os laboratórios de luz síncrotron, por meio de seus equipamentos operados de maneira simultânea, geram fótons de intensa energia, resultando na radiação síncrotron. A radiação é produzida sobre uma ampla faixa de energias, a partir da região do infravermelho, com energias <1 eV, até a região dos raios-X duros, com energias de 100 keV ou acima (KELLY; HESTERBERG; RAVEL, 2008). O uso da radiação para averiguar questões ambientais fornece indícios acerca dos mecanismos de reação dos metais pesados na interface entre as fases do adsorvente encontradas nos solos e na solução do solo (ROBERTS; NACHTEGAAL; SPARKS, 2005).

Existe um número considerável (67) de laboratórios de luz síncrotron no mundo (e.g., Estados Unidos, Japão, Canadá, Alemanha, França, China, Itália), dos quais apenas um localiza-se na América Latina, o Laboratório Nacional de Luz Síncrotron - LNLS, situado em Campinas-SP, Brasil, sendo o pioneiro no Hemisfério Sul (LIGHTSOURCES, 2013). Nesse laboratório, pesquisadores, do Brasil e do exterior, utilizam a fonte de luz para realizar pesquisas que visam a avançar no conhecimento sobre os átomos e as moléculas, sendo o laboratório mantido com recursos financeiros do Ministério da Ciência e Tecnologia - MCT (LABORATÓRIO NACIONAL DE LUZ SÍNCROTRON - LNLS, 2013).

A utilização da luz síncrotron possibilitou um grande salto no uso da técnica de espectroscopia de absorção de raios-X (XAS, *X-Ray Absorption Spectroscopy*) por proporcionar a geração de fótons de alta energia, imprescindíveis na aquisição de espectros com uma boa relação sinal/ruído. XAS é uma das técnicas mais utilizadas nos laboratórios síncrotron pelos cientistas de química do solo ambiental (ROBERTS; NACHTEGAAL; SPARKS, 2005).

XAS pode ser usada para estudar a maioria dos elementos nos estados sólido cristalino ou não cristalino, líquido ou gasoso, com uma ampla faixa de concentração (de poucos miligramas por litro ao elemento puro). É também uma técnica *in situ*, o que significa que é possível estudar as reações na presença de água. Esta é uma importante vantagem em relação a muitas técnicas de escala molecular, que exigem frequentemente a secagem do material de amostra, o que pode provocar alteração na amostra, impedindo a simulação das condições naturais do solo (SPARKS, 2003).

O processo básico do XAS consiste na atenuação dos raios-X pelos átomos de um dado elemento, produzindo uma absorção (aumento do espectro, Figura 1) em uma estreita faixa de energia. Esse aumento do espectro é denominado borda de absorção e corresponde à produção de fotoelétrons, devido à excitação de elétrons localizados nas camadas eletrônicas mais internas (K ou L) do átomo absorvedor pelos fótons de raios-X. Isto ocorre quando a energia dos raios-X incidente (E) é igual à energia de ligação dos elétrons do nível mais interno do átomo (Eb), o que torna a XAS uma técnica sensível para um elemento específico e até mesmo sensível a seu estado de oxidação (KELLY; HESTERBERG; RAVEL, 2008).

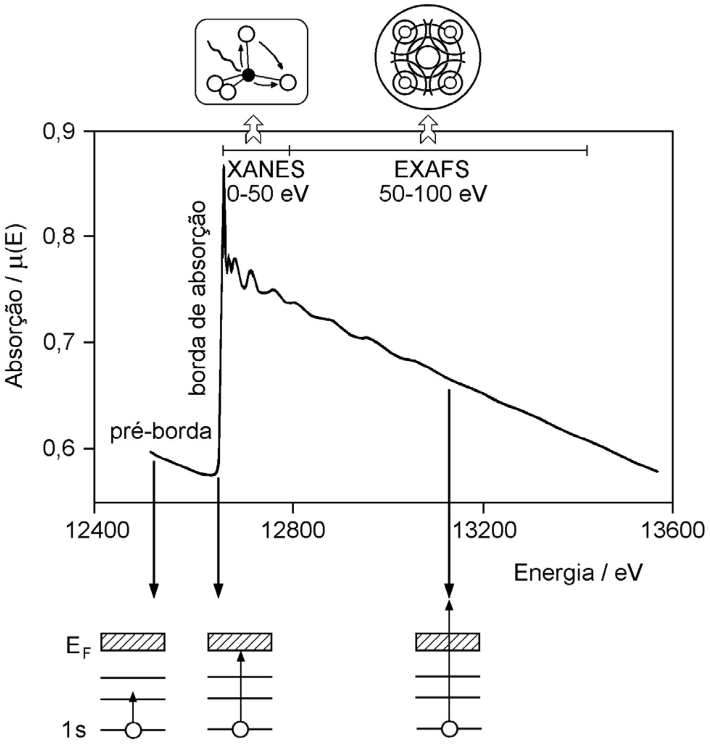

Figura 1 Espectro de absorção de raios-X da borda K do selênio
Fonte: Gonçalves (2000)

Após a borda de absorção, o espectro de XAS pode ser separado em duas regiões (Figura 1). A primeira consiste na espectroscopia de alta resolução da borda de absorção - XANES (*X-Ray Absorption Near Edge Structure*), a qual permite obter informações a respeito do estado de oxidação do átomo fotoabsorvedor, do arranjo espacial dos átomos da sua vizinhança e da densidade de estados desocupados referente ao átomo fotoabsorvedor estudado. Esta região é usada frequentemente para comparar compostos conhecidos (referência) com amostras desconhecidas. A segunda, por sua vez, compreende a espectroscopia da estrutura fina de absorção - EXAFS (*Extended X-Ray Absorption Fine Structure*), a qual fornece informações estruturais de curto alcance, como o número de coordenação e as distâncias interatômicas ao redor do átomo estudado, permitindo uma estimativa da desordem local do sistema (TEO; JOY, 1981).

O diâmetro médio do feixe de raios-X em um experimento convencional de XAS (*bulk*-XAS) é de alguns centímetros. Com espelhos de focagem e outros dispositivos, o feixe de raios-X atingindo uma amostra pode ir até alguns micrômetros quadrados em área (análises de micro-XAS), aproximando-se do tamanho das espécies mais reativas nos solos e permitindo a distinção de espécies individuais em um sistema heterogêneo. A fim de determinar a localização exata para direcionar o feixe de raios-X focalizado na amostra, micro-XAS é combinado com micro-fluorescência de raios-X (µ-XRF), permitindo a obtenção de mapas elementares antes da análise. Enquanto a microssonda eletrônica não é sensível o suficiente para detectar elementos-traço em solo, µ-XRF apresenta alta sensibilidade para investigar a distribuição espacial dos elementos-traço e sua correlação espacial com outros elementos (SPARKS, 2003).

Experimentos utilizando XAS com o objetivo de discriminar as espécies de um dado elemento têm adotado a técnica de ajuste da combinação linear (*linear combination fit* - LCF), em que os espectros das espécies de referência (conhecidos) são ajustados com o espectro da amostra desconhecida. LCF tem sido empregada com sucesso para identificar e quantificar as principais espécies nas amostras, incluindo os minerais e os complexos de sorção. O sucesso da especiação depende criticamente de um banco de dados espectrais contendo todas as principais espécies coexistentes na amostra desconhecida (ROBERTS; NACHTEGAAL; SPARKS, 2005).

Há vários estudos no mundo reportando relevantes informações (e.g., especiação, mobilidade, biodisponibilidade, tipo de ligação) sobre elementos-traço em solos/rejeitos de áreas contaminadas utilizando a técnica XAS

(CANCÈS et al., 2008; KREIDIE et al., 2011; MCNEAR; CHANEY; SPARKS, 2007; MORIN; CALAS, 2006; PAKTUNC; FOSTER; LAFLAMME, 2003; STRAWN et al., 2002; WALKER et al., 2005). Embora a técnica seja muito utilizada e difundida em outros países, no Brasil seu uso é ainda incipiente na área de geociências e de ciência do solo.

Meunier et al. (2010), investigando os efeitos da composição e mineralogia do solo na bioacessibilidade de As em amostras de rejeitos de uma mina de ouro no Canadá, utilizaram a técnica XAS e reportaram que a forma de As predominante nas amostras era a pentavalente, e que a maior parte da arsenopirita presente nos rejeitos foi oxidada durante as reações de intemperismo. Além disso, associou-se a maior bioacessibilidade de As (até 49%) com a presença de arsenato de Ca-Fe, e a menor bioacessibilidade (<1%) para as amostras que continham predominância de arsenopirita e escorodita. Niazi, Singh e Shah (2011), avaliando a especiação de As via XAS em solos contaminados, indicaram que a forma de As predominante nas amostras de solos era As(V), sendo este, na sua maior parte, associado com óxidos de Fe amorfos. Em poucas amostras também foi encontrado As na forma de As(III) ou como mineral escorodita.

3 CONSIDERAÇÕES FINAIS

No presente estudo foram analisadas amostras de solos/rejeitos de duas áreas, sendo a primeira uma área de processamento de minério de Zn e a segunda uma área de mineração de ouro, ambas situadas na região Noroeste do estado de Minas Gerais, Brasil.

A área de beneficiamento de Zn situa-se próximo à área urbana da cidade de Três Marias-MG e ao lado do rio São Francisco. Durante o processamento do Zn geram-se resíduos (rejeitos) com altos teores de metais pesados, os quais vêm sendo depositados ao longo dos anos em uma área de 18 ha ao redor da planta de beneficiamento. Os solos pertencentes a essa área recebem os rejeitos de modo localizado ou por processos físicos, como carreamento pela ação erosiva da chuva e do vento.

A área de mineração de ouro localiza-se a menos de 2 km da área urbana da cidade de Paracatu e possui uma mina a céu aberto, uma planta de processamento e uma barragem (lagoa) de rejeitos, além da infraestrutura de superfície. A mineradora está em operação desde 1987, tendo seu tempo de vida útil estimado até 2042. É a maior produtora de ouro no Brasil (25% da produção nacional em 2011), mas possui o menor teor de ouro comercialmente explorável do mundo (KINROSS GOLD CORPORATION, 2013). Nessa área ocorre a geração de resíduos sólidos (estéril e rejeito) com concentrações significativas de As. O resíduo estéril é depositado em pilhas e o rejeito, lançado em uma barragem de contenção, formando uma “lagoa” de rejeitos.

O objetivo do presente trabalho foi, no primeiro estudo (artigo 1), avaliar a bioacessibilidade e a cinética de dessorção de Cd e Pb em amostras de rejeitos de uma área de beneficiamento de zinco; e, no segundo (artigo 2), avaliar os teores de As nos particulados de poeira e investigar, via análises de espectroscopia baseada na radiação síncrotron, a especiação de As em amostras de rejeitos de mina e em particulados de poeira de uma área de mineração de ouro.

Com base no estudo conduzido no artigo 1, altas concentrações de Cd e Pb foram encontradas nos rejeitos da área de beneficiamento de Zn e, com base no artigo 2, elevados teores de As foram observados nos rejeitos da área de mineração de ouro. Levando-se em consideração os altos teores de elementos-traço encontrados nos rejeitos e o fato de que ambas as áreas situam-se muito próximo a áreas urbanas, é importante salientar que o descarte final desses materiais requer um planejamento adequado com o intuito de evitar a contaminação do ambiente por elementos-traço.

Vale mencionar, ainda, que embora os estudos tenham apontado elevados teores de elementos-traço nos rejeitos das áreas, as mesmas são fechadas e inacessíveis a pessoas não autorizadas, o que torna o risco de exposição aos materiais relativamente baixo.

De acordo com o artigo 1, a bioacessibilidade de Cd e Pb na fase intestinal foi bem abaixo da concentração total dos metais, indicando que uma significativa fração dos metais não é disponível para absorção. Os experimentos de cinética de dessorção revelaram que a fração de Pb nas amostras é menos lábil e a de Cd mais lábil, estando esses resultados de acordo com os de bioacessibilidade. O desenvolvimento de estudos com enfoque na especiação de Cd e Pb nas amostras são ainda necessários e podem contribuir significativamente no entendimento dos resultados de bioacessibilidade encontrados na presente pesquisa.

Conforme o artigo 2, as amostras apresentaram as frações de As predominantemente na sua forma mais oxidada (AsV), como arsenato de Fe pouco cristalino, e, em menor proporção, na sua forma reduzida, como arsenopirita. Estes resultados confirmam a baixa bioacessibilidade de As encontrada nas amostras em estudos prévios. Todas as amostras de particulados de poeira apresentaram As, sendo os maiores teores averiguados para as amostras coletadas próximo à área da mina. Os particulados de poeira apresentaram as mesmas formas de As encontradas nas amostras de rejeitos da mina.

É de extrema importância a criação de uma regulamentação que estabeleça valores de referência para elementos-traço em particulados em suspensão ao ar no Brasil, a fim de que seja possível a avaliação da qualidade do ar. A necessidade é ainda mais emergencial em locais próximos a áreas de mineração, uma vez que, como previamente afirmado, todos os particulados de poeira coletados apresentaram As, e também em zonas industriais, já que estas apresentam níveis de contaminação extremamente altos.

A técnica XAS ainda é pouco aplicada e difundida no Brasil na área de ciência do solo, muito embora sua utilização seja bastante comum em outros países. Essa subutilização pode ser atribuída à carência de equipamentos, ao reduzido número de grupos de pesquisa envolvidos com tais estudos e à escassez de oportunidades de treinamento para um número maior de pesquisadores. Nota-se, dessa forma, a necessidade do país treinar estudantes, tanto para o manuseio dos aparelhos e realização das análises, quanto para a interpretação dos resultados, para haver avanços significativos nas pesquisas realizadas em ciência do solo.

Diante dos tópicos abordados no presente trabalho, diversas outras pesquisas podem ser conduzidas em solos, sedimentos e rejeitos do território brasileiro com a utilização dos ensaios de bioacessibilidade e das análises com a radiação síncrotron (e.g., absorção de raios-X), contribuindo para a ampliação do conhecimento de tais informações no país.

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SEGUNDA PARTE - ARTIGOS

ARTIGO 1 Assessing bioaccessibility of cadmium and lead in tailings from a zinc smelting area in Brazil

Normas da revista *Journal of Hazardous Materials*

Assessing Bioaccessibility of Cadmium and Lead in Tailings from a Zinc Smelting Area in Brazil

Fábio Benedito Ono[§], Evanise Silva Penido[§], Ryan Tappero[£], Donald Sparks[€], Luiz Roberto Guimarães Guilherme[*,§]

[*]Corresponding author phone: + 55 35 3829 1259; fax: + 55 35 3829 1251; e-mail: guilherm@dcs.ufla.br

[§]Department of Soil Science, Federal University of Lavras, CP 3037, Campus UFLA, 37200-000, Lavras, MG (Brazil)

[£]Photon Sciences, Beamline X27A, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973 (USA)

[€]University of Delaware, Delaware Environmental Institute, Interdisciplinary Science and Engineering Lab, Suite 250a, Newark, DE 19716 (USA)

Abstract

Soils and wastes enriched with heavy metals may present significant ecological and human health risks. A considerable number of mining/smelting areas exist in Brazil, where high levels of metals have been found, as well as in their surrounding soils and sediments. However, studies of bioaccessibility of metals in soils/tailings from these areas are scarce, despite their potential informational contribution concerning exposure risks for residents near these areas. This study evaluated tailing samples collected from four sites of a smelting area with aims to: (i) evaluate the presence of metals of potential concern; (ii) investigate Cd and Pb bioaccessibility; and, (iii) determine the desorption kinetics of Cd and Pb. Five composite samples were collected from each site, at two depths, from a zinc smelting area located near Três Marias city-MG, Brazil. Availability of Cd and Pb was measured using a bioaccessibility test and a desorption experiment. High concentrations of total Cd and Pb and great variability were found in the tailings (up to 1743 mg Cd kg^{-1} and 8675 mg Pb kg^{-1}), indicating the importance of adequate planning for their final disposal, in order to avoid contamination in the surrounding environment. Cadmium and Pb bioaccessibility percentages in the intestinal phase were less than 47 and 4%, respectively, which represents significant fractions not available for absorption in the intestinal tract. However, this material has to be monitored since its bioaccessibility may increase with eventual physicochemical changes, releasing Cd and Pb. Desorption kinetics experiments revealed that the Pb in the samples remained in less labile fractions whereas Cd was found in more labile fractions, which is in accordance with the bioaccessibility results.

Keywords: trace elements; anthropogenic impacts; in vitro test; environmental contamination.

Introduction

Mining and smelting of metals are important economic activities since they contribute to the income of the country and generate employment, besides producing a range of different metals that can have countless uses in various contexts. Yet, mining and smelting activities have resulted in the generation of large quantities of wastes, which can be a relevant source of environmental contamination by trace elements

(Alloway, 1990), such as cadmium (Cd), lead (Pb), and zinc (Zn). These metals may be transferred to the water, soils, plants and other environmental compartments, and eventually enter human bodies through food chains or direct ingestion, representing a considerable threat to human health (Bi et al., 2006).

Trace elements such as Cd and Pb have been investigated in several compartments (e.g. water, plants, food, soil dust, agricultural soil, wastes) due to their potential toxic effects on humans and animals. Lead and Cd are ranked number two and seven, respectively, in the priority list of 275 hazardous substances to human health by ATSDR (2011). Human exposure to Cd can result in kidney dysfunction, skeletal disorders (i.e., Itai-Itai disease), and respiratory problems (Jarup, 2003). Lead poisoning can cause serious reactions in the infant human body, affecting children's nervous system and reducing their intelligence (Han et al., 2012).

There are a significant number of metal mining/smelting areas in Brazil, especially in the state of Minas Gerais, and relatively high concentrations of trace elements have been found in the wastes from these areas and in surrounding soils and sediments (Dias-Júnior et al., 1998; Ribeiro-Filho et al., 1999; Matschullat et al., 2000; Bundschuh et al., 2012). According to Carrizales et al. (2006), metal concentrations in soils from urban areas located in the vicinity of mine/smelter sites is higher than background levels. Total metal content analysis (e.g. acid digestion) has been used in the characterization of contaminated soils/wastes by trace elements in order to address human health risk. However, the total concentration of elements does not reflect the proportion that might be available to humans and other forms of life (Demetriades et al., 2010). Thus, bioaccessibility tests such as IVG (Rodriguez et al., 1999) and PBET (Ruby et al., 1996), among others, have been suggested in order to obtain a more realistic health risk assessment. Ruby et al. (1996, 1999) define the term bioaccessibility, regarding human exposure by soil ingestion, as the fraction of a potential toxicant in soil/wastes that becomes soluble in the gastrointestinal tract and is then available for absorption. If this fraction crosses a biological membrane it is then bioavailable. Bioavailability is considered a tool for better decision making regarding risk assessments and remediation purposes (Harmsen and Naidu, 2013). Inaccurate risk assessments for human health or for ecological purposes often result in an unnecessary clean-up of ‘contaminated’ sites and, consequently, a substantial and needless cost for the industries and the government (Lamb et al., 2009).

Incidental ingestion of soils/tailings particles via hand-to-mouth contact by children is a highly significant pathway of direct heavy metal exposure contributing to human health risk (Rodriguez et al., 1999; Hemond and Solo-Gabriele, 2004; Kwon et al., 2004). Based on studies of soil ingestion by children, guideline values were set by the USEPA (2002), at a mean of 100 mg day^{-1} for children between 1 and 6 years old. For metals that are strongly adsorbed to soil particles, this route of exposure might be the most relevant form of human contamination. Therefore, we emphasize the relevance of characterization studies, especially bioaccessibility analyses and metal desorption experiments of tailings from mining/smelting areas located in urban surroundings. Such studies are scarce in Brazil and may give relevant information on the risk from exposure of residents living around these areas.

Tailing samples collected from four sites of a smelting area were used in this study with the aim of: (i) assessing the presence of metals of potential concern;

(ii) investigating the bioaccessibility of Cd and Pb, and (iii) determining the desorption kinetics of Cd and Pb from such tailings. The study area is a zinc smelting area located very close to Três Marias city - MG, Brazil, and to the São Francisco River, which is one of the most important Brazilian rivers.

Materials and Methods

Site description and sampling

The smelter tailing samples selected for this study were collected at the facilities of a zinc smelting area located in Três Marias, in the Northwest of Minas Gerais - Brazil, from four sites, as follows: Eu, EB, pH9 and Tailings. Eu and EB represent experimental areas of a revegetation project (conducted in 2001-2002) where constant long-term Zn smelting activities in the past left a significant contaminated tailing deposit. In both areas, *Eucalyptus camaldulensis* was planted with a 2-m spacing between the plants and a mixture of non-contaminated soil, limestone, organic residue and fertilizer (N-P-K) was placed into the planting holes. In the EB area, a 2-cm limestone layer and a 20-cm non-contaminated soil layer were applied in between the rows of eucalyptus and then *Brachiaria decumbens* was seeded. The pH9 site comprises an inactive area of waste deposits with alkaline characteristics. When the samples were collected the area had several plant species of Cerrado vegetation. “Tailings” hereafter is used to describe an area (pond) used for waste depositions from the Zn smelting.

Five composite samples were randomly collected from each site at two depths (0-2 and 2-10 cm), using a stainless steel straight blade. Each composite sample consisted of five sub-samples from a 4-m^2 area. The samples were transported to the Soil

Science Department at the Federal University of Lavras, Brazil, air-dried and sieved to less than 2 mm.

Basic chemical characterization

Two composite samples from each site (one at 0-2 cm and the other at 2-10 cm) were selected for chemical characterization analysis. The concentration of the elements in the samples (disaggregated and sieved to <250 µm fraction) was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after microwave-assisted acid digestion by the EPA method 3051. The organic matter (OM) content in the tailings (<2 mm) was measured using Walkley-Black method (Nelson and Sommers, 1996).

Procedure for total Cd and Pb extraction

Total (or pseudototal) Cd and Pb contents in the smelter tailing samples were carried out using microwave-assisted acid digestion of the samples by the EPA method 3051A. For this procedure, 0.5 g of the samples (only sieved to <250 µm fraction) was transferred to microwave vessels filled with 5 mL of concentrated HNO_3. After digestion, the extract was filtered and diluted with ultrapure water (5 mL). The filtered extracts were preserved by refrigeration (4°C) until quantification using either graphite furnace atomic absorption spectroscopy (GFAAS) or flame atomic absorption spectroscopy (FAAS) using a Perkin Elmer AAnalyst 800 spectrometer.

Bioaccessibility of Cd and Pb

An in vitro Physiologically Based Extraction Test (PBET) protocol – a simulation of sequential digestion in the stomach and intestine proposed by Ruby et al. (1996) – was performed to determine the contents of bioaccessible Cd and Pb in the smelter tailing samples. The gastric phase consisted of a mixture of 1 g of air-dried tailings (only sieved to a <250 µm fraction – these particles very likely adhere to the hands of children and may be eventually ingested (Maddaloni et al., 1998)) with 100 mL of a gastric solution that was prepared using 1 L of ultrapure water, 1.25 g of pepsin (Sigma-Aldrich, Cat. No. P7000), 0.5 g of citrate (Sigma-Aldrich), 0.5 g of malate (Sigma-Aldrich), 420 µL of lactic acid (syrup – 85% w/w, Sigma-Aldrich) and 500 µL of acetic acid (>99.7%, Sigma-Aldrich). The gastric solution was acidified, before adding the samples, with concentrated HCl (37%, Merck) to reach a pH = 2.50±0.05. The Erlenmeyer flasks containing the gastric solution and the solid material were placed in a water bath at 37±0.5°C and placed under constant horizontal shaking (100±2 rpm) for 1 hour.

The intestinal medium consisted of adjusting the gastric solution pH with saturated $NaHCO_3$ (pa, Merck) solution to 7.0±0.1 and then adding 175 mg of bile salts (Sigma-Aldrich, Cat Nº B8631) and 50 mg of pancreatin (Sigma-Aldrich, Cat Nº P1500). The container with the mixture was also subjected to horizontal shaking (100±2 rpm) for 2 hours at 37±0.5°C. At the end of each phase (gastric and intestinal), 5 mL were collected and centrifuged at 10,000 rpm for 10 min and the supernatant was filtered through a membrane filter of 0.45 µm pore size. The extracts were preserved under refrigeration (4°C) until analysis by GFAAS or FAAS.

The percentages of bioaccessible Cd and Pb were calculated using the following equation:

$$\text{Bioaccessible metal (\%)} = \frac{\text{In vitro metal}}{\text{Total metal}} \times 100$$

Desorption kinetics experiments

Kinetics of Cd and Pb release from the smelter tailing samples were performed using a stirred-flow technique, which lessens diffusion effects and re-adsorption phenomena through constant mixing in the reaction chamber, and removal of the metals in the effluent solutions (Sparks, 2003). Similarly to the experimental set up illustrated by Strawn and Sparks (2000), our experiments were carried out using two different desorptive solutions: (1) a 0.1 M $CaCl_2$ solution adjusted (with NaOH or HCl solutions) to the smelter tailings pH, and (2) a Mehlich-1 (0.05 M HCl + 0.0125 M H_2SO_4) solution. The desorbing solution passed through the chamber containing the solid sample at a constant flow rate of 0.9 mL min^{-1} using a peristaltic pump. The chamber was covered with a 25-mm filter membrane of 0.45 µm pore size to separate the solids from the solution. The chamber volume of 12 mL contained a suspension of 0.6 g of sample (<250 µm, this being the same particle size used for total and bioaccessible analyses), which was stirred at 400 rpm with a magnetic stir bar. The experiments were performed in duplicate for 210 min, and the effluent was collected every 2 minutes for the first 10 min and every 10 min thereafter for a total of 210 min. Cadmium and Pb concentrations were analyzed using ICP-AES, to subsequently calculate cumulative Cd and Pb desorption percentages, in accord with Shi (2006).

Quality assurance and quality control

All reagents used in this work were analytical grade. Ultrapure water with a resistivity of 18.2 MΩ-cm was used to prepare all solutions. Glassware, flasks and materials were treated with a 10% HNO_3 solution for 24 hours, and rinsed three times with distilled water before use. All chemical analyses were performed in triplicate, except for the desorption experiment, which was carried out in duplicate, with blank samples conducted in parallel for quality control purposes.

Certified reference materials (BCR 143R, NIST 2710 and NIST 2710a) were used to evaluate the reproducibility and the accuracy/precision of the tested analytical procedures. Recovery percentages of trace elements in the samples showed a reliable analytical data accuracy for the analyses of total contents. The percentages of bioaccessible Cd (78% - gastric and 44% - intestinal) and Pb (25% - gastric and 12% - intestinal) found in the certified material NIST 2710 were in good agreement with the values found in other studies. Hamel et al. (1998) reported the bioaccessibility of Cd and Pb for NIST 2710 as 51.4±18.5% and 36±14%, respectively, at a liquid-to-solution ratio of 100:1 in the gastric phase. Rodriguez et al. (1999) found Pb bioaccessibility in the gastric phase (with dough) of 28%. Ellickson et al. (2001) reported bioaccessibility of Pb in the intestinal step as 10.7%. Cadmium bioaccessibility values found for the NIST 2710a and BCR 143R were 33% (gastric), 33% (intestinal) and 46% (gastric), 38% (intestinal), respectively. For Pb, the values were 33% (gastric), 3% (intestinal) and 1% (gastric), 1% (intestinal), respectively. To the best of the authors’ knowledge, no previous research has indicated the bioaccessibility values for these standards that could be used as a reference for us to compare to the results from this study.

Results and Discussion

Chemical characteristics of the smelter tailings

Smelter tailing samples from the studied sites showed intermediate values of pH (Table 1). The highest pH value found was for the pH9 site due to the alkaline conditions of the wastes disposed in this area. The OM contents in the samples were low, ranging from 0.5 to 1.5%, with the highest values – 1.5 and 1.3% – for the EB and the pH9 sites, respectively. This occurred because of the existence of plants in these areas, the pH9 site being naturally covered with plants of Cerrado vegetation, and EB the area where the revegetation project took place. Comparing the revegetation sites (Eu and EB), the content of the surface OM (0-2 cm) and the pH of the EB site were higher than the values found in Eu. This difference is a result of the surface application of limestone and the growth of brachiaria in between the rows of eucalyptus in EB. The Eu site had no plant species in between the rows.

Concentrations of trace elements in the smelter tailings determined in this study were compared with the industrial investigation threshold established by Conama (2009), since there are no guideline values for trace elements in tailings in the Brazilian legislation. The threshold values (in mg kg^{-1}) are: As (150), Cd (20), Cr (400), Cu (600), Pb (900), and Zn (2000). The samples showed levels of As and Cr well below these values (Table 1). The Eu site had Cd contents above the threshold, as well as EB (0-2 cm depth), which also showed high levels of Zn. The pH9 sample was the only one that showed low levels of trace elements, which was expected since this area had several species of plants growing normally. Therefore, this site is considered to be non-contaminated by trace elements – taking into consideration the industrial investigation threshold. On the other hand, Tailings is the most contaminated site, with the highest levels of Cd (621 mg kg^{-1}), Cu (2518 mg kg^{-1}), Pb (7431 mg kg^{-1}), and Zn (45,058 mg kg^{-1}). Studies carried out by Lamb et al. (2009) showed very high concentrations of Cd, Cu, Pb, and Zn in contaminated soils from Australia – up to 302 mg Cd kg^{-1}, 6841 mg Cu kg^{-1}, 12,000 mg Pb kg^{-1}, and 39,000 mg Zn kg^{-1}. The authors reported that, despite the high total metal concentration of the contaminated soil, Zn, Cd, and Pb were not generally found at elevated levels in the pore-water. A previous study on geochemical position of metals in soils near a mine/smelter in Poland reported the highest concentrations of Cd, Pb, and Zn in a forest soil – 200 mg kg^{-1}, 25,000 mg kg^{-1} and 20,000 mg kg^{-1}, respectively (Chrastný et al., 2012).

Considering their importance in terms of human health effects, for the present study, we selected the trace elements Cd and Pb for investigation of total and bioaccessible contents in all samples collected (five samples from each site at two depths) and desorption kinetics for one sample from each site at the 0-2 cm depth.

Table 1. Chemical characteristics of the smelter tailings from a zinc smelting area

Samples	pH	OM	As	Ca	Cd	Cr	Cu	K	Mn	P	Pb	S	Zn	Al	Fe
	(H_2O)	(%)	mg kg^{-1}											(%)	
Eu[1]	5.1	1.0	2	172	52	25	19	340	55	95	23	340	819	1.2	2.0
Eu[2]	4.8	0.8	2	144	39	18	27	266	81	57	45	309	1104	1.1	1.8
EB[1]	6.1	1.5	3	1438	30	35	58	896	800	230	157	657	3301	2.5	4.1
EB[2]	6.3	1.2	8	564	11	22	77	507	1108	184	293	468	3268	1.1	3.5
pH9[1]	6.5	1.3	2	994	15	64	29	661	452	190	46	3261	954	0.6	3.1
pH9[2]	6.7	0.9	1	421	6	23	27	1020	134	179	26	2085	403	0.7	3.0
Tailings[1]	5.5	0.6	59	48521	621	2	2518	1647	29169	147	7431	66200	45058	0.3	2.5
Tailings[2]	5.0	0.5	36	25678	525	14	561	711	9044	223	3455	40843	25321	0.4	2.8
NIST 2710[3]	Recovery (%)		90	Dm	99	Nc	94	29	92	86	92	83	88	36	86
BCR 143R[3]			Nc	Nc	97	105	98	Nc	103	Nc	97	Nc	89	Nc	Nc

[1,2] Collected at the depths of 0-2 and 2-10 cm, respectively; [3] Certified reference material

OM determined by the Walkley-Black method; EPA method 3051 – ICP analyses

Dm = analyzed by different methods; Nc = noncertified value

Industrial threshold (mg kg^{-1}) for As (150), Cd (20), Cr (400), Cu (600), Pb (900) and Zn (2000) established by Conama (2009)

Total Cd and Pb contents

The samples showed a great variability in the contents of Cd and Pb not only among the different sites, but also in replicate samples from the same site and from the same sampling depth, with average values ranging from 6 up to 773 mg kg^{-1} for Cd and from 32 up to 6256 mg kg^{-1} for Pb (Figure 1). The Tailings site showed extremely high concentrations of the elements – up to 1743 mg kg^{-1} for Cd and 8675 mg kg^{-1} for Pb. Such heterogeneity in trace elements contents in samples of the same area is common in tailings from smelting areas due to constant waste disposal with variable contamination levels. Various studies have reported great variability in metal concentrations among different sites. Rieuwerts and Farago (1996) reported contents of Cd ranging from 0.1 to 48 mg kg^{-1} and of Pb ranging from 55 to 37,300 mg kg^{-1} in soils from the vicinity of a mining and smelting area in the Czech Republic. The levels of metals decreased with increasing distance from the smelter, i.e., the larger the distance from the smelter, the lower the levels of metals. Studies carried out by Bi et al. (2006) of samples from Zn smelting areas in China revealed that soil from a cornfield near the smelting sites had elevated concentrations of Cd (5.8 to 74 mg kg^{-1}), Pb (60 to 14,000 mg kg^{-1}), and Zn (260 to 16,000 mg kg^{-1}). High concentrations of heavy metals were also found in corn plants and in the moss samples from the smelting sites.

For an interpretation of the contents found in this study, the values established by Conama (2009) for Cd and Pb were once again considered. For Cd, most of the sites had values above 20 mg kg^{-1}, except for pH9 (Figure 1). The Tailings sample stood out for having mean contents approximately 38 times higher than the industrial threshold. It also exceeded the limit for Pb, with average content approximately 7 times greater. The other sites showed Pb concentrations well below the threshold.

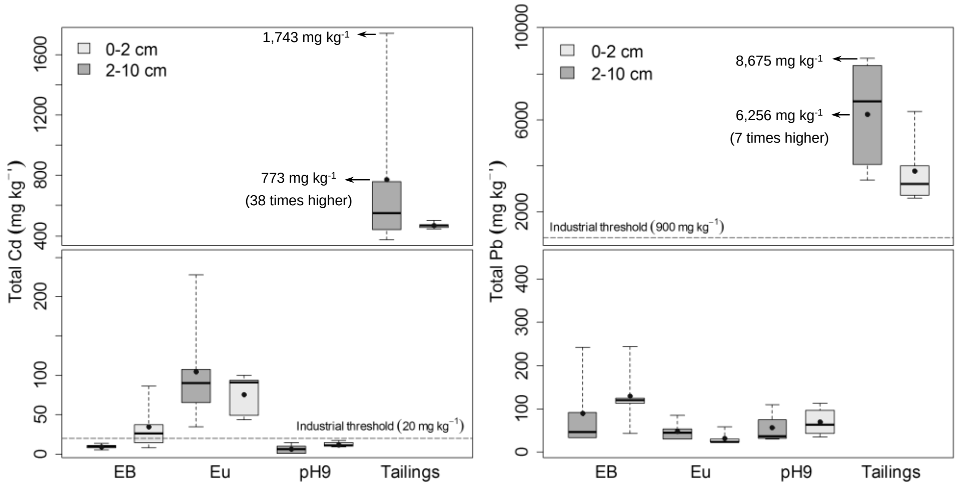

Figure 1. Box plot of total Cd and Pb contents in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Cd and Pb values. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the right and left boxes represent the depths of 0-2 and 2-10 cm, respectively. Industrial threshold = soil guideline value for industrial areas established by Conama (2009). Recovery (%) of the certified materials: Nist2710 (Cd: 84; Pb: 83), Nist2710a (Cd: 119; Pb: 103), BCR143R (Cd: 99; Pb: 81).

Contamination by multiple metals (such as Pb, Zn, Cd, Cu, and Ni, that can co-occur in mineral deposits) is rather common in the surrounding mining/smelting areas, with substantial variation in the bioavailable levels among the sites (Schaider et al., 2007). However, total concentration of trace elements in soils/tailings does not usually provide enough information for determining the element bioavailability and mobility. Metals in soils/tailings are related to certain physicochemical parameters that control the availability of metals in the environment (Anju and Banerjee, 2011).

No pattern was noticed in the contents of Cd and Pb among the stratified samples (0-2 and 2-10 cm) (Figure 1). For a risk assessment considering involuntary ingestion of soils/tailings by children (i.e. hand-to-mouth activity), the most important layer of soil to be considered is the most superficial one (the first few cm). However, it is relevant to have samples collected from different stratifications in a risk assessment because the particles on the top layer of the soil/tailing can be eroded by wind and water (rain and surface run off) and transported to urban areas, rivers, farmland, etc, causing the layer underneath to become the top layer (Ono et al., 2012).

Bioaccessibility of Cd and Pb

Similarly to the total content, a great variability was noticed in the concentration of bioaccessible Cd and Pb both among and within the sites, with the Tailings site showing the highest contents (Figures 2 and 3). The mean contents of bioaccessible Cd in the Eu and in the Tailings sites for both depths were above the industrial threshold (Figure 2). In addition, very high Cd contents (up to 807 mg kg^{-1}) were observed for the Tailings site at the 2-10 cm depth, this value being 40 times higher than the industrial threshold.

The bioaccessible Pb contents were well below the industrial threshold in all sites at both depths (Figure 3), which confirms the necessity of not taking into consideration only the total content of the element when assessing human health risks, since the results can be overestimated. Several studies have indicated that the bioaccessibility of a contaminant is well less than 100%, and have therefore suggested the use of bioaccessible contents instead of total contents when assessing health risk, due to their greater accuracy (Ruby et al., 1996; Hamel et al., 1998; Rodriguez et al., 1999; Turner and Ip, 2007; Girouard and Zagury, 2009; Juhasz et al., 2010; Lu et al., 2011; Ono et al., 2012; Toujaguez et al., 2013). No pattern was observed in the contents of bioaccessible Cd and Pb (Figures 2 and 3) among the stratified samples (0-2 and 2-10 cm), showing a similar behavior to that found for total contents (Figure 1).

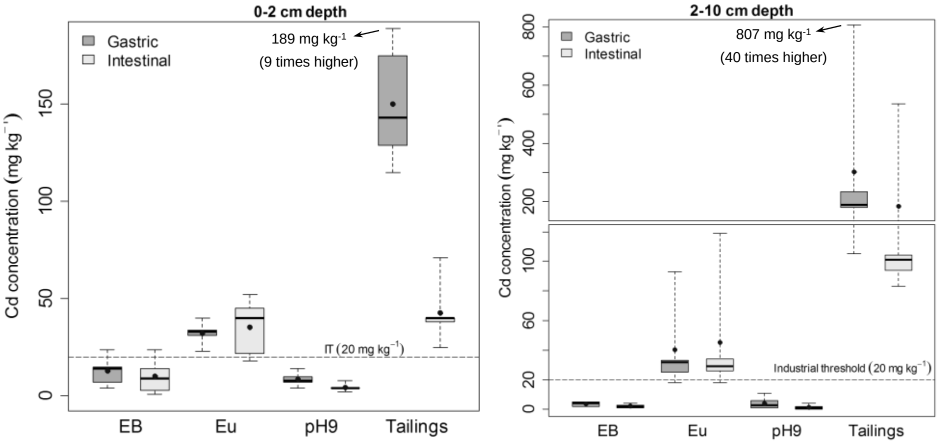

Figure 2. Box plot of bioaccessible Cd content in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Cd value. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the left and right boxes represent the gastric and intestinal phases, respectively. Industrial threshold = soil guideline value for industrial areas established by Conama (2009).

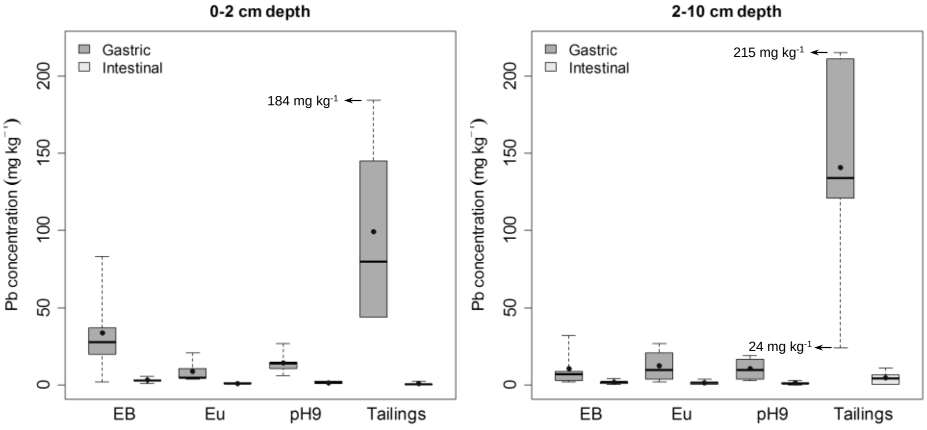

Figure 3. Box plot of bioaccessible Pb content in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Pb value. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the left and right boxes represent the gastric and intestinal phases, respectively.

Percentages of bioaccessible Cd and Pb

The percentages of bioaccessible Cd and Pb for each area and depth were calculated as the ratio between the average content (mg kg^{-1}) of bioaccessible metal and total metal (Figure 4). The pH9 site showed a high percentage of bioaccessible Cd in the gastric phase at both sampling depths (75 and 67%, at 0-2 and 2-10 cm, respectively) (Figure 4). Despite that, its bioaccessible contents (Figure 2), as well as the total (Figure 1), were below the industrial threshold, being thus considered a non-contaminated area. The other sites presented moderate bioaccessible Cd (%) in the gastric phase, ranging from 32 to 44% (Figure 4). The Eu site, besides having bioaccessible and total Cd contents (Figures 1 and 2) above the industrial threshold, showed the highest bioaccessible Cd (%) in the intestinal phase (Figure 4) for both depths (47 e 43%, at 0-2 and 2-10 cm, respectively).

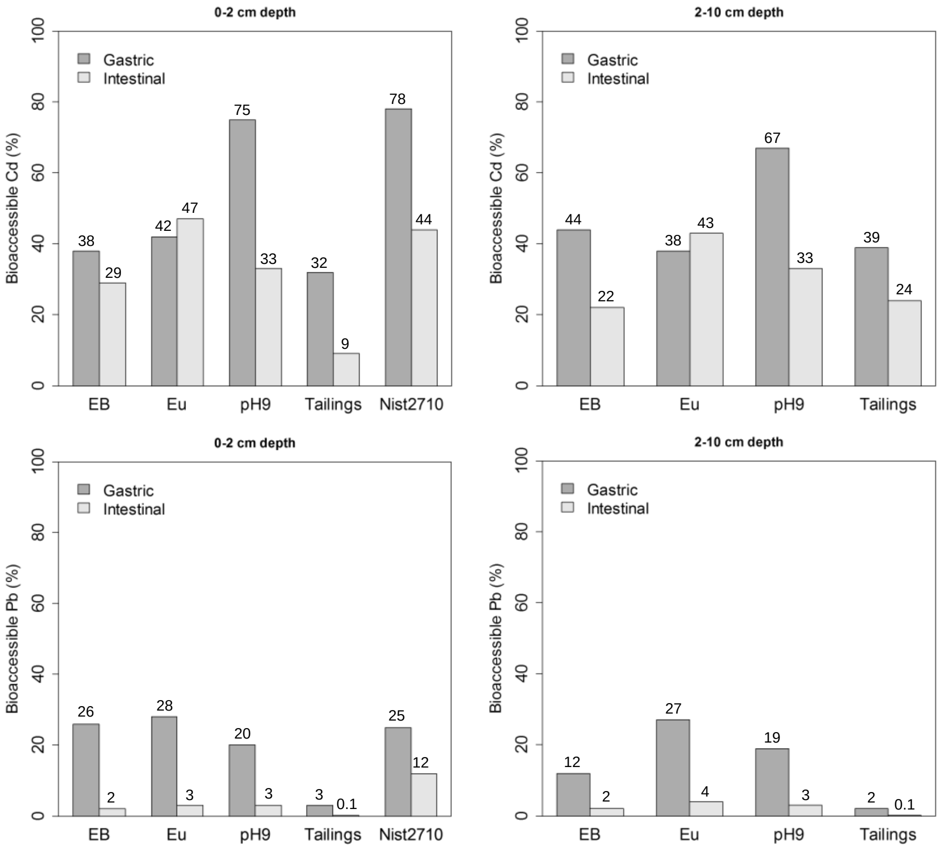

Figure 4. Percentage of bioaccessible Cd and Pb in tailings from a zinc smelting area and in a certified reference material.

The Tailings site showed one of the lowest percentages of bioaccessible Cd and the lowest percentage of bioaccessible Pb (<3%) (Figure 4), even though it showed the highest contents of total and bioaccessible Cd (Figures 1 and 2) – above the industrial threshold – and total and bioaccessible Pb (up to 8675 and 215 mg kg^{-1}, respectively) (Figures 1 and 3), the latter being below the industrial threshold. However, there is still a need to monitor this material because a range of physicochemical changes may occur over time, increasing the bioaccessibility and generating Cd and Pb release to the environment. A study on bioavailability of Cd, Pb, and As in an abandoned mine site in Spain indicated that pH and mineralogical composition were important factors controlling metal bioavailability in the materials (Navarro et al., 2006). Another study reported that the bioaccessibility of Cd, Pb, and Zn in smelter-contaminated agricultural soils from France was affected by various physicochemical parameters, such as sand, carbonates, organic matter, assimilated P, free Al oxides, and total Fe contents (Pelfrêne et al., 2011a).

Mean bioaccessible Cd and Pb (%) were higher in the gastric phase when compared to the intestinal phase (except for Cd in the Eu site), the difference between the two phases being higher for Pb (Figure 4). This indicated that most of the Cd and the Pb was dissolved in the stomach and after that a portion remained soluble in the intestine, being potentially available for absorption. This result is relevant since the absorption of metals occurs mainly in the intestines and insignificantly in the stomach (Charman et al., 1997; Daugherty and Mrsny, 1999). Similarly, Lu et al. (2011) pointed out that the bioaccessibility of Pb in the gastric phase (39.1%) was much greater than in the intestinal phase (6.9%) in soils from different land uses (urban parks, roadsides, industrial sites and residential areas) in China. They attributed this to the reduced solubility of Pb at a much higher pH in the intestinal phase than in the gastric phase. The dissolution of Pb in the acidic gastric phase is strongly dependent on pH, i.e., its solubility decreases significantly (by 65%) with increasing gastric pH from 1.3 to 2.5 (Ruby et al., 1996). Also, it was reported that the adsorption of Cd in the soil increased rapidly with increasing solution pH within the range of 2 to 5 (Naidu et al., 1994).

However, the highest percentages of bioaccessible metals do not necessarily occur in the gastric phase. A previous study on bioaccessibility of metals in dust from several domestic and working settings reported that, compared to the accessibility in the stomach, the accessibility in the more alkaline carbonate-rich intestine was either lower (Al, Ca, Cd, Mn, Ni, Sn, Pb, Zn), similar (Co, Cu, Fe) or greater (Cr, U) (Turner and Ip, 2007). The authors attributed these observations to precipitation and/or readsorption in the intestine, stabilization by complexation, or anion-like adsorption of negatively charged polyatomic species, respectively. Several studies indicate that Cd and Pb bioaccessibility is greater in gastric phase extracts when compared to intestinal phases (Carrizales et al., 2006; Tang et al., 2006; Turner and Ip, 2007; Juhasz et al., 2010; Lu et al., 2011; Pelfrêne et al., 2011b).

Percentages of bioaccessible Cd were much higher than the bioaccessible Pb values, especially in the intestinal phase (Figure 4), indicating that Cd occurs in more labile forms than Pb. Navarro et al. (2006) reported that in a mine site Cd was the most bioavailable metal in both the stomach and the intestinal phases (47 and 27.8%, respectively), followed by Pb (25.3 and 11.5%). In smelter-contaminated agricultural soils, Pelfrêne et al. (2011a) found a mean bioaccessibility (%) in the gastric and intestinal phases of 82 and 45% for Cd, and 55 and 20% for Pb, respectively, indicating that Cd was mainly found in more available fractions and Pb was mostly present as adsorbed or occluded by Fe/Mn oxides. Several studies have shown bioaccessible values higher for Cd than for Pb in soils, urban dust, and mine tailings (Turner and Ip, 2007; Pelfrêne et al., 2011a; Okorie et al., 2012).

Some studies have investigated the effects of amendments in the reduction of the availability of metals in contaminated soils/tailings. The addition of P-containing amendments (P fertilizers) was found to effectively reduce the bioaccessibility of Pb in contaminated soils (Tang et al., 2004). In general, the effectiveness of the treatments in the intestinal phase was, in decreasing order: hydroxyapatite, phosphate rock, hydroxyapatite plus single super-phosphate, and single super-phosphate. In a study on Pb toxicity reduction in a highly contaminated military shooting range soil in Korea, Ahmad et al. (2012) found that, compared to the unamended soil, the bioavailability and bioaccessibility of Pb decreased by 92.5% and 48.5% with mussel shell, by 84.8% and 34.5% with cow bone, and by 75.8% and 12.5% with biochar, respectively.

Desorption kinetics experiments

In order to assess the exchangeable metal fraction and the phytoavailable metal (or not stable at lower pH – relevant in the presence of acid rain or near the roots of plants) fraction, stirred-flow desorption experiments were conducted using a 0.1 M $CaCl_2$ (adjusted to the samples pH) or a Mehlich-1 (pH = 1.6±0.1) solution. The small sample chamber, the relatively low solid:solution ratio and the constant flow rate ensured that none of the desorption products would be re-adsorbed onto the solid sample (Sparks, 2003). To compare the desorption behavior of smelter tailings, the amount of metal released was plotted as the cumulative metal desorption (% of total concentrations) as a function of time (Figure 5).

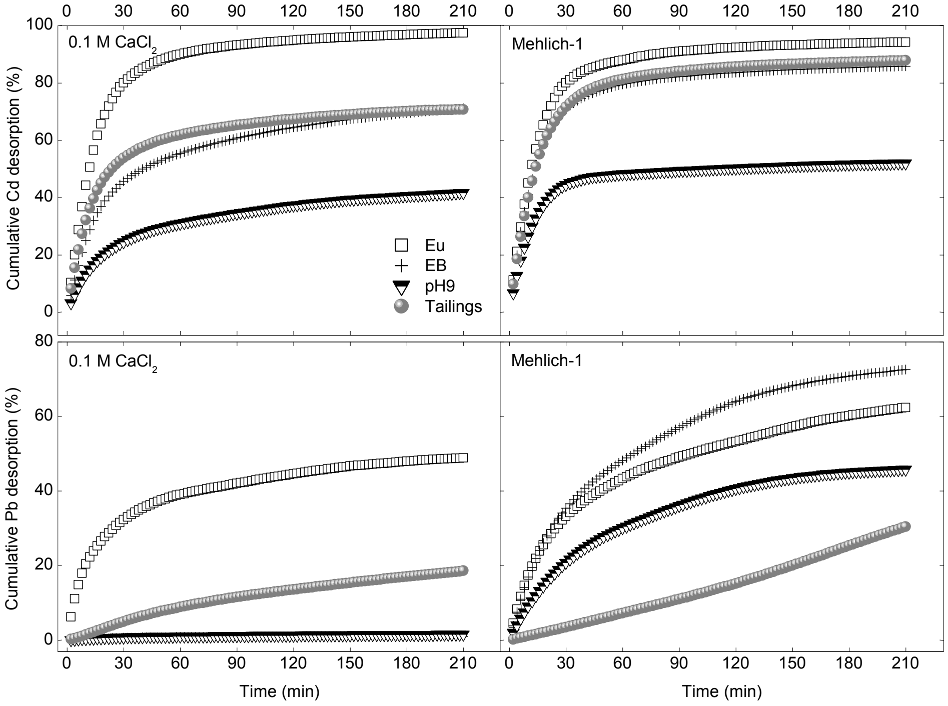

Figure 5. Percentage of Cd and Pb release from smelter tailing samples during a stirred-flow dissolution experiment using a 0.1 M $CaCl_2$ solution adjusted to the smelter tailings pH and a Mehlich-1 solution.

The experimental data indicated an initially rapid desorption of Cd by both extraction solutions ($CaCl_2$ and Mehlich-1) in the first 30 minutes (Figure 5). After that, small quantities of Cd were released until the end of the experiment (210 min), when equilibrium was reached. At the completion of the 210 min dissolution experiment, Cd desorption was over 94% for Eu, 71% for EB, 42% for pH9 and 71% for Tailings. The $CaCl_2$ solution desorbed a slightly lower amount of Cd from the samples than the Mehlich-1, except for the Tailings sample. This result shows that most of the Cd present in the samples was in labile forms (exchangeable).

The percentage of Pb released by $CaCl_2$ was 49% and 19% for Eu and Tailings samples, respectively, whereas with Mehlich-1 it was 62% and 31% for the same samples, during the 210-min experiment (Figure 5). For the EB and pH9 samples, however, percentages of Pb were very low (1 and 1.5%, respectively) when desorbed by $CaCl_2$ and high (73 and 46%, respectively) when desorbed by Mehlich-1.

Lead desorption by the Mehlich-1 solution did not reach an equilibrium during the dissolution experiment, indicating that more of this element would have been released after 210 min. The percentage of Pb removed from the Tailings sample by both solutions tended to be linear (increased rapidly) during 210 min and did not reach equilibrium. In general, this study showed that the exchangeable Pb fraction was not predominant in the samples. The greatest Pb release occurred in the extraction solution with lowest pH, indicating that Pb fractions appeared in more recalcitrant forms in the samples. The fact that Cd appeared in the more labile forms (exchangeable) and Pb in the more recalcitrant forms (less labile) is in agreement with the results of bioaccessibility (Figure 4), in which Cd was shown to be more bioaccessible and Pb less bioaccessible.

Conclusions

The smelter tailing samples from the Zn smelting area, especially from the Tailings site, have high concentrations of Cd, Cu, Pb and Zn. More detailed analyses revealed that Cd and Pb concentrations were considerably elevated in the Tailings site and highly variable among and within the sites. Thus, we point out that the final disposal of these materials requires adequate planning, in order to avoid Cd and Pb contamination of the surrounding environment. Even though the study detected elevated levels of Cd and Pb, it has to be considered that the population does not have free access to the sites studied, which results in a rather low risk of exposure.

The bioaccessibility of Cd and Pb in the intestinal phase (less than 47 and 4%, respectively) was less than half the total concentration of the metals. This indicates that a considerably high fraction of the elements was not available for absorption in the intestinal compartment (where the absorption takes place). Desorption kinetics experiments revealed that the Pb fraction in the samples was less labile (more recalcitrant) and the Cd fraction more labile (i.e. exchangeable fraction). This finding is in accordance with the bioaccessibility results.

Acknowledgments

We gratefully acknowledge funding received from the CNPq, CAPES and FAPEMIG - Brazil. We would like to thank the Delaware Environmental Institute (DENIN) and Environmental Soil Chemistry research group of the University of Delaware, especially Matt Siebecker and Jerry Hendricks, for their assistance during the experimental analyses. Fábio Ono appreciates the Sandwich Doctorate fellowship for this work funded by Capes, and also the support of the University of Delaware.

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ARTIGO 2 Investigation of arsenic species in tailings and windblown dust from a gold mining area

Normas da revista *Environmental Science and Technology*

Investigation of Arsenic Species in Tailings and Windblown Dust from a Gold Mining Area

Fábio Benedito Ono[§], Ryan Tappero[£], Donald Sparks[€], Luiz Roberto Guimarães Guilherme[*,§]

[*]Corresponding author phone: + 55 35 3829 1259; fax: + 55 35 3829 1251; e-mail: guilherm@dcs.ufla.br

[§]Department of Soil Science, Federal University of Lavras, CP 3037, Campus UFLA, 37200-000, Lavras, MG (Brazil)

[£]Photon Sciences, Beamline X27A, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973 (USA)

[€] University of Delaware, Delaware Environmental Institute, Interdisciplinary Science and Engineering Lab, Suite 250a, Newark, DE 19716 (USA)

Abstract

Research has shown the presence of high levels of arsenic (As) in tailings from a gold mining area of Brazil. This is a critical problem, generating concerns about impacts on human health. Yet, a recent study showed that As bioaccessibility in the same area was very low. Thus, determination of the direct solid-phase speciation of As in the mine tailings and windblown dust is needed to explain this low bioaccessibility. Tailing samples were collected from four subareas and windblown dust from eight sites. Synchrotron-based bulk-X-ray absorption near edge structure (XANES) spectroscopy, µ-XANES and µ-X-ray fluorescence (µ-SXRF) spectroscopy were applied to determine As speciation. Bulk-XANES spectra indicated that As occurs as the As(V) oxidation state. Micro-XANES and µ-SXRF analyses revealed that As was also present as arsenopyrite (FeAsS) and its weathering products, but mostly it was As(V) as poorly crystalline ferric arsenate. This supports the finding of low bioaccessible As and highlights the importance of Fe oxides in immobilizing As in the terrestrial environment. All air particulate samples exhibited As-rich particles. The air particulates exhibited solid-phase As species very similar to those found in the mine tailings.

Keywords: trace elements; arsenic speciation; micro-XANES; air particulates.

Introduction

Arsenic (As) is considered a trace element of great interest in studies concerning environmental contamination due to its high toxicity and consequent risks to humans and animals.[1,2] The element is strongly associated with skin, bladder and lung cancers in humans[3] and it has been found in significant levels in soils, sediments and mine wastes from gold mining areas and nearby, raising serious environmental concerns.[4-12]

Studies have indicated an association of natural sources of As especially with gold deposits containing sulfide minerals worldwide, including in Brazil.[13-15] Generally, As exists in these materials in the form of reduced sulfide minerals (e.g. arsenopyrite FeAsS)[16,17] and the gold mining activities enable the weathering of As sulfides, releasing As together with Fe sulfates and hydroxides, generating secondary compounds and forming more oxidized As forms.[16] Usually, As in sulfide minerals (e.g. arsenopyrite, realgar) is slightly soluble – low bioavailability. Thus, if As remains in these mineral forms, it tends to be less mobile and bioavailable than in the oxidized forms.[17,18] It is worth pointing out the stability of arsenopyrite under reducing conditions, and the probable chemical stability of mine tailings containing this mineral during long-term storage if they are kept water-saturated and moderately reduced.[19]

The release of As from mine wastes is controlled by precipitation-dissolution and adsorption-desorption reactions involving the secondary compounds generated during the weathering of arsenopyrite.[20] In mine tailings, As usually occurs integrated with sulfide minerals such as arsenopyrite, arsenian pyrite, arsenates, and As-bearing Fe oxyhydroxides.[8,21] In soils from mining areas, however, As is mainly associated with amorphous Fe oxyhydroxides.[22,23] In well-aerated environments, As(V) is the predominant form of As and it adsorbs on Fe oxyhydroxides by formation of inner-sphere surface complexes as a result of a ligand exchange reaction with hydroxyl groups at the mineral surface, resulting in the formation of predominantly bidentate binuclear surface species.[24,25]

Previous studies have shown high levels of As in soils, substrates and tailings from gold mining areas of Brazil,[4,13,26,27] especially in mine tailings from an open pit gold mine located very close to the city of Paracatu - MG.[11] The site includes an open pit mine, a processing plant, and a tailings impoundment area, besides some office buildings. It is the biggest gold producer in Brazil (2011: 453,396 oz ~ 25% of national production) and it has been in operation for 25 years, with a lifespan estimated to 2042. The mine has the lowest gold grade in the world (0.4 grams of gold per ton of ore).

Despite the high levels of As found in the tailings of this mine area, the samples showed a very low As bioaccessibility.[11] The bioavailability, mobility and toxicity of As depend on its speciation – chemical form and oxidation state.[28] However, studies concerning the solid-phase chemical speciation of As have not yet been carried out neither for these samples nor for the windblown dust collected at the city located very near the mine area. Knowing the As levels as well as the species in windblown dust is relevant in terms of human health. Open pit metal mining activities may cause aerosol emission to the air and these particulates could be transported by aerial processes long distances and deposited in urban areas. According to Cebrian et al.[29], in mining regions or near active smelters, there is also the risk of contamination by ingestion or inhalation of As-bearing particulates dispersed through hydraulic transport or aerosol emissions.

The aim of this study was to identify the direct solid-phase speciation of As in mine tailings and windblown dust from a gold mining area using synchrotron-based spectroscopy analyses such as bulk-X-ray absorption near-edge structure (bulk-XANES), micro-X-ray fluorescence (μ-SXRF) and micro-X ray absorption near-edge structure (μ-XANES) spectroscopy, and also evaluate the As levels present in windblown dust. Such studies are scarce in Brazil and may provide relevant information on the risk from exposure of residents near these areas.

Materials and Methods

Studied site and sampling procedure

The mine samples were collected on the grounds of an open pit gold mine located near the Paracatu city (Figure 1), in the Northwest of Minas Gerais - Brazil, at the following sites: 1) PNR - Private Natural Land Reserve (our control area), which is an area of native vegetation; 2) B1 - mined oxidized soil layer, comprising a slightly weathered material from which gold had been extracted; 3) Exp.B1 - experimental area of revegetation over B1 material; 4) Undisturbed - a non-commercially mined ore body, because of its low gold content; and 5) Pond tailings - waste materials from gold smelting. In a previous study,[11] five composite samples were collected from each of these five areas at two depths. These materials were once again analyzed in the present study. We selected the composite sample with the highest As content from each area at the 0-2cm depth. The samples were air-dried and sieved to less than 2 mm.

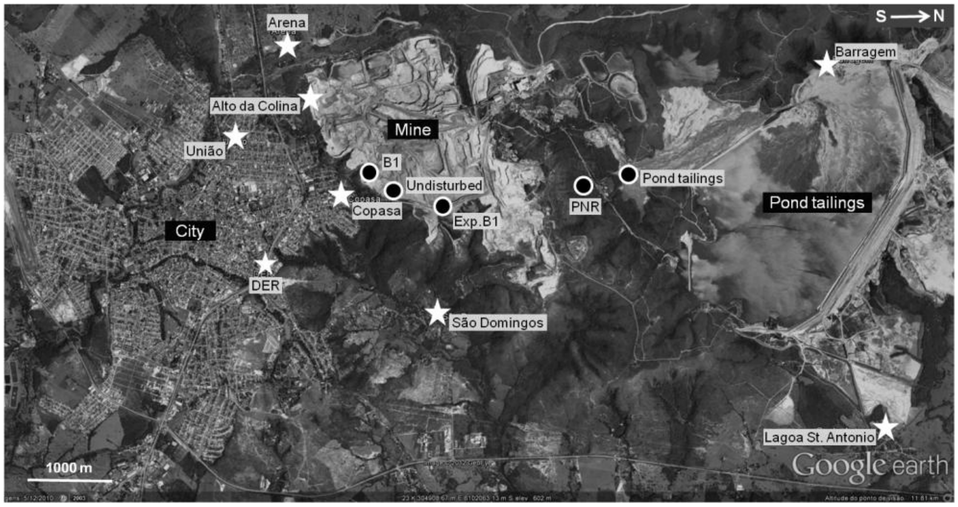

Figure 1. Map of the sampling sites from a gold mining area located in the Paracatu city. The stars and circles indicate the collection sites of air particulates and mine tailings samples, respectively.

The windblown dust samples (particles <100 µm) were collected around the mine area – urban and industrial area, Figure 1 – using a high volume (Hi-Vol) air sampler with a glass-fiber filter (20.3 x 25.4 cm). The air samplers were installed at eight sites: 1) Alto da Colina, 2) Arena, 3) Copasa, 4) União, 5) Barragem, 6) DER, 7) Santo

Antônio, and 8) São Domingos, for an exposure time of 1440 minutes. The filters were weighed before and after their installation in order to determine the total deposited dust.

Wet-chemical characterization

The mine tailings samples were air-dried and sieved to 2 mm. The concentration of the elements in the samples was determined by ICP-AES after microwave-assisted acid digestion by the EPA method 3051 and the organic matter content was measured through the Walkley-Black method.[30]

Total As content in windblown dust was quantified using acid digestion of the filters by the EPA method 3052. For this process, an 80-cm^2 section of filter was cut and transferred to microwave vessels filled with 3 mL of HF plus 9 mL of HNO_3. After digestion, the extracts were diluted with bidistilled water (5 mL), centrifuged, filtered and analyzed by graphite furnace atomic absorption spectrometry - GFAAS.

Arsenic Fraction

Phytoavailable

The same procedure as recommended for the routine analysis of phytoavailable phosphorus was adopted, due to similarities between phosphate and arsenate in soils. For that, 2.5 g of mine sample and 10 mL of a Mehlich-1 solution (0.05 M HCl + 0.0125 M H_2SO_4) were used according to Kuo[31]. The solid material and the solution were placed in a 15-mL centrifuge tube and, after shaking (150 rpm) for 5 minutes, samples were centrifuged, filtered and analyzed by GFAAS.

Non-specifically adsorbed As and Specifically adsorbed As

These two As fractions in the mine samples (<150 µm) were determined using the first two steps of the sequential-extraction method developed by Wenzel et al.[32]. The first step (0.05 M $(NH_4)_2SO_4$, 4 h shaking, 20°C) removes the non-specifically bound – easily exchangeable – As fraction (Fraction 1), which approximates the outer-sphere surface bound As fraction, and the second step (0.05 M $(NH_4)_2HPO_4$, 16 h shaking, 20°C) is used to extract specifically sorbed As fraction (Fraction 2), which approximates the inner-sphere surface bound As fraction. The As concentrations of the supernatants were determined by GFAAS after filtration.

Bulk-XANES analyses

The redox state of As in the mine samples was determined by X-ray absorption near edge structure (XANES) spectroscopy. The analyses were conducted at the As K-edge (11,867 eV) at the Brazilian Synchrotron Light Laboratory-LNLS (Campinas, Brazil) on the D08B-XAFS2 beamline. The spectra were recorded at room temperature using a Si (111) double crystal monochromator with an upstream vertical aperture of 0.5 mm and calibrated with Au L3-edge (11,919 eV). Air-dried, finely ground mine samples were mounted behind Kapton tape in a Teflon holder and analyzed in fluorescence or transmission mode depending on As concentration. Three scans were collected for each sample, and then merged. The spectra were baseline-corrected and normalized using Athena software.[33] The following natural minerals were used as reference standards for As: arsenopyrite (FeAsS), realgar (As_4S_4), orpiment (As_2S_3), and scorodite

($FeAsO_4•2H_2O$). These standard materials were selected to cover a wide range of oxidation states exhibited by As.

Micro-SXRF, µ-XANES and µ-XRD analyses

Micro-focused synchrotron based X-ray fluorescence (µ-SXRF), micro-focused XANES (µ-XANES) and micro-X-ray diffraction (µ-XRD) spectroscopic analyses in the mine tailings and windblown dust samples were conducted at beamline X27A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY, USA, to determine elemental distributions and direct solid-phase speciation of As. Two mine tailings (Undisturbed and Pond tailings) and three windblown dust (Alto da Colina, União and Barragem) samples were selected. The fine particulates were mounted behind Kapton tape in a cardboard slide-holder. The µ-SXRF maps were 3x3 mm in size, with a 10 µm step size, and beam energy was set to 12.5 keV. Micro-XANES spectra were then collected for the As K-edge (11,867 eV), at points of interest observed in µ-SXRF maps, where As was relatively highly concentrated. Micro-XRD spectra were collected at the same points. Linear-combination fitting (LCF) of the µ-XANES spectra of samples with those of various model compounds was performed using the Athena software[33] to estimate As species in the mine tailings and windblown dust samples. Based on the R-factor value, the best fit and possible combination of reference compounds with the samples spectra were selected. The following materials were included as As standards: arsenopyrite (FeAsS), realgar (As_4S_4), sodium arsenite (NaH_2AsO_3), sodium arsenate (NaH_2AsO_4), scorodite ($FeAsO_4•2H_2O$), and poorly crystalline ferric arsenate ($FeAsO_4•2.4H_2O$). The poorly crystalline ferric arsenate was synthesized following the procedures of Jia et al.[34]. The compound is characterized as a scorodite-like mineral (poorly crystalline scorodite) due to its structural likeness.[35]

Quality assurance and quality control

All of the reagents were analytical grade. Ultra pure water with a resistivity of 18.2 MΩ-cm was used to prepare all solutions. All wet-chemical analyses were performed in triplicate with blank samples conducted in parallel for quality control purposes. Arsenic concentrations in blank samples were always lower than the detection limit for the GFAAS (4 µg As L^{-1}). Certified reference materials BCR 143R and NIST 2709 were analyzed by the EPA methods 3051 and 3052, respectively.

Results and Discussion

Chemical characteristics of mine tailings

The mine tailing samples had low pH (Table 1), with the highest value (5.5) for the Exp.B1 site, where limestone was used in order to provide a pH value more appropriate for plant growth. The low pH of the mine tailings was probably caused by the weathering of sulfide ore (e.g. pyrite, arsenopyrite), whose products cause strongly acid reaction.

PNR (control area) and Exp.B1 samples showed the highest OM content – 3.0 and 1.5%, respectively. This was related to growth of plants in these areas. The PNR is an area with native vegetation and Exp.B1 is an area that has been revegetated.

Table 1. Chemical characteristics of the mine tailings from a gold mining area

Samples	pH	OM	Al	Ca	Cd	Cr	Cu	Fe	K	Mn	P	Pb	S	Zn
	(H_2O)	(%)	mg kg^{-1}											
PNR - Control	4.5	3.0	23373	158	0.5	38	82	40503	3141	122	460	19	143	25
B1	4.6	0.5	2276	90	1.3	5	30	17428	502	5	115	15	49	5
Exp.B1	5.5	1.5	2302	1245	1.1	4	41	27427	686	160	234	70	304	57
Undisturbed	3.3	0.4	9188	821	0.5	9	72	34870	759	1274	139	11	12103	157
Pond tailings	4.0	0.9	5361	2261	9.3	6	59	49496	2010	899	146	89	15164	168
BCR 143R	Recovery (%)		Nc	Nc	97	105	98	Nc	Nc	103	Nc	97	Nc	89

OM determined by the Walkley-Black method; EPA Method 3051 – ICP analyses; Nc = noncertified value

Industrial threshold (mg kg^{-1}) for As (150), Cd (20), Cr (400), Cu (600), Pb (900) and Zn (2000) established by Conama[36]

All samples had high levels of Fe and the Undisturbed and Pond tailings samples also had high levels of S – sulfide materials (Table 1). In addition, all samples contained Cd, Cr, Cu, Pb, and Zn (Table 1) well below the industrial threshold established by Brazilian legislation.[36] In a previous study,[11] high As concentrations were found in these samples – higher than the industrial threshold – except for the control area (37 mg kg^{-1}) (Table 2).

Selective chemical extractions

A previous study showed that the As bioaccessibility (IVG method) in the tailing samples was very low (<4.4%) (Table 2). Thus, As fractionation by Mehlich-1 (phytoavailable), $(NH_4)_2SO_4$ (easily exchangeable) and $NH_4H_2PO_4$ (inner-sphere surface bound As) was performed to confirm that As is not mostly labile (easily available) in the mine samples.

The proportion of phytoavailable, exchangeable and specifically sorbed As represented less than 4.7, 0.5 and 4.6% of the total As, respectively (Table 2). Therefore, these results confirmed the low As availability found in the samples through a bioaccessibility test, and indicated that the greatest proportion of As in the mine tailings was probably associated with Fe oxyhydroxides and/or the residual phase. A previous study reported that most of the As in river sediments was associated with Fe oxyhydroxides (62.1%), with moderate proportions of specifically sorbed As (17.9%), and a low proportion of exchangeable As (1.1%).[37] The authors showed that the last two chemical forms are extremely important from an environmental point of view, since they are claimed to be the most mobile As fractions and are able to generate a high level of toxicity.

Table 2. Total As content and available As fractions in the mine tailings from a gold mining area

Samples	Total As[&] mg kg^{-1}	Bioaccessible[&] (%)	Mehlich-1 (%)	Fraction 1[§] (%)	Fraction 2[§] (%)
PNR - Control	37	<DL	0.3	<DL	<DL
B1	262	3.1	1.6	0.2	2.2
Exp.B1	335	2.0	2.4	0.4	2.0
Undisturbed	527	1.6	1.0	0.5	4.6
Pond tailings	2666	4.4	4.7	0.1	2.1

[&] Modified according to Ono et al.[11]

<DL = below the detection limit (4 µg As L^{-1})

[§] As fractions associated with (1) non-specifically sorbed – extracted by $(NH_4)_2SO_4$ – and (2) specifically sorbed – extracted by $NH_4H_2PO_4$ – according to Wenzel et al.[32]

The As contents determined by Mehlich-1 were similar to the bioaccessible fractions, which might have been caused by the similarity in the pH values of these extracting solutions (Mehlich-1 pH~1.6; IVG method pH~1.8). A previous study indicated a significant correlation between bioaccessible and Mehlich-1-extracted As for samples from the same mining area.[38]

Total suspended particulates and Total As in windblown dust

The total suspended particulates (TSP) ranged from 43.1 to 148.8 µg m^{-3}, for the União and Lagoa St. Antonio sites, respectively (Table 3). All sites showed TSP values below the daily primary limit (240 μg m^{-3} in an exposure time of 24 h) established by Brazilian guidelines.[39] Primary limits for air quality are based on levels of pollutants that might present risks to human health.

Total As content analysis in the air filter samples indicated the presence of As in the air particulates, ranging from 38 to 313 mg As kg^{-1} (Table 3). The lowest As content was found at Lagoa St. Antonio – the farthest site from the mine area – and the highest As content was found at Alto da Colina – the nearest site to the mine area. In general, the closer the filters were to the mine area, the higher the As content. It is important to mention that this mine area is rather close to an urban area (Figure 1).

Table 3. Filter sample information and total As content in windblown dust from the Paracatu city

Sites	Collection date	Air volume (m^3)	TDD (g)	TSP (μg m^{-3})	Total As (mg kg^{-1})
Alto da Colina	05/12/2011	1475	0.0823	51.3	313
Arena	05/12/2011	1159	0.1199	95.1	250
Copasa	05/12/2011	2493	0.1808	66.7	147
União	05/12/2011	2205	0.1035	43.1	166
Barragem	06/29/2011	1571	0.0949	55.5	110
DER	05/18/2011	1809	0.1058	51.9	103
Lagoa St. Antônio	08/10/2011	2519	0.4079	148.8	38
São Domingos	05/13/2011	1796	0.1060	54.2	266

TDD = total deposited dust; TSP = total suspended particulates

EPA Method 3052 – GFAAS analyses; Recovery of the NIST 2709 = 84%

Air particulates around the tailings pond had low As content (Table 3), even though the tailings presented a concentration of up to 2666 mg As kg^{-1} (Table 2). This occurred due to the fact that these tailings are not easily suspended because they are immersed in the water (pond).

There is no regulation establishing reference values for trace elements in suspended air particulates in Brazil, which makes it difficult to compare and classify the As values as high or low. The existing regulations indicate criteria for the evaluation of air quality taking into consideration only the amount and the size of the suspended particulates. Thus, we emphasize the necessity of a regulation establishing reference values for trace elements in suspended air particulates in Brazil, to enable the evaluation of air quality, especially in sites close to mining/industrial areas.

Bulk-XANES analyses of mine tailings

The mobility and toxicity of As are related to its speciation and it is well known that As(III) is much more toxic for humans and animals and more mobile than As(V).[40,41] Thus, mine tailings were analyzed by bulk-XANES spectroscopy at the As K-edge to determine the predominant oxidation state of As (Figure 2). When comparing the absorption edge position of mine tailings and reference compounds (where the oxidation state is known) the XANES spectra indicated that in all mine tailings As occurred mainly in the As(V) oxidation state. This result could have been expected, since the mine tailings were collected at 0-2 cm and were therefore well aerated, except for the Pond tailings sample, which was originally under water-saturated conditions, but was not kept like that during the measurements. This condition change may have oxidized lowervalent As. Similarly, Paktunc et al.[5] in a study on As speciation in exposed and water-saturated mine tailings from a former gold mine, reported that As occurred as As(V) in both exposed and water-saturated tailings (air-dried prior to analysis). Also, no reduced As species were found in the bulk-XANES spectra.

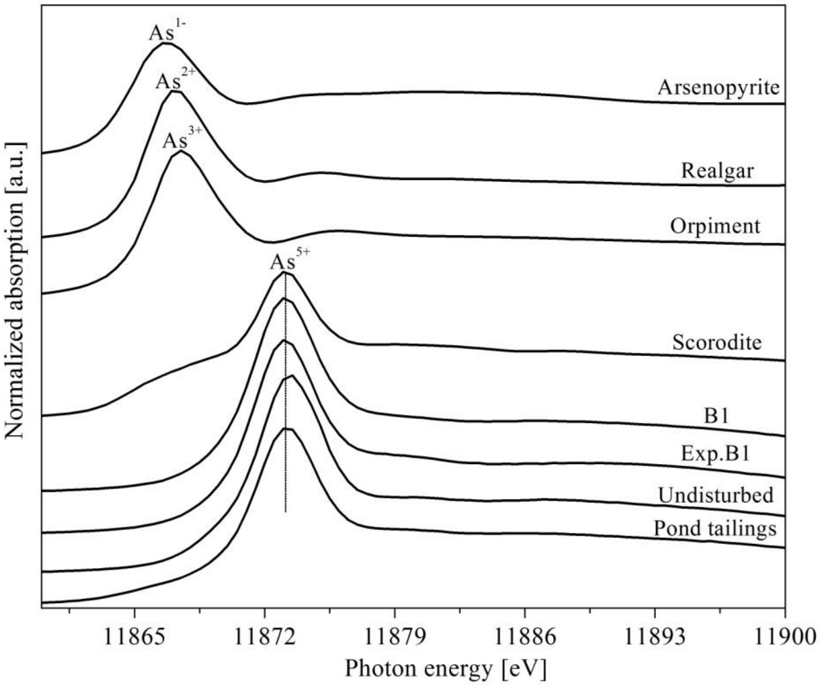

Figure 2. Normalized As K-edge XANES spectra of mine tailings. Also shown are XANES spectra of arsenopyrite (As^{1-}), realgar (As^{2+}), orpiment (As^{3+}) and scorodite (As^{5+}) for comparison of the edge positions.

Generally, the predominant forms of As found in mine tailings are As(V) and As(III). A study on mine tailings from three different mining areas indicated the predominance of As(V) in the samples, and mixed oxidation states [As(0) and As(V)] were observed in the Argonaut Mine waste.[8] Kreidie et al.[42] reported that in tailing samples and nearby samples As occurred in two oxidation states [As(III) and As(V)] simultaneously, while in the samples at longer distances from the mine As(V) species was the predominant state.

Due to the heterogeneity of the mine tailing samples, bulk-XANES analysis only detects the dominant speciation over mm^2 of the sample. Micro-analyses such as µ-XANES combined with µ-SXRF are capable of identifying also the species present in minor abundance – in other words, they enable the identification of the species that are less predominant in the samples, but may be the most important for controlling metal(loid) bioavailability.

Micro-SXRF, µ-XANES and µ-XRD analyses

Micro-focused synchrotron based X-ray fluorescence (µ-SXRF) and micro-focused XANES (µ-XANES) spectroscopic analyses were used to generate elemental distribution maps and to determine the direct solid-phase As species of two mine tailings (Undisturbed and Pond tailings) and three windblown dust (Alto da Colina, União and Barragem) samples (Figures 3 and 5). Linear-combination fitting (LCF) was performed to identify and estimate the proportion of each As species in the samples. Micro-X-ray diffraction (µ-XRD) analyses were used to confirm some As mineral species (Figure 4).

Micro-SXRF images taken from powder-on-tape mine tailings samples showed evident association of As and Fe (Figure 3). Usually, Fe is the element that best associates with As in soil/sediment/tailing samples, which occurs due to its high concentrations and the strong binding of As with Fe-oxides.[43]

Mine tailings

The LCF results from µ-XANES spectra of mine tailings showed that As was also present as arsenopyrite and its transformation products, but mostly it was in the form of As(V) as poorly crystalline ferric arsenate (Figure 3). Out of 13 selected spots where µ-XANES spectra were collected, 3 (23%) were associated with arsenopyrite and 10 (77%) were associated with poorly crystalline ferric arsenate. These results were confirmed by µ-XRD analyses (Figure 4). Our results also indicated that As(III) was also found with As(V) in the same spots (e.g. spot 3, Figure 3). Nevertheless, it was not clear what mineral phase could be present, which could be attributed to its very low abundance in the sample and the few reference compounds of As(III) used in the study.

We also found that arsenopyrite was preserved under gold extraction conditions. This was due to the presence of arsenopyrite in both the Undisturbed (exposed tailings) and the Pond tailings (water-saturated tailings) samples, which are samples obtained before the gold extraction (raw ore) and after the gold extraction (waste of processed ore), respectively.

Our results did not indicate the presence of scorodite – which is the most common arsenate mineral found in the weathering environment of As-bearing sulphide deposits[44] – or the sulphide mineral realgar (As_4S_4) in the samples. Murciego et al.[16] identified scorodite, pharmacosiderite and amorphous ferric arsenates as arsenopyrite weathering products in mine wastes. Filippi et al.[6], in a study on As speciation in soils above a gold deposit, identified as products of arsenopyrite and/or pyrite oxidation: scorodite, Fe(III) oxyhydroxides, K(-Ba) pharmacosiderite, arseniosiderite, and jarosite.

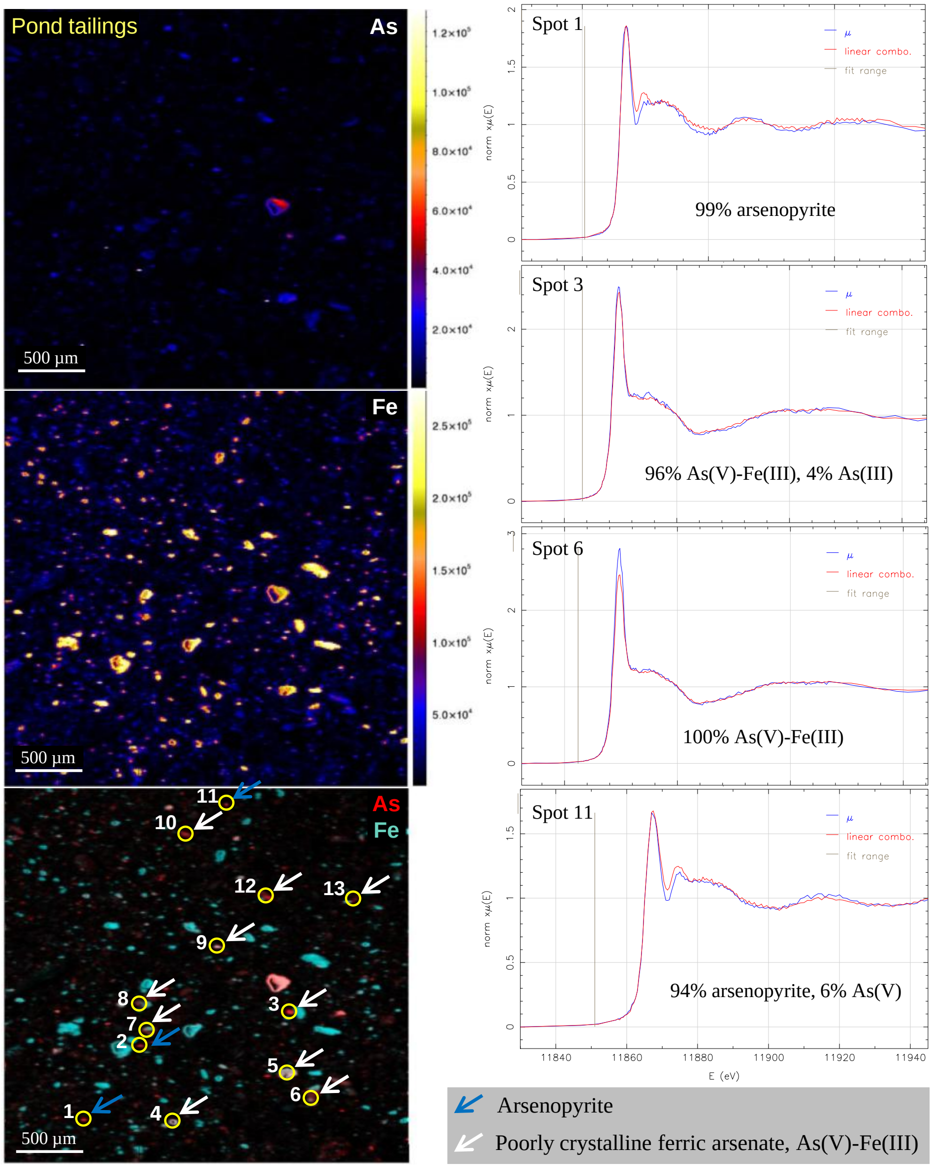

Figure 3. Micro-SXRF maps (left) using an AsFe filter and µ-XANES analyses (right) for the Pond tailings sample. The numbers (1-13) indicate the spots where µ-XANES spectra were collected. The red line is the linear-combination best fit for results shown and the blue line is a XANES scan. The blue arrow is indicative of arsenopyrite and the white arrow of poorly crystalline ferric arsenate.

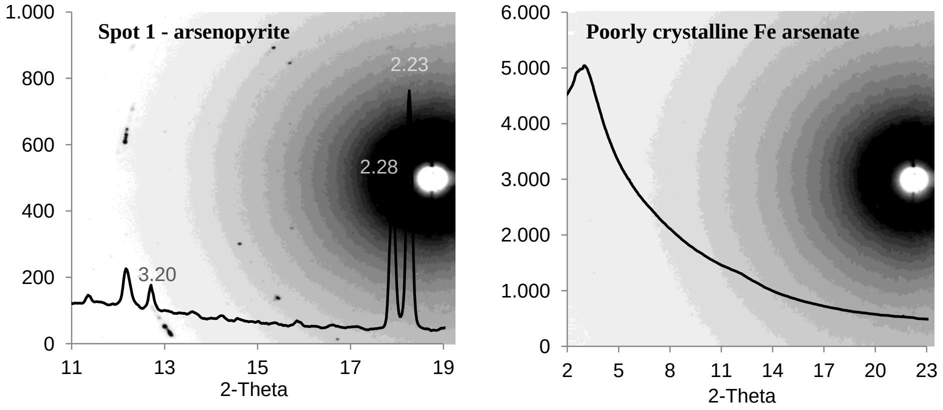

Figure 4. Micro-XRD patterns for two analyzed spots. One XRD pattern shows the presence of arsenopyrite and the other shows the low crystallinity of the iron arsenate.

Based on the solid-phase As species and the proportions found in the present study, we can infer that the As fractions present in these tailings were not readily available and therefore are not considered a great source of As release to the environment, as long as no physicochemical changes occur (e.g. pH, redox potential). This study highlights the importance of Fe oxides in controlling the mobility and availability of As in tailings following dissolution of the sulphide minerals of As. Meunier et al.[17] investigated As in tailings and mining-impacted soils and found that As was present in minerals such as arsenopyrite, scorodite, realgar, and kankite. The authors measured bioaccessible As and reported that it represented <1% in samples containing more arsenopyrite and scorodite, and ranged from 2 to 10% in samples with a greater proportion of As-bearing amorphous Fe arsenate and Fe oxyhydroxides minerals.

According to Wang et al.[37], despite the low mobility presented by As associated with Fe oxides in non-acidic oxidizing environments, changes in the redox potential or pH can cause As release. The poorly crystalline ferric arsenate can release As due to its low stability with increasing pH values.[45] Thus, it is important to point out the relevance of studies of long-term stability of As in these mine tailings taking into account the physicochemical changes, in order to better predict the behavior of As.

It should be mentioned, however, that despite the high levels of As and its species in the mine tailings, the actual risk of exposure is rather low, since the population does not have free access to this area.

Windblown dust

Air particulate samples from the Alto da Colina, União and Barragem sites were selected for μ-SXRF and μ-XANES analyses. For this selection of samples, we considered the total As levels (high, intermediate, and low) in the air particulates and the distance between the sampling site and the mine area (Alto da Colina: highest As content – at the borders between the urban area and the mine; União: intermediate As – urban area; Barragem: low As – distant from mine area and very near the tailings pond). Micro-SXRF maps from powder-on-tape windblown dust samples showed an association of As with Fe (data not shown), similarly to the mine tailings (Figure 3).

The LCF results from μ-XANES spectra indicated in all three samples the existence of a minor amount of arsenopyrite and a greater abundance of poorly crystalline ferric arsenate (Figure 5). Thus, this analysis showed that the speciation of As in the windblown dust was very similar to that in the mine tailings.

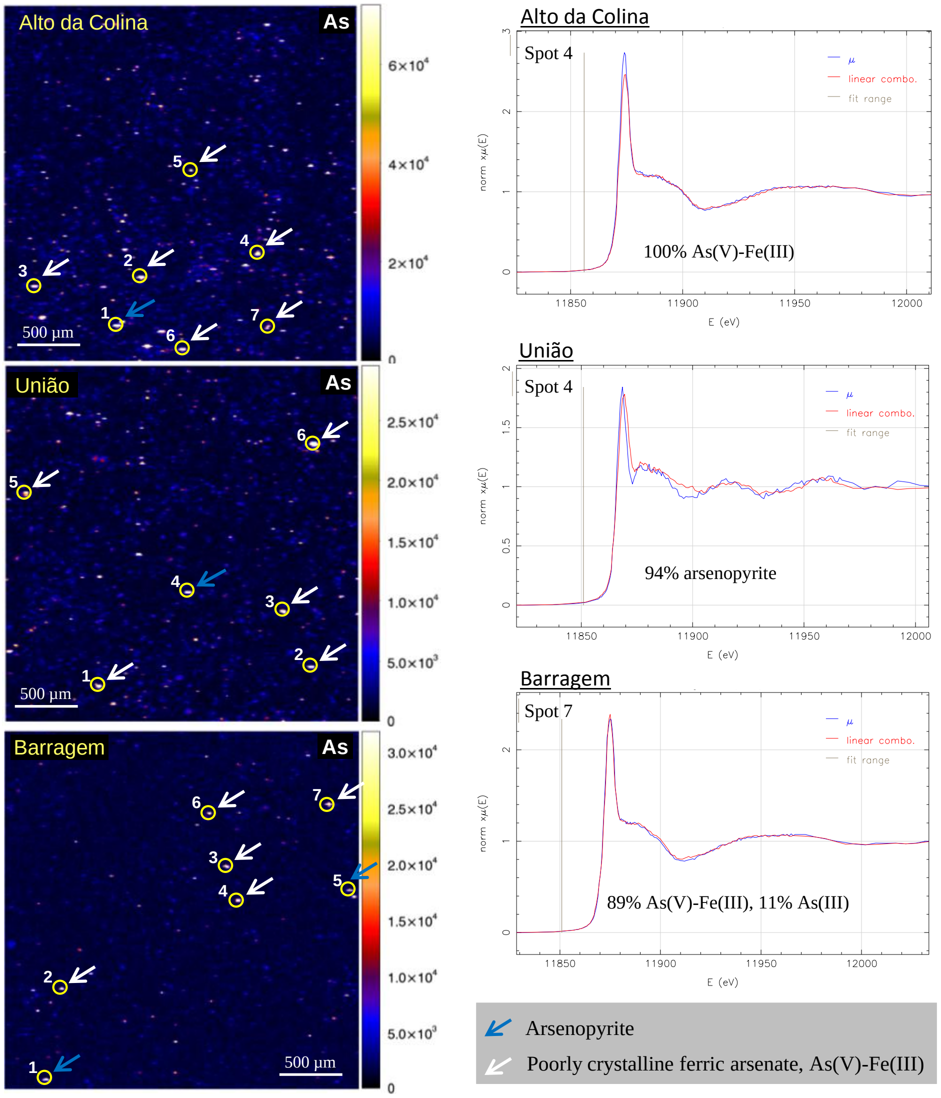

Figure 5. Micro-SXRF maps (left) and µ-XANES analyses (right) for the windblown dust samples. The numbers indicate the spots where µ-XANES spectra were collected. The red line is linear-combination best fit results shown and the blue line is a XANES scan. The blue arrow is indicative of arsenopyrite and the white arrow of poorly crystalline ferric arsenate.

Based on the speciation of As and its proportions found, we can infer that As occurs in less labile forms, resulting, in these conditions, in low mobility and availability. Therefore, these results confirmed the low As availability found in the samples via a bioaccessibility test and selective chemical extractions (Table 2).

Acknowledgments

We gratefully acknowledge funding received from the CNPq, CAPES and FAPEMIG - Brazil. We acknowledge the Brazilian Synchrotron Light Laboratory-LNLS technical, scientific, and administrative staff for assisting with the bulk-XAS analysis (project 11781, supported by LNLS/ABTLuS/MCT). Use of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Beamline X27A at NSLS is supported in part by the U.S. Department of Energy – Geosciences (DE-FG02-92ER14244 to The University of Chicago - CARS). We would like to thank the Delaware Environmental Institute (DENIN) and Environmental Soil Chemistry research group of the University of Delaware, especially Cecily Moyer and Matt Siebecker for their assistance during the experimental analyses. Fábio Ono appreciates the Sandwich Doctorate fellowship for this work funded by Capes, and also the support of the University of Delaware.

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