BRUNA WURR RODAK

EXPLORING A NOVEL NICKEL SOURCE FOR TROPICAL AGROECOSYSTEMS

LAVRAS - MG
2018

BRUNA WURR RODAK

EXPLORING A NOVEL NICKEL SOURCE FOR TROPICAL AGROECOSYSTEMS

> Tese apresentada a Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Fertilidade do Solo e Nutrição de Plantas, para obtenção do título de Doutor.

Orientador
Dr. Luiz Roberto Guimarães Guilherme

Coorientador
Dr. André Rodrigues dos Reis

LAVRAS – MG
2018

BRUNA WURR RODAK

EXPLORING A NOVEL NICKEL SOURCE FOR TROPICAL AGROECOSYSTEMS

EXPLORANDO UMA NOVA FONTE DE NÍQUEL PARA AGROECOSSISTEMAS TROPICAIS

> Tese apresentada a Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Fertilidade do Solo e Nutrição de Plantas, para obtenção do título de Doutor.

APROVADA em 10 de agosto de 2018.

Dr. Luiz Roberto Guimarães Guilherme	UFLA
Dr. Guilherme Lopes	UFLA
Dr. Adônis Moreira	EMBRAPA SOJA
Dr.ª Larissa Alexandra Cardoso Moraes	EMBRAPA SOJA
Dr. José Lavres Junior	CENA/USP

Dr. Luiz Roberto Guimarães Guilherme
Orientador

Dr. André Rodrigues dos Reis
Coorientador

LAVRAS – MG
2018

Para minha mãe Jacinta Wurr, como sempre.

DEDICO

AGRADECIMENTOS

"Todo caminho da gente é resvaloso. Mas também, cair não prejudica demais –
a gente levanta, a gente sobe, a gente volta!...
O correr da vida embrulha tudo, a vida é assim: esquenta e esfria, aperta e daí
afrouxa, sossega e depois desinquieta. O que ela quer da gente é coragem. O
que Deus quer é ver a gente aprendendo a ser capaz de ficar alegre a mais, no
meio da alegria, e inda mais alegre ainda no meio da tristeza! Só assim de
repente, na horinha em que se quer, de propósito – por coragem. Será? Era o
que eu às vezes achava. Ao clarear do dia."

João Guimarães Rosa em "Grande Sertão: Veredas"

RESUMO

O manejo de solos ácidos com subprodutos promove a reutilização desses materiais e pode combinar práticas agrícolas (e.g., calagem e fertilização), tornando a cadeia produtiva mais sustentável. Subprodutos da mineração, como cinzas da queima de coque de petróleo, podem ser eficientes corretivos de acidez do solo e fornecer o micronutriente Ni às plantas. Emergente na agricultura, o Ni é constituinte da urease e hidrogenase, enzimas chave no metabolismo do N. A fertilização de plantas com esse micronutriente, embora promissora, ainda precisa ser melhor compreendida. Esse estudo investigou o uso benéfico de cinzas de coque de petróleo na agricultura como um produto rico em Ni e corretivo de acidez do solo, bem como os efeitos da fertilização do Ni no sistema solo-planta. Na primeira parte do estudo, as propriedades físicas, químicas e mineralógicas das cinzas foram caracterizadas, com posterior criação de um produto – *Blended limestone* (BL). Sua viabilidade agronômica e ambiental foi testada em condições de casa de vegetação, com diferentes solos e plantas cultivadas. O BL corrigiu a acidez do solo e forneceu nutrientes às plantas, funcionando também como um fertilizante portador de Ni. Dessa forma, esse produto é uma tecnologia viável e sustentável para o uso de subprodutos derivados do coque de petróleo na agricultura. Na segunda parte do estudo, foram investigados os efeitos residuais, a curto prazo, da aplicação de Ni no sistema solo-planta, bem como sua segurança ambiental e alimentar. Para tal, uma aplicação única de corretivos de acidez do solo enriquecidos com Ni (um contendo um subproduto rico em Ni – BL – e outro com adição de um sal de Ni) foi avaliada em condições de cultivo a campo, conduzindo duas safras agrícolas. As fontes enriquecidas forneceram Ni às plantas e neutralizaram a acidez do solo. No primeiro ano-safra, o Ni alcançou níveis ótimos no solo e na planta, promovendo ganhos produtivos e fisiológicos nas plantas. Pequeno efeito residual dos teores de Ni foram constatados no segundo ano e ganhos produtivos não mais foram observados. Nenhum impacto negativo da aplicação de Ni ao ambiente e à segurança alimentar foi verificado. Nossos dados sugerem que a fertilização com esse micronutriente pode exigir ajustes ano a ano via fertilizantes, devendo ser monitorada. Aliando os resultados de ambas as partes do nosso estudo, conclui-se que além de gerarmos novos conhecimentos sobre a fertilização de Ni na agricultura, também desenvolvemos uma tecnologia viável e sustentável de reutilização de subprodutos da indústria de mineração no sistema agrícola, possibilitando aliar práticas de manejo do solo que contribuem para maior eficiência do sistema de cultivo. A melhor gestão e o uso eficiente de recursos com a integração das cadeias produtivas da mineração e agrícola estão em concordância com objetivo 12 Consumo e Produção Responsáveis da ONU.

Palavras-chave: Subproduto. Corretivo de acidez do solo. Fertilização com Ni. Efeito residual no sistema solo-planta.

ABSTRACT

The management of acidic soils with by-products promotes the reuse of these materials allowing combined agricultural practices (e.g., liming and fertilization), which increases the sustainability of food production chains. Mining by-products, such as petroleum coke ashes, can be efficient soil acidity amendments while providing Ni – an important micronutrient – to plants. Emergent in agriculture, Ni is a constituent of urease and hydrogenase, two key enzymes in N metabolism. Crop fertilization with this micronutrient, although promising, still needs to be better understood. This study investigated the beneficial use of petroleum coke ashes in agriculture as a Ni-rich soil acidity amendment, as well as the effects of Ni fertilization on the soil-plant system. In the first part of the study, the physical, chemical, and mineralogical properties of the ashes were assessed to create a product called blended limestone (BL). Its agronomic and environmental feasibility was tested under greenhouse conditions, with different soils and cultivated plants. The BL corrected soil acidity and provided nutrients to the plants, also functioning as a Ni fertilizer. In this way, this product is a viable and sustainable technology for promoting the beneficial use of byproducts of petroleum coke in agriculture. In the second part of the study, we investigated short-term residual effects of Ni application on the soil-plant system, as well as environmental and food safety aspects of such application. For this purpose, a single application of Ni-rich soil amendments (one containing a Ni-rich by-product – BL – and one containing a Ni salt) was evaluated under field conditions, after two cropping seasons. The enriched sources provided Ni to the plants and neutralized soil acidity. In the first cropping season, Ni reached optimal levels in soils and plants, promoting yield and physiological gains in plants. Small residual effects of Ni levels were observed in the second year, yet yield gains were no longer observed. No negative impacts to the environment and to food safety were verified following the application of Ni. Our data suggest that fertilization with this micronutrient may require year-to-year adjustments via Ni-fertilizers and should be monitored. The combined results of both parts of our study allow us to conclude that in addition to generating new knowledge concerning Ni fertilization in agriculture, we have also developed a viable and sustainable technology for reusing by-products from the mining industry in agroecosystems, making it possible the combination of soil management practices that contribute to greater efficiency of the cropping system. A better management and an efficient use of resources through integration of productive chains in the mining industry and in agriculture are actions in line with goal 12 – Ensure sustainable consumption and production patterns – of the 2030 Agenda for Sustainable Development.

Keywords: By-product. Soil acidity amendments. Ni-fertilization. Residual effect on soil-plant system.

SUMÁRIO

PRIMEIRA PARTE

1 INTRODUÇÃO

Em 25 de setembro de 2015, os 193 países membros da Organização das Nações Unidas assinaram um plano global composto por 17 objetivos e 169 metas para o desenvolvimento sustentável em todos os âmbitos até 2030. Cada objetivo e suas respectivas metas abordam aspectos diferentes que convergem para a viabilidade de uma sociedade sustentável, entre eles, o objetivo 12 "Consumo e Produção Responsáveis" visa "fazer mais e melhor com menos", aumentando os ganhos líquidos das atividades econômicas, reduzindo o uso de recursos, degradação e poluição ao longo de todo o ciclo de produção, sobretudo na agricultura, uma vez que impactos substanciais ocorrem na fase de produção de alimentos (ORGANIZAÇÃO DAS NAÇÕES UNIDAS – ONU, 2018).

Integrar as cadeias produtivas da indústria de mineração e agrícola pode ser uma alternativa para a gestão sustentável e o uso eficiente dos recursos naturais. Nesse cenário, a utilização de subprodutos da mineração na agricultura, além de possibilitar o reuso desses produtos, que geralmente são armazenados inadequadamente sem nenhuma finalidade causando impacto negativo ao ambiente, também pode combinar práticas de manejo do solo promovendo maior eficiência do sistema produtivo agrícola. O uso benéfico, na agricultura, de cinzas da queima de coque de petróleo – subproduto da produção de energia em indústrias de mineração (CHEN; LU, 2007), devido a suas características alcalinas e composição química, pode ser uma alternativa para aliar práticas de manejo do solo (CHEN; DICK; KOST, 2006; CHEN; DICK; NELSON, 2001; CHEN; KOST; DICK, 2008, 2010), como calagem, gessagem e fertilização, as quais são amplamente adotadas para superar limitações produtivas em solos ácidos (FAGERIA; NASCENTE, 2014). Contudo, essas cinzas apresentam alto conteúdo

de elementos-traço, como o Ni, o que pode representar uma restrição para seu uso agrícola (GONZÁLEZ; NAVIA; MORENO, 2009). Por essa razão, faz-se necessário aprofundar os estudos sobre a carga de elementos-traço nesses subprodutos para viabilizar seu uso benéfico na agricultura.

O estudo do elemento Ni vem recebendo uma nova abordagem científica nas últimas décadas, com pesquisas focando na sua toxicidade às plantas dando lugar àquelas ligadas à sua essencialidade (SEREGIN; KOZHEVNIKOVA, 2006; YUSUF et al., 2011). O Ni é considerado micronutriente de plantas (BROWN; WELCH; CARY, 1987; ESKEW; WELCH; CARY, 1983) por ser constituinte estrutural das metaloenzimas urease (DIXON et al., 1975) e hidrogenase (KLUCAS et al., 1983), as quais desempenham importante papel no metabolismo de N (POLACCO; MAZZAFERA; TEZOTTO, 2013; RUIZ-ARGÜESO; PALACIOS; IMPERIAL, 2001). Os benefícios do suprimento de Ni em plantas é demonstrado em uma ampla gama de processos fisiológicos, desde a germinação das sementes até o crescimento vegetativo (GERENDAS; SATTELMACHER, 1997; KUTMAN; KUTMAN; CAKMAK, 2014; NYCZEPIR; WOOD, 2012; SENGAR et al., 2008; URUÇ PARLAK, 2016). Na segunda metade dos anos 2000, esse micronutriente foi inserido na legislação agrícola de muitos países (BRASIL, 2018; NYCZEPIR; WOOD, 2012; WOOD; REILLY, 2007), permitindo a comercialização de fertilizantes contendo Ni na sua composição. Contudo, a recomendação da fertilização com Ni em espécies anuais cultivadas ainda é pouco compreendida necessitando de mais estudos.

Nesse cenário, a aplicação de Ni na agricultura está condicionada ao desenvolvimento de fertilizantes eficientes no fornecimento adequado desse micronutriente às plantas. Concomitantemente, faz-se necessário aprofundar os estudos acerca níveis críticos nos solos e nas plantas, bem como no efeito residual de Ni, para adequação da dose, forma e frequência de aplicação dessas fontes de Ni na agricultura.

Dessa forma, o objetivo desse estudo foi investigar se o uso das cinzas da queima de coque de petróleo na agricultura pode funcionar como um produto rico em Ni e corretivo de acidez do solo. Para tal, foram caracterizadas as propriedades físicas, químicas e mineralógicas das cinzas, com posterior avaliação da sua viabilidade agrícola e ambiental de acordo com as diretrizes da legislação brasileira pertinente ao assunto. Adicionalmente, esse estudo explorou importantes aspectos da fertilização com Ni na agricultura, avaliando os efeitos da fertilização com esse micronutriente no *status* nutricional, fisiologia, crescimento e produtividade das plantas – soja e milho, bem como o efeito residual do Ni em curto prazo no sistema solo-planta.

2 REFERENCIAL TEÓRICO

2.1 Objetivos do desenvolvimento sustentável

As informações sobre o desenvolvimento sustentável abordadas nessa sessão podem ser acessadas na plataforma do desenvolvimento sustentável da Organização das Nações Unidas (ONU) (ONU, 2018).

O tema desenvolvimento sustentável ganhou destaque na Conferência das Nações Unidas sobre o Meio Ambiente e Desenvolvimento, realizada no Rio Janeiro, em 1992. Conhecida como Rio-92 ou Eco-92, a Conferência discutiu o desenvolvimento e a proteção do meio ambiente, tendo como ênfase a busca do desenvolvimento sustentável. Durante a Rio-92, a Agenda 21 Global foi assinada por 179 países para promover o desenvolvimento sustentável. Nos anos 2000, 191 nações renovaram seu compromisso com o desenvolvimento sustentável na Declaração do Milênio, que estabelecia 8 Objetivos de Desenvolvimento do Milênio (ODM) a serem obtidos até 2015. Apesar de terem sido alcançadas concretizações importantes a muitas das metas dos ODM a nível mundial – as quais podem ser acessadas no "Relatório Sobre os Objetivos de Desenvolvimento do Milénio 2015" (ONU, 2015) –, os progressos foram irregulares entre as regiões e países, deixando lacunas significativas para obter um mundo mais próspero, sustentável e igualitário. Nesse contexto, em 2012, foi realizada a Rio+20, Conferência das Nações Unidas sobre o Desenvolvimento Sustentável, que serviu para a definição da Agenda pós-2015, a qual propôs ações e esforços mundiais de desenvolvimento até 2030. Nessa Conferência, foi criado o Grupo de Trabalho Aberto que, após mais de um ano de deliberações, propôs os 17 Objetivos de Desenvolvimento Sustentável (ODS) – ou, em inglês, *Sustainable Development Goals* (SDG).

Em setembro de 2015, na sede da Organização das Nações Unidas em Nova Iorque, 193 nações aprovaram o documento intitulado "Transformando nosso mundo: A agenda 2030 para o desenvolvimento sustentável", que oficializou o conjunto de 17 objetivos e 169 metas a serem alcançadas pelas nações até 2030, de modo a promover o desenvolvimento sustentável e a erradicação da pobreza. Os 17 ODS foram idealizados visando estimular ações em cinco áreas prioritárias: pessoas, planeta, prosperidade, paz e parceria.

Dentre os ODS da área "planeta", o de número 12 "Consumo e Produção Responsáveis" visa alcançar a gestão sustentável e o uso eficiente dos recursos naturais. Resumidamente suas metas relacionadas ao sistema de produção agrícola são: 1) Reduzir o desperdício de alimentos ao longo das cadeias de produção e abastecimento; 2) Alcançar a gestão ambientalmente adequada dos produtos químicos e resíduos; 3) Reduzir substancialmente a geração de resíduos por meio da prevenção, redução, reciclagem e reutilização; e 4) Incentivar empresas a adotar práticas e integrar informação sobre sustentabilidade.

Nesse cenário, a otimização do manejo de solos ácidos em países em desenvolvimento, seja pelo emprego de insumos alternativos ou empregando novas tecnologias, pode tornar o sistema agrícola mais eficiente e produtivo, i.e., mais sustentável (KUYLENSTIERNA et al., 2001; LAL, 2000), o que está em concordância com o ODS 12.

2.2 Manejo de solos ácidos

A acidez superficial e subsuperficial (pH < 5,5) afeta aproximadamente 30% e 75% da crosta terrestre, respectivamente, sendo uma das principais limitações na produção agrícola (SUMNER; NOBLE, 2003). O Brasil é um dos principais produtores agrícolas mundiais, notadamente na região do Cerrado, uma área de expansão agrícola do país que apresenta em torno de 205 milhões de

hectares de solos ácidos, correspondendo a 23% do território nacional. As principais ordens de solos dessa região são Latossolos (46%) e Argissolos (15%), os quais apresentam baixa fertilidade natural (FAGERIA; NASCENTE, 2014).

Esses solos são altamente intemperizadas e apresentam alta concentração de H^+, causando a lixiviação de nutrientes catiônicos, como Ca^{2+}, Mg^{2+} e K^+; consequentemente, saturação por Al^{3+} desses solos é elevada, enquanto sua saturação por bases (V%) é baixa, o que afeta negativamente a produção das culturas agrícolas (LOPES; GUILHERME, 2016). Estratégias para o manejo de solos ácidos vêm sendo adotadas para viabilizar seu uso agrícola. A calagem é uma dessas estratégias, visto que a aplicação de calcário ($CaMg[CO_3]_2$) eleva o pH do solo, a V% e a disponibilidade de Ca^{2+} e Mg^{2+} às plantas, além de reduzir a concentração de Al^{3+} disponível (FAGERIA; BALIGAR, 2008; FAGERIA; NASCENTE, 2014; GOULDING, 2016). O gesso agrícola ($CaSO_4 . 2H_2O$), devido à sua maior mobilidade no perfil do solo, é usado principalmente para o manejo da subsuperfície dos solos ácidos. A dissociação do gesso no solo, além de aumentar a disponibilidade de Ca e S às plantas, reduz a toxicidade do Al^{3+} devido à formação do par iônico $AlSO_4^+$ (SHAINBERG et al., 1989).

Além das práticas de calagem e gessagem, a fertilização mineral também é realizada para construção da fertilidade dos solos ácidos. Ênfase deve ser dada à fertilização com micronutrientes, como por exemplo o Ni, uma vez que a aplicação de calcário altera o pH do solo, o que influencia a solubilidade, concentração, forma iônica e mobilidade desse micronutriente no solo e, consequentemente, sua absorção pelas plantas (WESTFALL et al., 2005). A disponibilidade de Ni reduz com aumento do pH do solo (MA et al., 2013; MELLIS; CRUZ; CASAGRANDE, 2004). Associado com os baixos teores disponíveis naturais desse micronutriente nos solos (RODAK et al., 2015; UREN, 1992), seu fornecimento via adubação se faz necessário para evitar sintomas de deficiência das plantas.

Nesse cenário, desenvolver tecnologias integradas para o manejo dos solos ácidos, associando práticas como a calagem, para corrigir a acidez de superfície do solo, a gessagem, para minimizar a acidez potencial em subsuperfície, e a fertilização mineral, fornecendo nutrientes às plantas, possibilitaria maior sustentabilidade aos sistemas de produção agrícola. O uso benéfico de subprodutos da indústria de mineração, devido a suas características alcalinas e composição química, pode ser uma alternativa regional para aplicação combinada dessas práticas agrícolas.

2.3 Uso de cinzas da queima de coque de petróleo na agricultura

Subprodutos derivados da indústria de mineração usualmente são armazenados em aterros a céu aberto, tornando-se problemas ambientais devido à possibilidade de lixiviação de metais traço para o lençol freático (ETTLER et al., 2016). Por essa razão, faz-se necessário desenvolver tecnologias inovadoras e sustentáveis para o reaproveitamento desses subprodutos. Um caso bem sucedido é a utilização agrícola de cinzas de carvão, que reduz os efeitos prejudiciais de metais potencialmente tóxicos para o ecossistema, além de ser eficiente na correção da acidez do solo e no fornecimento de macro e micronutrientes às plantas, possibilitando ganhos produtivos em muitas culturas agrícolas (BASU et al., 2009; SINGH et al., 2010; SKOUSEN et al., 2013).

As cinzas de carvão são subprodutos oriundos da produção de energia a partir da queima de carvão mineral em caldeira de leito fluidizado (SILVA et al., 2014) (Figura 1). Nas últimas décadas, o carvão mineral vem sendo substituído pelo coque de petróleo (CHEN; LU, 2007), um produto terminal do processo de refinamento de petróleo (MURTHY et al., 2014), que apresenta alta disponibilidade e baixo preço, tornando-se atrativo para a geração de energia (HILL; KARIMI; MALEKSHAHIAN, 2014; WANG; ANTHONY;

ABANADES, 2004). Contudo, o uso exclusivo de coque pode aumentar a emissão de gases poluentes ao ambiente, e por isso, sua queima vem sendo realizada juntamente com calcário nas caldeiras fluidizadas (LI et al., 2006). A adoção desse processo resulta em considerável mudança da composição das cinzas e, consequentemente, da sua utilidade.
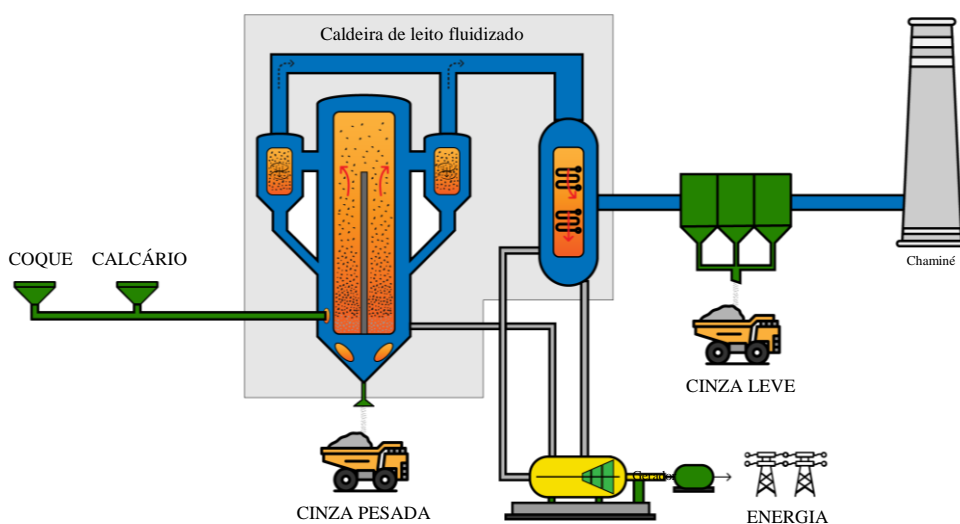
Figura 1 Esquema simplificado do processo de geração de energia da indústria de mineração a partir da queima de coque de petróleo e calcário em caldeira de leito fluidizado, resultando na formação das cinzas leve e pesada. Essas cinzas são subprodutos obtidos em fases distintas desse processo e separadas em função da sua densidade. A cinza leve, por apresentar menor densidade, é arrastada e resfriada por uma corrente de ar juntamente com gases residuais oriundos da queima, enquanto a cinza pesada é separada por sedimentação e depositada no leito da caldeira.
Fonte: adaptado de Mount Carmel Cogen (2018).

Atualmente, as cinzas derivadas de coque de petróleo vêm sendo destinadas principalmente para a indústria de cimento (OLMEDA et al., 2013), porém, apresentam grande potencial para uso benéfico na agricultura como corretivo de acidez do solo, devido a suas características alcalinas (ANTHONY

et al., 2006; ANTHONY; JIA; BURWELL, 2003). As cinzas também são ricas em Ca, S e metais-traço, como V e Ni (HOWER et al., 2005; IZQUIERDO et al., 2007), e o alto conteúdo desses metais pode ser uma restrição à sua utilização agrícola (GONZÁLEZ, NAVIA, MORENO, 2009).

Estudos pioneiros apresentam perspectivas promissoras do uso de subprodutos derivados do coque de petróleo na agricultura (CHEN; DICK; KOST, 2006; CHEN; DICK; NELSON, 2001; CHEN; KOST; DICK, 2008, 2010). Avaliando a aplicação das cinzas em um solo ácido da região de Ohio, Estados Unidos, cultivado com alfafa (*Medicago sativa* L.), esses estudos previamente citados verificaram melhor desenvolvimento das plantas e nenhuma contaminação por metais traço no solo e no lençol freático foi constatada, indicando que a aplicação das cinzas em solos agrícolas é segura. Contudo, esses trabalhos, embora relevantes, são restritos devido ao pequeno número de espécies vegetais testadas – alfafa, assim como pelas condições experimentais utilizadas – apenas um solo. Dessa forma, faz-se necessário aprofundar a compreensão do uso benéfico das cinzas da queima de coque na agricultura, principalmente em agroecossistemas tropicais, bem como do seu potencial uso como fertilizante provedor de Ni.

2.4 Essencialidade e toxidez do Ni em plantas

Mais de 40 anos antes de Martini (1930) considerar o Ni como um constituinte comum dos tecidos vegetais devido à sua ampla distribuição terrestre, pouca ou nenhuma informação sobre o papel do Ni na nutrição de plantas havia sido descoberta (MISHRA; KAR, 1974). No final da década de 1940, foi relatado que plantas de *Alyssum bertolonii,* crescidas na região da Toscana na Itália, apresentavam uma concentração extraordinariamente alta (10.000 mg kg^{-1}) de Ni na parte aérea (MINGUZZI; VERGNANO, 1948). Estava descoberta a primeira

planta hiperacumuladora de Ni, cerca de 30 anos antes da terminologia "hiperacumuladora" ser usada para descrever plantas que acumulam > 1.000 mg de Ni kg^{-1} na massa seca da parte aérea (BROOKS et al., 1977) e, também se iniciavam os estudos que culminariam no potencial uso dessas hiperacumuladoras como fitorremediadoras. A partir de então, mais de 318 táxons de hiperacumuladoras de Ni foram descobertos, principalmente, em solos ultramáficos ricos em Ni (serpentina), com destaque para os gêneros botânicos *Alyssum*, *Thlaspi* e *Sebertiu* (JAFFRÉ et al., 2018; KÜPPER et al., 2001). Concomitantemente, a maior parte da literatura gerada nesse período estudava também a toxicidade do Ni para as plantas sensíveis e moderadamente tolerantes, com aplicação de doses excessivamente elevadas desse metal, e os estudos da sua essencialidade foram deixados de lado até o início da década de 1980 (SEREGIN; KOZHEVNIKOVA, 2006; YUSUF et al., 2011).

O Ni foi o último elemento a ser inserido na lista de essenciais às plantas. A primeira evidência de sua essencialidade foi em plantas de soja (*Glycine max* [L.] Merrill) em 1983, quando em condições controladas sob depleção de Ni, essas plantas apresentaram acúmulo tóxico de ureia na ponta dos folíolos (ESKEW; WELCH; CARY, 1983). Contudo, foi apenas quatro anos mais tarde que o Ni foi considerado um micronutriente às plantas, quando, sob privação de Ni, plantas de cevada (*Hordeum vulgare* L.), após três gerações sucessivas de cultivo, não mais produziram grãos viáveis (BROWN; WELCH; CARY, 1987).

Em plantas, o Ni compõe o sítio ativo da metaloenzima urease (DIXON et al., 1975), que é responsável pela hidrólise da ureia em duas moléculas de amônia e gás carbônico, desempenhando função direta no metabolismo de N (POLACCO; MAZZAFERA; TEZOTTO, 2013).

Além da urease, o Ni é um cofator catalítico essencial em pelo menos mais oito enzimas em eubactérias, arqueobactérias e fungos, incluindo metil coenzima M redutase, superóxido dismutase, glioxilase Ni-dependente,

acireductona dioxigenase, NiFe-hidrogenase, monóxido de carbono desidrogenase, acetil-CoA descarboxilase sintase e metilenourease (LI; ZAMBLE, 2009). Dessas, merece destaque a NiFe-hidrogenase, que catalisa a oxidação do H_2 em prótons e elétrons (BAGYINKA, 2014). Essa reação é de grande importância em plantas leguminosas que realizam a fixação biológica de N_2 (FBN). Durante o processo de fixação, a nitrogenase catalisa a produção de amônia a partir do N_2 atmosférico e também produz H_2 (REES et al., 2005). Nessa etapa da FBN é que a NiFe-hidrogenase atua, reoxidando o H_2 e gerando energia adicional para a nitrogenase e, dessa forma, potencializando a fixação de N_2 (RUIZ-ARGÜESO; PALACIOS; IMPERIAL, 2001).

Recentes estudos acerca da deficiência de Ni na ruptura do metabolismo de ureideos, aminoácidos e ácidos orgânicos em plantas de pecã (*Carya illinoinensis* [Wangenh.] K. Koch) sugerem que esse micronutriente possa exercer papeis adicionais na nutrição das plantas que ainda não foram descobertos (BAI; REILLY; WOOD, 2006, 2007).

2.5 Uso do micronutriente Ni na agricultura

O reconhecimento do Ni como um micronutriente para as espécies cultivadas, juntamente com inúmeros resultados de pesquisas comprovando seu efeito benéfico no crescimento das plantas (GERENDAS; SATTELMACHER, 1997; KUTMAN; KUTMAN; CAKMAK, 2014; NYCZEPIR; WOOD, 2012; SENGAR et al., 2008; URUÇ PARLAK, 2016), promoveu uma rede crescente de estudos avaliando sua aplicação na agricultura. O fornecimento de Ni visa aumentar sua disponibilidade às plantas, uma vez que solos naturais e agrícolas usualmente apresentam baixos teores desse micronutriente, em torno de 0,1 a 1,0 mg kg^{-1} (RODAK et al., 2015; UREN, 1992), podendo causar sintomas de deficiência às plantas.

Até o presente momento, a deficiência de Ni a campo foi relatada em plantas de pecã e bétula (*Betula nigra* L.), espécies arbóreas cultivadas em solos arenosos com baixa disponibilidade de Ni no sudeste dos Estados Unidos (RUTER, 2005; WOOD; REILLY; NYCZEPIR, 2004a, 2004b, 2006). A sintomatologia de deficiência de Ni é conhecida popularmente como "orelha-de-rato" e caracteriza-se pelo arredondamento da ponta das folhas associado à clorose ou necrose devido ao acúmulo tóxico de ureia no tecido foliar, semelhantemente ao observado por Eskew, Welch e Cary (1983), quando evidenciaram a essencialidade do Ni em plantas de soja.

Estudo recente de Freitas et al. (2018) constatou haver deficiência oculta (latente) de Ni em uma ampla gama de genótipos de soja cultivados em solos tropicais a campo. Segundo esses autores, a deficiência de Ni não permite que o máximo potencial produtivo desses genótipos seja expresso. Essa questão já havia sido levantada por Wood (2013), que sugere que a deficiência de Ni em muitas espécies vegetais não apresenta sintomas visíveis. Esses resultados evidenciam a necessidade da fertilização com esse micronutriente no cultivo agrícola.

A maioria dos estudos sobre fertilização com Ni foram desenvolvidos em plantas de soja, pecã e bétula, sendo que, para as demais espécies cultivadas, a fertilização desse micronutriente ainda é pouco compreendida. Na soja, pesquisas com doses e formas de aplicação já se encontram adiantadas, embora ainda sem uma recomendação oficial (FREITAS et al., 2018; LAVRES; FRANCO; CÂMARA, 2016; MACEDO et al., 2016; RODAK et al., 2015). Atualmente, o Ni vem sendo aplicado com sucesso apenas nos pomares de pecã e bétula dos Estados Unidos, onde, usualmente, doses anuais de 10 a 100 mg L^{-1} são pulverizadas nas folhas, usando sais solúveis (LIU; SIMONNE; LI, 2011; NYCZEPIR; WOOD, 2012; OJEDA-BARRIOS et al., 2016; RUTER, 2005; WOOD; REILLY, 2007).

Nesse cenário, a aplicação de Ni na agricultura está condicionada ao desenvolvimento de fertilizantes eficientes no fornecimento desse micronutriente, ou seja, que apresentem granulometria (tamanho, forma e uniformidade de partículas) e composição (concentração e solubilidade) que favoreçam uma aplicação homogênea e absorção adequada pelas plantas. Concomitantemente, faz-se necessário aprofundar os estudos sobre níveis críticos desse micronutriente nos solos e nas plantas, bem como do seu efeito residual, para adequação da dose, forma e frequência de aplicação dessas fontes de Ni na agricultura.

2.6 Legislação brasileira sobre fertilizantes niquelados

As Instruções Normativas (IN) da legislação brasileira de insumos agrícolas que serão abordadas nessa sessão podem ser acessadas em Brasil (2018).

O Ministério da Agricultura, Pecuária e Abastecimento (MAPA), através da IN Nº 53, de 23/10/2013, estabelece oito categorias de insumos destinados a agricultura: 1) Fertilizante mineral, que pode ser enquadrado em cinco características adicionais – simples, simples em solução, simples em suspenção, complexo e misto; 2) Fertilizante orgânico, com quatro características adicionais – simples, composto, misto e organomineral; 3) Corretivo, com três características adicionais – de acidez, de alcalinidade e de sodicidade; 4) Condicionador de solo; 5) Inoculante; 6) Biofertilizante; 7) Remineralizador; e 8) Substrato para plantas.

Em 2007, o MAPA reconheceu o Ni como um micronutriente de plantas e o inseriu na legislação, sendo possível, a partir de então, que as diferentes categorias de insumos contenham Ni na sua composição e possam ser comercializadas como fonte desse micronutriente (IN Nº 05, de 23/02/2007). Atualmente, sete INs estabelecem as definições, exigências, especificações, garantias e análises laboratoriais para o Ni, sendo, a seguir, apresentados os principais aspectos para cada categoria de insumo.

A especificação para a categoria de fertilizantes minerais que contém Ni se encontra na IN Nº 46, de 22/11/2016. A garantia mínima exigida dos teores totais de Ni nesses produtos não pode ser inferior a 0,005% ou 0,05%, sendo esta diferença estabelecida de acordo com a característica adicional do fertilizante. Para fertilizantes minerais simples de Ni as especificações são mais restritivas, devendo cumprir garantia mínima específicas para os teores, forma, solubilidade e obtenção, como apresentado na Tabela 1. Ressalta-se que a determinação do teor total de Ni, independente da categoria de insumo, deve ser realizado conforme USEPA Método 3050-B (IN Nº 24, de 20/06/2007).

Tabela 1 Especificações dos fertilizantes minerais simples de Ni.

| Fertilizante | Garantia mínima | | Obtenção |
	Teor e forma	Solubilidade	
Carbonato de Ni ($NiCO_3$)	39% de Ni	Ni teor total	Reação do sulfato de Ni com carbonato de Na, posterior purificação
Fosfito de Ni	4% de Ni	Ni solúvel em água	Reação do ácido fosforoso com hidróxido ou carbonato de Ni
Quelato de Ni	2% de Ni	Nutrientes solúveis em água ligados a um quelante	Reação do sal inorgânico com um agente quelante
Sulfato de Ni ($NiSO_4.6H_2O$)	10% de S 19% de Ni	S e Ni teores solúveis em água	Reação de ácido sulfúrico com Ni metálico ou com carbonato de Ni

Para a categoria de remineralizadores, os teores mínimos de Ni podem ser declarados somente se forem iguais ou superiores a 0,005% do teor total (IN Nº 05, de 10/03/2016).

A IN Nº 25, de 23/07/2009, estabelece para a categoria de fertilizantes orgânicos de aplicação via solo, uma garantia mínima exigida dos teores totais de 0,005% de Ni e, para os produtos de aplicação via foliar, fertirrigação e hidroponia, teores solúveis em água de 0,005%. Ressalta-se que para essa categoria, independentemente das características adicionais, a IN Nº 27, de 05/06/2006, sobre carga de metais pesados tóxicos, estabelece limites para concentração máxima de Ni de 70 mg kg^{-1}.

Para as categorias de substrato de plantas (IN Nº 05, de 10/03/2016) e condicionadores de solo (IN Nº 35, de 04/07/2006) não existem especificações

para garantias mínimas de Ni, contudo o valor máximo admitido desse metal nesses produtos é de 175 mg kg^{-1} e de 70 mg kg^{-1}, respectivamente (IN Nº 27, de 05/06/2006).

Nenhuma exigência, seja de teores mínimos ou máximos admitidos, vigora para as categorias de inoculante (IN Nº 13, de 24/03/2011), biofertilizante (IN Nº 25, de 23/07/2009) e corretivo (IN Nº 35, de 04/07/2006).

Nesse cenário, um corretivo de acidez enriquecido e, ou, rico em Ni, devido ao fato de não haver especificações nesses produtos para esse micronutriente, deve apenas cumprir as especificações da IN Nº 35, de 04/06/2006. Segundo a IN Nº 35, corretivo de acidez é um produto que promove a correção da acidez do solo, além de fornecer Ca, Mg ou ambos, sendo constituído de partículas que deverão passar totalmente na peneira de 2 mm (10 mesh), no mínimo 70% na peneira de 0,84 mm (20 mesh) e 50% na de 0,3 mm (50 mesh). Quanto às propriedades químicas, o corretivo deve apresentar especificações mínimas de 38% de soma de óxidos (CaO + MgO), 67% de poder de neutralização (PN) e 45% de poder relativo de neutralização total (PRNT), além de não ultrapassar o limite máximo admitido de 20 mg kg^{-1} de Cd e 1.000 mg kg^{-1} de Pb (IN Nº 27, de 05/06/2006).

3 CONSIDERAÇÕES FINAIS

Nosso estudo promoveu o uso inovador e sustentável de um subproduto derivado de cinzas da queima de coque de petróleo na agricultura, com ênfase em solos ácidos. A adequação das cinzas como um produto rico em Ni e corretivo de acidez do solo, além de reduzir os efeitos prejudiciais do contaminante para o ecossistema devido ao seu armazenamento inadequado, possibilita aliar práticas de manejo do solo, como calagem, gessagem e fertilização, tornando o agroecossistema mais eficiente e produtivo. Também atende à demanda atual do mercado por fertilizantes a base do micronutriente Ni.

Concomitantemente, nosso estudo explorou a fertilização do micronutriente Ni na agricultura. Para tal, o efeito residual em curto prazo da sua aplicação a campo no cultivo de soja foi estudado, gerando também informações sobre dose, forma e frequência de aplicação do Ni a níveis seguros em solos agrícolas. Dessa forma, nossos resultados podem servir de base para adequação da recomendação agronômica de Ni em insumos e dos níveis críticos desse micronutriente no sistema solo-planta, principalmente no cenário agrícola brasileiro. Além disso, gerou informação incremental que possibilitou maior compreensão do papel do Ni na nutrição de plantas cultivadas.

Finalizando, é sabido que a integração das cadeias produtivas da indústria de mineração e agrícola, proporcionada pelo desenvolvimento de um novo insumo agrícola com a reutilização de subprodutos – produto rico em Ni e corretivo de acidez do solo –, possibilita uma melhor gestão e uso eficiente de recursos em ambas as cadeias produtivas. Nesse contexto, nosso estudo está em concordância com as metas da Agenda 2030 dos Objetivos do Desenvolvimento Sustentável da ONU, particularmente no tocante ao ODS12 – Consumo e Produção Responsáveis.

REFERÊNCIAS

ANTHONY, E. J. et al. Understanding the behavior of calcium compounds in petroleum coke fluidized bed combustion (FBC) ash. **Journal of Energy Resources Technology**, New York, v. 128, n. 4, p. 290–299, Dec. 2006.

ANTHONY, E. J.; JIA, L.; BURWELL, S. M. **Petroleum coke FBC ash: a detailed look at calcium in the ash.** New York. 2003. Disponível em: <http://proceedings.asmedigitalcollection.asme.org/proceeding.aspx?articleid=1 574547>. Acesso em: 24 jul. 2018.

BAGYINKA, C. How does the ([NiFe]) hydrogenase enzyme work? **International Journal of Hydrogen Energy**, New York, v. 39, n. 32, p. 18521–18532, Oct. 2014.

BAI, C. Nickel deficiency disrupts metabolism of ureides, amino acids, and organic acids of young pecan foliage. **Plant Physiology**, Rockville, v. 140, n. 2, p. 433–443, Jan. 2006.

BAI, C.; REILLY, C. C.; WOOD, B. W. Nickel deficiency affects nitrogenous forms and urease activity in spring xylem sap of pecan. **Journal of the American Society for Horticultural Science**, Washington, v. 132, n. 3, p. 302–309, May 2007.

BASU, M. et al. Potential fly-ash utilization in agriculture: a global review. **Progress in Natural Science,** Beijing, v. 19, n. 10, p. 1173-1186, Oct. 2009.

BRASIL. **Legislações.** Brasília, 2018. Disponível em: <http://www.agricultura.gov.br/assuntos/insumos-agropecuarios/insumos-ag ricolas/fertilizantes/legislacoes>. Acesso em: 24 jul. 2018.

BROOKS, R. et al. Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. **Journal of Geochemical Exploration,** Amsterdam, v. 7, n. 1977, p. 49-57, Jan. 1977.

BROWN, P. H.; WELCH, R. M.; CARY, E. E. Nickel: a micronutrient essential for higher plants. **Plant Physiology,** Rockville, v. 85, n. 3, p. 801-803, Nov. 1987.

CHEN, J.; LU, X. Progress of petroleum coke combusting in circulating fluidized bed boilers–a review and future perspectives. **Resources, Conservation and Recycling**, Amsterdam, v. 49, n. 3, p. 203–216, Jan. 2007.

CHEN, L.; DICK, W. A.; KOST, D. Circulating fluidized bed combustion product addition to acid soil: Alfalfa (*Medicago sativa* L.) composition and environmental quality. **Journal of Agricultural and Food Chemistry**, Washington, v. 54, n. 13, p. 4758–4765, June 2006.

CHEN, L.; DICK, W. A.; NELSON, S. Flue gas desulfurization by-products additions to acid soil: alfalfa productivity and environmental quality. **Environmental Pollution**, Barking, v. 114, n. 2, p. 161–168, Sept. 2001.

CHEN, L.; KOST, D.; DICK, W. A. Petroleum coke circulating fluidized bed combustion product as a sulfur source for alfalfa. **Communications in Soil Science and Plant Analysis**, New York, v. 39, n. 13–14, p. 1993–2008, July 2008.

CHEN, L.; KOST, D.; DICK, W. A. Petroleum coke circulating fluidized bed combustion product effects on soil and water quality. **Soil Science**, Baltimore, v. 175, n. 6, p. 270–277, June 2010.

DIXON, N. E. et al. Jack bean urease (EC 3.5.1.5). Metalloenzyme. Simple biological role for nickel. **Journal of the American Chemical Society**, Washington, v. 97, n. 14, p. 4131–4133, July 1975.

ESKEW, D. L.; WELCH, R. M.; CARY, E. E. Nickel: an essential micronutrient for legumes and possibly all higher plants. **Science**, New York, v. 222, n. 4624, p. 621–623, Nov. 1983.

ETTLER, V. et al. Leaching behaviour of slag and fly ash from laterite nickel ore smelting (Niquelândia, Brazil). **Applied Geochemistry**, New York, v. 64, p. 118–127, Jan. 2016.

FAGERIA, N. K.; BALIGAR, V. C. Ameliorating soil acidity of tropical oxisols by liming for sustainable crop production. **Advances in Agronomy**, Orlando, v. 99, p. 345–399, Dec. 2008.

FAGERIA, N. K.; NASCENTE, A. S. Management of soil acidity of South American soils for sustainable crop production. **Advances in Agronomy**, Orlando, v. 128, p. 221–275, Dec. 2014.

FREITAS, D. S. et al. Hidden nickel deficiency? Nickel fertilization via soil improves nitrogen metabolism and grain yield in soybean genotypes. **Frontiers in Plant Science**, Lausanne, v. 9, n. 614, p. 1–16, May 2018.

GERENDAS, J.; SATTELMACHER, B. Significance of Ni supply for growth, urease activity and the concentrations of urea, amino acids and mineral nutrients of urea-grown plants. **Plant and Soil,** Netherlands, v. 190, n. 1, p. 153–162, Mar. 1997.

GONZÁLEZ, A.; NAVIA, R.; MORENO, N. Fly ashes from coal and petroleum coke combustion: current and innovative potential applications. **Waste Management and Research**, London, v. 27, n. 10, p. 976–987, Dec. 2009.

GOULDING, K. W. T. Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom. **Soil Use and Management**, Wallingford, v. 32, n. 3, p. 390–399, Sept. 2016.

HILL, J. M.; KARIMI, A.; MALEKSHAHIAN, M. Characterization, gasification, activation, and potential uses for the millions of tonnes of petroleum coke produced in Canada each year. **The Canadian Journal of Chemical Engineering**, Ottawa, v. 92, n. 9, p. 1618–1626, Sept. 2014.

HOWER, J. C. et al. Impact of co-combustion of petroleum coke and coal on fly ash quality: case study of a Western Kentucky power plant. **Applied Geochemistry**, New York, v. 20, n. 7, p. 1309–1319, July 2005.

IZQUIERDO, M. et al. Influence of a modification of the petcoke/coal ratio on the leachability of fly ash and slag produced from a large PCC power plant. **Environmental Science and Technology**, Washington, v. 41, n. 15, p. 5330–5335, Aug. 2007.

JAFFRÉ, T. et al. The discovery of nickel hyperaccumulation in the New Caledonian tree *Pycnandra acuminata* 40 years on: an introduction to a Virtual Issue. **New Phytologist**, London, v. 218, n. 2, p. 397–400, Apr. 2018.

KLUCAS, R. V. et al. Nickel: a micronutrient element for hydrogen-dependent growth of *Rhizobium japonicum* and for expression of urease activity in soybean leaves. **Proceedings of the National Academy of Sciences**, Washington, v. 80, n. 8, p. 2253–2257, Apr. 1983.

KÜPPER, H. et al. Cellular compartmentation of nickel in the hyperaccumulators *Alyssum lesbiacum*, *Alyssum bertolonii* and *Thlaspi goesingense*. **Journal of Experimental Botany**, Oxford, v. 52, n. 365, p. 2291–2300, Dec. 2001.

KUTMAN, B. Y.; KUTMAN, U. B.; CAKMAK, I. Effects of seed nickel reserves or externally supplied nickel on the growth, nitrogen metabolites and nitrogen use efficiency of urea- or nitrate-fed soybean. **Plant and Soil**, Netherlands, v. 376, n. 1–2, p. 261–276, Mar. 2014.

KUYLENSTIERNA, J. C. I. et al. Acidification in developing countries: ecosystem sensitivity and the critical load approach on a global scale. **AMBIO: A Journal of the Human Environment**, Stockholm, v. 30, n. 1, p. 20, Feb. 2001.

LAL, R. Soil management in the developing countries. **Soil Science**, Baltimore, v. 165, n. 1, p. 57–72, Jan. 2000.

LAVRES, J.; FRANCO, G. C.; CÂMARA, G. M. S. Soybean seed treatment with nickel improves biological nitrogen fixation and urease activity. **Frontiers in Environmental Science**, Lausanne, v. 4, n. 37, p. 1–11, May 2016.

LI, F. et al. Characterization of fly ashes from circulating fluidized bed combustion (CFBC) boilers cofiring coal and petroleum coke. **Energy and Fuels**, Washington, v. 20, n. 4, p. 1411–1417, July 2006.

LI, Y.; ZAMBLE, D. B. Nickel homeostasis and nickel regulation: an overview. **Chemical Reviews**, Washington, v. 109, n. 10, p. 4617–4643, Oct. 2009.

LIU, G.; SIMONNE, E. H.; LI, Y. Nickel nutrition in plants. **Horticultural Sciences,** Gainesville, v. 1191, p. 1–5, June 2011.

LOPES, A. S.; GUILHERME, L. R. G. A career perspective on soil management in the Cerrado Region of Brazil. **Advances in Agronomy**, Orlando, v. 137, p. 1–72, Mar. 2016.

MA, Y. et al. Aging of nickel added to soils as predicted by soil pH and time. **Chemosphere**, Oxford, v. 92, n. 8, p. 962–968, Aug. 2013.

MACEDO, F. G. et al. Nickel availability in soil as influenced by liming and its role in soybean nitrogen metabolism. **Frontiers in Plant Science**, Lausanne, v. 7, n. 1358, p. 1–12, Sept. 2016.

MARTINI, A. Der phytomikroehemisehe Nachweis des Nickels und sein Vorkommen im Pflanzenreieh. **Mikroehemie,** Berlin, v. 8, p. 41-45, Jan. 1930.

MELLIS, E. V.; CRUZ, M. C. P.; CASAGRANDE, J. C. Nickel adsorption by soils in relation to pH, organic matter, and iron oxides. **Scientia Agricola**, Piracicaba, v. 61, n. 2, p. 190–195, Apr. 2004.

MINGUZZI, C., VERGNANO, O. II contenuto del nichel nelle ceneri di *Alyssum bertolonii.* **Atti della Società Toscana di Scienze Naturali,** Toscana, v. 55, p. 49–71, Jan. 1948.

MISHRA, D.; KAR, M. Nickel in plant growth and metabolism. **The Botanical Review**, Washington, v. 40, n. 4, p. 395–452, Oct. 1974.

MOUNT CARMEL COGEN. **The Cogeneration Process.** Pennsylvania, 2018. Disponível em: <http://mountcarmelcogen.com/cogen-process.html>. Acesso em: 25 jul. 2018.

MURTHY, B. N. et al. Petroleum coke gasification: a review. **The Canadian Journal of Chemical Engineering**, Ottawa, v. 92, n. 3, p. 441–468, Mar. 2014.

NYCZEPIR, A. P.; WOOD, B. W. Foliar nickel application can increase the incidence of peach tree short life and consequent peach tree mortality. **Horticultural Sciences,** Gainesville, v. 47, n. 2, p. 224–227. Feb. 2012.

OJEDA-BARRIOS, D. L. et al. The impact of foliar nickel fertilization on urease activity in pecan trees. **Journal of soil science and plant nutrition**, Temuco, v. 16, n. 1, p. 237–247, Mar. 2016.

OLMEDA, J. et al. Effect of petroleum (pet) coke addition on the density and thermal conductivity of cement pastes and mortars. **Fuel**, Washington, v. 107, p. 138–146, May 2013.

ONU – ORGANIZAÇÃO DAS NAÇÕES UNIDAS. **The Millennium Development Goals Report 2015.** New York, 2015. Disponível em: <http://www.un.org/millenniumgoals/2015_MDG_Report/pdf/MDG%202015%20rev%20%28July%201%29.pdf>. Acesso em: 01 Sept. 2018.

ONU – ORGANIZAÇÃO DAS NAÇÕES UNIDAS. **Sustainable development: knowledge platform.** New York, 2018. Disponível em: <https://sustainabledevelopment.un.org/>. Acesso em: 24 Jul. 2018.

POLACCO, J. C.; MAZZAFERA, P.; TEZOTTO, T. Opinion – nickel and urease in plants: still many knowledge gaps. **Plant Science**, Shannon, v. 199–200, p. 79–90, Feb. 2013.

REES, D. C. et al. Structural basis of biological nitrogen fixation. **Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences**, United Kingdom, v. 363, n. 1829, p. 971–984, Apr. 2005.

RODAK, B. W. et al. Methods to quantify nickel in soils and plant tissues. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 39, n. 3, p. 788–793, June 2015.

RUIZ-ARGÜESO, T.; PALACIOS, J. M.; IMPERIAL, J. Regulation of the hydrogenase system in *Rhizobium leguminosarum*. **Plant and Soil,** Netherlands, v. 230, n. 1, p. 49–57, Mar. 2001.

RUTER, J. M. Effect of nickel applications for the control of mouse ear disorder on river birch. **Journal of Environmental Horticulture**, Washington, v. 23, n. 1, p. 17–20, Mar. 2005.

SENGAR, R. S. et al. Occurrence, uptake, accumulation and physiological responses of nickel in plants and its effects on environment. **Research Journal of Phytochemistry**, Washington, v. 2, n. 2, p. 44–60, Feb. 2008.

SEREGIN, I. V.; KOZHEVNIKOVA, A. D. Physiological role of nickel and its toxic effects on higher plants. **Russian Journal of Plant Physiology**, Moscow, v. 53, n. 2, p. 257–277, Mar. 2006.

SHAINBERG, I. et al. Use of gypsum on soils: a review. In: STEWART, B. A. (Ed.). **Advances in Soil Science**. New York: Springer, 1989. p. 1–111.

SILVA, L. F. O. et al. Geochemistry and mineralogy of coal-fired circulating fluidized bed combustion fly ashes. **Coal Combustion and Gasification Products**, Lexington, v. 6, p. *6–28.* Apr. 2014.

SINGH, R. P. et al. Coal fly ash utilization in agriculture: its potential benefits and risks. **Reviews in Environmental Science and Bio/Technology**, Dordrecht, v. 9, n. 4, p. 345–358, Dec. 2010.

SKOUSEN, J. et al. Review of fly ash as a soil amendment. **Geosystem Engineering**, London, v. 16, n. 3, p. 249–256, Sept. 2013.

SUMNER, M. E.; NOBLE, A. D. Soil acidifcation: the world story. In: RENGEL, Z. (Ed.). **Handbook of soil acidity**. New York: Marcel Dekker Inc., 2003. p. 1–28.

UREN, N. C. Forms, reactions, and availability of nickel in soils. **Advances in Agronomy**. Orlando, v. 48, p. 141–203, May 1992.

URUÇ PARLAK, K. Effect of nickel on growth and biochemical characteristics of wheat (*Triticum aestivum* L.) seedlings. **NJAS - Wageningen Journal of Life Sciences**, Wageningen, v. 76, p. 1–5, Mar. 2016.

WANG, J.; ANTHONY, E. J.; ABANADES, J. C. Clean and efficient use of petroleum coke for combustion and power generation. **Fuel**, Washington, v. 83, n. 10, p. 1341–1348, July 2004.

WESTFALL, D. G. et al. Efficient and environmentally safe use of micronutrients in agriculture. **Communications in Soil Science and Plant Analysis**, New York, v. 36, n. 1–3, p. 169–182, Jan. 2005.

WOOD, B. W. Iron-induced nickel deficiency in pecan. **Horticultural Sciences,** Gainesville, v. 48, n. 9, p. 1145–1153, Sept. 2013.

WOOD, B. W.; REILLY, C. C. Nickel and plant disease. In: DATNOFF, L. E.; ELMER, W. H.; HUBER, D. M. (Eds.). **Mineral nutritional and plant disease**. Minnesota: The American Phytopathological Society, 2007. p. 215–231.

WOOD, B. W.; REILLY, C. C.; NYCZEPIR, A. P. Mouse-ear of pecan: I. Symptomatology and occurrence. **Horticultural Sciences,** Gainesville, v. 39, n. 1, p. 87–94, Feb. 2004a.

WOOD, B. W.; REILLY, C. C.; NYCZEPIR, A. P. Mouse-ear of pecan: II. Influence of nutrient applications. **Horticultural Sciences,** Gainesville, v. 39, n. 1**,** p. 95–100, Feb. 2004b.

WOOD, B. W.; REILLY, C. C.; NYCZEPIR, A. P. Field deficiency of nickel in trees: symptoms and causes. **Acta Horticulturae**, Washington, v. 1, n. 721, p. 83–98, Oct. 2006.

YUSUF, M. et al. Nickel: an overview of uptake, essentiality and toxicity in plants. **Bulletin of Environmental Contamination and Toxicology**, New York, v. 86, n. 1, p. 1–17, Jan. 2011.

SEGUNDA PARTE – ARTIGOS

Artigo redigido conforme a norma do periódico científico *Journal of Cleaner Production* (versão aceita e publicada)

ARTIGO 1 – Beneficial use of Ni-rich petroleum coke ashes: product characterization and effects on soil properties and plant growth

Bruna Wurr Rodak [a], Douglas Siqueira Freitas [a], Geraldo Jânio Eugênio de Oliveira Lima [b], André Rodrigues dos Reis [c], Joachim Schulze [d], Luiz Roberto Guimarães Guilherme [a, *]

[a] Department of Soil Science, Federal University of Lavras, 3037, Lavras, Minas Gerais, CEP 37200-000, Brazil
[b] Agriculture and Environmental Technology Center, Alto do Córrego, Lindolfo Garcia St., 1,000, Paracatu, Minas Gerais, CEP 38600-000, Brazil
[c] School of Sciences and Engineering, São Paulo State University, Tupã, São Paulo, CEP 7602-496, Brazil
[d] Department of Crop Science, University of Goettingen, Carl-Sprengel-Weg 1, 37075, Goettingen, Germany
* Corresponding author. guilherm@dcs.ufla.br

Abstract
Fly and bottom ashes – by-products of petroleum coke combustion – contain important plant nutrients (e.g., Ca, S) and may be used as soil acidity amendments, yet their metals content might be a concern. Finding innovative alternatives for the beneficial use of such by-products is key for assuring their environmental sustainability. In this study, we first carried out a comprehensive characterization of fly and bottom ashes, i.e., physical, chemical, mineralogical, and structural analyzes. Next, we created a new product based on these ashes to meet the demand of the Brazilian legislation. To test the agronomic efficiency of the product and the environmental implications of its agricultural use, greenhouse experiments were performed with two Oxisols, cultivated with maize and soybean. The treatments consisted on the application of two doses of different products, aiming to increase soil base saturation to 50% and 70%, and three sources: 1) a blend of fly and bottom ashes with commercial limestone (blended limestone, BL); 2) a positive control, commercial limestone enriched with Ni and S (enriched

limestone, EL); and, 3) a negative control (commercial limestone, CL). The BL was efficient for soil acidity correction, providing Ca, Mg, S, and Ni to maize and soybean plants. Plant dry weight did not change following the application of the product, yet the BL was effective as a Ni-fertilizer, since it was able to increase soil-Ni up to 5-fold, as well as Ni content in maize and in soybean leaves by 5- and 4-fold, respectively, positively affecting N metabolism. Our findings revealed that, while improving many soil attributes, the BL is a viable and sustainable technology for the use of petroleum coke combustion ashes in agriculture, working as a Ni-fertilizer to plants, which meets a current market demand for this micronutrient.

1 Introduction

Disposal of by-products from mining industries in open landfills has become an environmental concern in many countries, mainly due to potential leaching of trace metals to groundwater (Ettler et al., 2016), which speaks for the need to develop innovative and sustainable uses for such materials (Costa et al., 2012; Park et al., 2014; Valle et al., 2016). Applying coal ashes to agricultural soils is a current example of beneficial use of such by-products, as many of these materials are not only efficient to correct soil acidity, but also to provide plant nutrients, leading to yield gains in many crops (Basu et al., 2009; Pandey and Singh, 2010; Singh et al., 2010; Skousen et al., 2013; Ram and Masto, 2014; Shaheen et al., 2014).

Coal ashes are by-products obtained in the energy production process from mineral coal burning in fluidized bed combustion (FBC) boilers (Silva et al., 2014). During the last decades, mineral coal has been replaced by petroleum coke (Chen and Lu, 2007), a terminal product from the petroleum refining process (Murthy et al., 2014). Coke has high availability and low price, making it very attractive as energy source (Wang et al., 2004; Hill et al., 2014). However, the exclusive use of coke in FBC boilers may increase the emission of pollutant gases. In order to reduce environmental impacts of its use, coke burning has been associated with limestone (Li et al., 2006). This process causes a significant change in ash composition, and consequently in its usefulness.

Ashes from petroleum coke are used mainly in the cement industry (Olmeda et al., 2013). However, due to their high CaO content, they might be used

in agriculture as soil acidity amendments (Anthony et al., 2003, 2006; Chen et al., 2010). These ashes are also normally rich in S and metals, mainly V and Ni (Hower et al., 2005; Izquierdo et al., 2007), though their content might be a restriction to use in agriculture (Gonzalez et al., 2009). A pioneer study performed by Chen et al. (2006) has demonstrated that petroleum coke ashes application in some soils did not reach levels of theses metals that might cause environmental problems. To the best of our knowledge, no work has demonstrated the beneficial using of petroleum coke ashes in Brazilian agriculture.

This type of product should be of special interest to the Brazilian agriculture market, since many Brazilian soils are naturally acidic and have low contents of basic cations, which speaks for the need of adequate use of lime, gypsum, and fertilizers to correct surface and subsurface soil acidity, as well as nutrient deficiencies (Lopes and Guilherme, 2016). Much of these soils, particularly in the Cerrado region, have been intensively cultivated with maize (*Zea mays* L.) and soybean (*Glycine max* [L.] Merr.), high nutrient-demanding plants (Fageria and Baligar, 2008; Caires et al., 2011; Fageria and Nascente, 2014, Lopes and Guilherme, 2016). One of such nutrients – which has become especially important in Brazilian agriculture – is Ni, a structural component of urease metalloenzyme (Eskew et al., 1983, 1984; Brown et al., 1987). Ni-fertilizers have been recently regulated in the Brazilian fertilizer legislation (Brazil, 2017).

Considering the aforementioned scenario, studies assessing the beneficial use of coke ashes in Brazil may well be of interest, as: 1) a product can be formulated based on coke ashes, with high soil acidity neutralization power and appropriate trace element contents to plants, as well as environmental adequacy; 2) this product could also supply Ni to plants, since available contents of this micronutrient in tropical soils are usually low (Rodak et al., 2015).

This study aimed: 1) to characterize fly and bottom petroleum coke ashes and to adequate their agronomic and environmental use; and, 2) to evaluate the effects of a product based on these ashes on soil attributes and on growth and physiology of maize and soybean plants, focusing on Ni role in these plants. We expected that our findings might promote an innovative and sustainable use of by-products derived from petroleum coke ashes in tropical agroecosystems, with a special focus on their sustainable use in Brazilian agriculture.

2 Material and Methods

2.1 Process to obtain ashes from petroleum coke

Fly and bottom ashes are by-products obtained from different phases of the energy generation process in the mining industry. This process includes calcination (800 to 900 °C) of a mixture containing 68% petroleum coke, 30% limestone, and 2% sand. Separation of ashes is due to their density (fly ash ~ 0.9 g cm^{-3}; bottom ash ~ 1.4 g cm^{-3}). The fly ash is dragged and cooled by an air current, along with residual gases from combustion, while the bottom ash is separated by sedimentation, remaining deposited in the FBC boiler. It is then removed by a transporting platform, while being cooled during this step.

This energy generation process is adopted by Votorantim Metais, a Brazilian company located in Niquelândia (State of Goiás, Brazil), from which the ashes were collected for this study. The average proportion produced from this company is 70% of fly ash and 30% bottom ash. These ashes are stored in open fields, without proper destination. The existing ash stockpile contains approximately 150 thousand tons of material (Fig. 1).

2.2 Ashes characterization

To ensure the reliability and representativeness of the raw material used in experimentation, 20 petroleum coke ash samples were collected (10 of the fly ash and 10 of the bottom ash). To constitute each sample, five sub-samples were collected per day (alternating schedule), right after the production process in the end of the transporting platform. The sampling took place during one month, every two days.

The collected samples were submitted to physical (fineness), chemical, mineralogical, and structural characterization. Chemical and physical characterizations were performed according to standard methods of the Brazilian Ministry of Agriculture (Brazil, 2017).

Fineness was determined by using 10-mesh (2 mm), 20-mesh (0.84 mm), and 50-mesh (0.3 mm) sieves. Briefly, 100 g of each sample was added to the sieve set and then shacked during 5 min. Retained fractions were weighted and calculation of the passing percentage was done to determine total fineness efficiency (TFE). For moisture analysis, each ash sample was preliminary

weighed and then oven-dried until reaching constant weight (105 °C). The moisture was calculated by the ash mass loss data.

Content of macro- and micronutrients (Ca, Mg, Mo, Ni, and S), beneficial elements (Co and Si), and potentially hazardous elements (Ag, Al, As, B, Ba, Be, Cd, Cu, Cr, Fe, Hg, Mn, Pb, Sb, Sr, Se, V, and Zn) were determined by the USEPA 3050-B method, with quantification done through plasma optical emission spectrometry (ICP-OES). The content of calcium oxide (CaO) and magnesium oxide (MgO) were determined by the volumetric method, using ethylenediaminetetraacetic acid (EDTA). Neutralization power (NP) was determined by the acid-base titration method, while effective neutralization power (ENP) was obtained by the product of TFE and NP. The results were analyzed by descriptive statistics.

In addition to the chemical and physical analyzes, four samples of each ash, fly and bottom, were submitted to X-ray diffraction analysis (XRD) to obtain the mineralogical identification. These samples were previously sieved with a 200-mesh sieve (0.074 mm) and data were processed in a Miniflex II System, bench XRD, using Cu kα radiation (λ = 0.1540562 nm), operated at 30 kV and 15 mA, amplitude of 3 to 80° 2θ with Ni filter for suppression of Kβ, and detection with a NaI scintillator and Be window. The minerals were identified by the Match! 3.2.1. Software (Crystal Impact), using Crystallography Open database (COD 2016).

In order to refine the mineralogical analyzes, four samples from a mixture of each ash (50% ratio) were submitted to a synchrotron X-ray diffraction analysis (SXRD) at the Brazilian Synchrotron Light Laboratory, Campinas, Brazil. After 20-mesh sieving (0.841 mm), samples were inserted into capillary quartz samplers. The incident beam was monochromatic and obtained by a DCM-double crystal monochromator, with Si (111). Measurements were made with a radiation Au kα (λ = 1.04021 nm), with amplitude of 5 to 120° 2θ, and 2.0 s/step. The mineral phases were identified as described for XRD.

Characterization of ashes structure was performed by electronic microscopy. Two samples of each ash were fixed in aluminum stubs and sprayed with carbon for Ni distribution and speciation. The images were obtained through energy dispersive X-ray spectroscopy (EDS). For detailing particle size and homogeneity, the same samples were sprayed with gold and then submitted to scanning electronic microscopy (SEM). Each sample was observed in five homogeneous points, employing a tension equivalent to 25 kV.

After characterization, chemical and physical features of both fly and bottom ashes were compared with guidelines set by the current legislation of liming material ruled by the Brazilian Ministry of Agriculture (Brazil, 2017).

2.3 Agricultural and environmental feasibility of the ashes

Agricultural and environmental adequacy was tested by applying a mixture of fly and bottom ashes in soil-containing pots under greenhouse conditions. Four experiments (Fig. 2) were simultaneously performed, two cultivated with soybean and two with maize plants. Each plant species was cultivated in two types of soils. The adopted design was 3 x 2 completely randomized factorial (3 sources of soil acidity amendment in 2 doses), with four replicates. The tested sources were identified as: 1) a blend of fly (47%) and bottom (20%) ashes with commercial limestone (33%) (hereafter called blended limestone, BL); 2) a positive control, commercial limestone enriched with the same content of Ni and S found in the ashes (enriched limestone, EL); and, 3) a negative control (commercial limestone, CL). All sources were applied in two doses, i.e., to increase soil base saturation (V%) to 50% and to 70%. Focusing on Ni supply, the application of BL and EL added 1.4 kg ha^{-1} of Ni in Typical Red Dystrophic Latosol (LVd) soil and 0.9 kg ha^{-1} of Ni in Typical Red-Yellow Dystrophic Latosol (LVAd) soil in 50% dose, and 1.6 kg ha^{-1} of Ni in LVd soil and 1.4 kg ha^{-1} of Ni in LVAd in 70% dose.

2.3.1 Greenhouse experiments

Two Oxisols were used in greenhouse experiments, both collected at a depth of 0-20 cm. The first was a Typical Red Dystrophic Latosol (LVd), with a clay texture and the second was a Typical Red-Yellow Dystrophic Latosol (LVAd), with a loamy sand texture (Embrapa Solos, 2013). The soils were collected in Paracatu and Lagoa Grande (State of Minas Gerais, Brazil), respectively. Chemical and physical soil characteristics are detailed on Table 1. The soils were air dried, sieved through a 10-mesh sieve, and placed in 3.5-L pots. During that procedure, treatments (sources and doses) were incorporated to the soils, followed by homogenization.

In order to reproduce S and Ni contents from the BL, we have added gypsum (CaSO$_4 \cdot$ 2H$_2$O) and nickel sulfate (NiSO$_4 \cdot$ 6H$_2$O) in the EL. Gypsum was originated from a phosphogypsum (i.e., calcium sulfate dihydrate formed as a by-

product of the production of fertilizer from phosphate rock) commercial company (Agronelli, Brazil), while Ni sulfate was a pure Ni-salt (Sigma-Aldrich).

After soil acidity correction, the pots were kept incubated for 55 days until fertilization. Soil moisture was kept at approximately 60% of the water holding capacity. Fertilization of maize plants (cultivar 30F53YH) and soybean plants (cultivar M6210 IPRO) was performed by application via soil of P - 200 mg kg^{-1}, K - 100 mg kg^{-1}, Cl - 5 mg kg^{-1}, Mn - 3 mg kg^{-1}, Zn - 3 mg kg^{-1}, B - 1 mg kg^{-1}, Cu - 1 mg kg^{-1}, Mo - 0.5 mg kg^{-1}, and Co - 0.1 mg kg^{-1}. Additional 200 mg kg^{-1} of N and 100 mg kg^{-1} of P were applied for maize, and 50 mg kg^{-1} of S was applied in CL. Calcium and Mg were supplied by limestone.

Soybean seeds were inoculated with a stationary liquid culture of *Bradyrhizobium japonicum* N$_2$-fixing bacteria (SEMIA 5079 and 5080 strains), containing 10^9 mL^{-1} colony-forming units. Experiments were terminated when maize plants reached the vegetative stage V8 – eight leaves completely developed (Ritchie et al., 1993), and for soybean plants at R1 – flowering stage (Fehr and Caviness, 1977).

2.3.2 Soil analyzes

Soil analyzes (pH, H + Al, Al, Ca, Mg, S, and Ni) were performed at the end of the experiments (Embrapa Solos, 2011). Since there are no recommendations for Ni critical levels in soils, three extractors were employed (diethylenetriaminepentaacetic acid – DTPA, citric acid, and Mehlich-1).

2.3.3 Plant nutritional status

Plant leaves were collected at the end of the experiments. The leaf analyses included N, Ca, Mg, S, and Ni. Nutrients determination was done after nitric-perchloric digestion, by using ICP-OES, with the exception of N, which was done by the Kjeldahl method. Details regarding methodologies can be found in Embrapa Solos (2000).

2.3.4 Plant growth and physiological evaluation

The SPAD index as well as photosynthetic rate and urease activity were determined on leaves. The SPAD index was obtained by green color intensity portable measuring device. Photosynthetic rate was measured through Infrared

Gas Analyzer readings (Pearcy et al., 2000). Methodologies from McCullough (1967) and Hogan et al. (1983) were adopted in order to determine activity of leaf urease.

At the end of the experiments, plants were collected to determine the shoot dry weight.

2.3.5 Statistical analysis

Normality tests were performed and, since modeled with a normal distribution, the data were submitted to a two-way variance analysis (F-test). When significant, averages were compared by the Tukey test ($p < 0.05$). Statistical analyses for all four experiments were performed independently.

3 Results

3.1 Characterization of fly and bottom ashes

The fly ash had a fine granulometry (10 mesh - 100%, 20 mesh - 99%, and 50 mesh - 99%) with a homogenous light grey color, while the bottom ash had a coarser granulometry (10 mesh - 98%, 20 mesh - 91%, and 50 mesh - 28%) and a darker color (Fig. 3 and Table 2). We observed the presence of heterogeneous compounds in bottom ash, such as petroleum coke and a fine material sprayed over the bigger particles (Fig. 3e and 3f). Moisture was similar for both ashes, ~ 1.1% for fly ash and ~ 1.7% for bottom ash.

Chemical composition of fly ash was equivalent to 43% of CaO and 0.7% of MgO, as well as 31% of Ca, 0.4% of Mg, and 7% of S (Table 2). These properties were higher in fly ash, except for S content, which was 5% higher in bottom ash. Regarding micronutrients and benefic elements content, fly and bottom ashes had similar average values for Si, Mo, and Co (Table 2). However, Ni content was higher in bottom ash, 769 mg kg^{-1} of Ni, then in fly ash, 525 mg kg^{-1} of Ni. Regarding potentially hazardous elements in the ashes, their contents fit within values considered safe by Brazilian legislations. Aluminum, Fe, and V occurrence was noteworthy, with levels remarkably higher than those observed for other elements in both ashes (Table 3).

Predominant mineral phases in the fly ash were identified as anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), and lime (CaO) (Fig. 4a). Bottom ash had the same mineralogical phases verified for fly ash, besides quartz (SiO_2) and calcite

(CaCO$_3$) (Fig. 4b). These phases were more clearly identified in the diffractogram obtained with the synchrotron light (Fig. 4c), even though no other phase was detected.

Speciation of Ni through the EDS technique demonstrated a predominant occurrence of this element as sulfate (NiSO$_4 \cdot$ nH$_2$O) in the fly (Fig. 5a and 5b), as well as in the bottom ash (Fig. 5c and 5d). In the bottom ash, other chemical forms were eventually found, such as Ni sulfite (Ni$_x$S$_y$) (Fig. 5c) and Ni oxide (Ni$_x$O$_y$) (Fig. 5d). It is worthwhile to mention that non-identified chemical components were also found (Fig. 5c). Significant structural differences were not found between the replicates.

3.2 Ashes adequacy to legislation

Based on the Brazilian legislation concerning the TFE of liming materials, soil acidity amendments must pass 100% through a 10-mesh sieve, with a 70% minimum passing through a 20-mesh sieve, and 50% through a 50-mesh sieve. As for their chemical properties, such amendments must have a 38% minimum sum of CaO + MgO, 67% of NP, and 45% of ENP. Concerning the maximum level of hazardous elements, the material must have less than 20 mg kg^{-1} of Cd and less than 1,000 mg kg^{-1} of Pb (Brazil, 2017).

The ashes, when separated, do not fulfill some specifications required by Brazilian legislation. The fly ash does not fit for NP criterion, with a value 3% smaller than demanded. The bottom ash did not follow the specifications for sum of oxides, NP, ENP, and TFE, i.e., having values 3% lower for sum of oxides, 25% lower for NP, and 17% lower for ENP, 2% passing through the 10-mesh sieve, and 22% passing through the 50-mesh sieve (Table 2).

In order to fit the requirements of the Brazilian legislation, a blend of the ashes was prepared along with a commercial limestone. The final blend, blended limestone (BL), was composed of 46.7% fly ash, 20% bottom ash, and 33.3% commercial limestone, satisfying all requirements of the current legislation. When compared with the Brazilian legislation, the new product, BL, now fits the requirements. The new sum of oxides has exceeded the legislation demands in 7%, NP in 3%, and ENP in 19%. For fineness, 26% more material has passed through the 20-mesh sieve and 27% through the 50-mesh sieve. It is important to mention that BL passed completely through a 10-mesh sieve (Table 2) and that the heavy metals content (i.e., Cd and Pb, for the case of soil acidity amendments) also fulfilled the Brazilian requirements (Table 3).

3.3 Agricultural and environmental feasibility

3.3.1 Effects on soil chemical properties

The effect of treatments on soil chemical properties is detailed on Table 4.

All sources (i.e., BL, EL, and CL) were efficient to correct acidity in both soils, equally promoting an increase of pH and V%, yet the intensity of this effect has differed between doses (i.e., 50% and 70%). The soil acidity amendments were also efficient to reduce H + Al, differing between doses. Aluminum content also reduced in all treatments.

Soil acidity amendments were capable of supplying Ca and Mg to maize and soybean plants in both soils. The dose of 70% provided the highest contents of such nutrients in the soil, except for Mg in soybean. With regards to the sources, the BL generally resulted the highest content of Ca and the smallest content of Mg in soil.

Available S content in the soils treated with BL and EL were higher than with CL, since S supply in CL was calculated in the exact amount required by plants, i.e., with no residual effect. Likewise, available Ni content in soils were higher in BL and EL treatments. The dose of 70% provided the highest contents of S and Ni in both soils.

Focusing on Ni supply, BL and EL treatments, independently of the doses and plant species, increased the available soil-Ni content when compared with the CL, with values ranging from 0.13 to 0.42 mg kg^{-1} of Ni in DTPA and from 0.09 to 0.54 mg kg^{-1} of Ni in citric acid. The available Ni content for DTPA and citric acid extractions did not differ between the soils. On the other hand, the Mehlich-1 Ni content differed between soils, increasing from 0.21 to 1.05 mg kg^{-1} of Ni in the LVd and from 0.18 to 0.65 mg kg^{-1} of Ni in the LVAd. In specific cases, EL provided higher available soil Ni content than BL.

3.3.2 Effect in plant nutritional status

The effect of treatments in nutritional status of the plants is detailed on Table 5. In maize leaves, Ca, S, and Ni contents differed between sources, with BL providing higher Ca content, though not differing from the EL for S and Ni. In addition, the leaf Ni content was higher for the dose of 70%. Magnesium

content differed only between doses, with the higher values for the dose of 70%. Nitrogen content did not differ among the treatments.

In soybean leaves, Ca, S, and Ni contents had the same behavior verified for maize, with some particularities. Magnesium content had difference between the sources, with the lowest values being verified in BL. The treatment with EL resulted in the highest Ni content, when applied in LVd soil.

Compared with the negative control (CL), irrespectively of doses and soils, BL and EL increased the leaf Ni content, with averages ranging from 0.25 to 1.26 mg kg^{-1} of Ni in maize plants and from 0.35 to 1.64 mg kg^{-1} of Ni in soybean plants.

3.3.3 Effect on plant growth and physiology

Both plant species tested had positive physiological responses (Fig. 6), though shoot dry weight has not increased with treatments (Table 5). For photosynthetic rate (Fig. 6a, 6b, 6g, and 6h), SPAD index (Fig. 6c, 6d, 6i, and 6j) and urease activity (Fig. 6e, 6f, 6k, and 6l), BL and EL had higher average values than CL. Urease activity was even more responsive in soybean plants, which showed higher average value with addition of EL. There was no difference between doses for these variables.

4 Discussion

During the energy generation process, addition of limestone to the FBC boilers, associated with high concentration of SO_2 in the petroleum coke, resulted in considerable content of anhydrite ($CaSO_4$) and lime (CaO), derived from removal of CO_2 from calcite ($CaCO_3$) in fly and bottom ashes (Fig. 4). Besides this, quick slaking of lime with water generated portlandite [$Ca(OH)_2$], while carbonation of portlandite resulted in colloidal calcite, as verified by Anthony et al. (2000, 2003, 2006), Jia et al. (2002), Duan et al. (2010), and Sheng et al. (2007, 2012).

The presence of these mineral phases allowed the BL to have a high efficiency in soil acidity correction (Table 4). Acidity neutralization occurred due to by-product dissolution and dissociation. Effective chemical bases in the BL, such as carbonates (1, 2, and 3) and oxides (4) (Primavesi, 2004; Fageria and Baligar, 2008), reacted with H^+ or, through hydrolysis, resulted in OH^- formation in soil. At the same time, the attenuation of Al^{3+} toxicity in soil solution occurred

through dissociation of $CaSO_4$ and consequent formation of the ionic pair $AlSO_4^+$ (5 and 6) (Caires et al., 2011), as well as its precipitation as hydroxide (7) (Uchida and Hue, 2000). Such reactions also release Ca, Mg, and S into soil solution (Table 4), thus increasing the content of these nutrients in leaves (Table 5), as verified by Chen et al. (2006, 2008).

$$CaCO_3, MgCO_3 + 2H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \tag{1}$$

$$2HCO_3^- + 2H^+ \Leftrightarrow 2CO_2 + 2H_2O \tag{2}$$

$$CaCO_3, MgCO_3 + 4H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \tag{3}$$

$$CaO, MgO + 2H_2O \Rightarrow Ca^{2+} + Mg^{2+} + 4OH^- \tag{4}$$

$$CaSO_4 \cdot 2H_2O \Rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{5}$$

$$SO_4^{2-} + Al^{3+} \Rightarrow Al(SO_4)^+ \tag{6}$$

$$Al^{3+} + 3OH^- \Rightarrow Al(OH)_3 \tag{7}$$
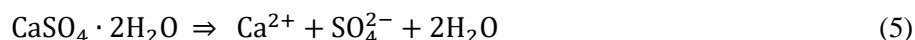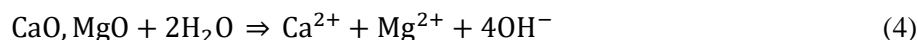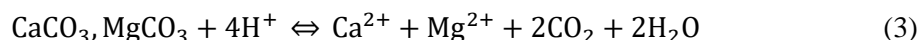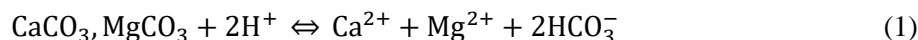
Besides supplying macronutrients to plants, BL also supplied the micronutrient Ni to maize and soybean (Table 5). In the bottom ash, this metal occurred with higher average content and with a higher variation (769 ± 216 mg kg^{-1} of Ni) in comparison to fly ash (525 ± 24 mg kg^{-1} of Ni) (Table 2). The higher Ni content in the bottom ash comes from the greater coke concentration in this fraction (Hower et al., 2005). Besides this, as reported by Milenkova et al. (2003), the variation of this element in the ash depends on the efficiency of the devolatization step, which can release trace elements from coke in a higher or smaller intensity. The production process of the BL (Table 2) resulted in reduction of Ni content and lower Ni dispersion (400 ± 87 mg kg^{-1} of Ni), even when compared with other coke ashes reported in the literature (Font et al., 2005; Hower et al., 2005; Izquierdo et al., 2007; González et al., 2010; Silva et al., 2013).

Although recommendation for Ni fertilization is still a matter of debate, the leaf Ni content considered as appropriate for crop plants usually range from 0.01 to 5 mg kg^{-1}, while soil Ni available content should be around 1 mg kg^{-1}

(Uren, 1992; Liu et al., 2011; Stankovic et al., 2011; Broadley et al., 2012). When compared with these values, BL provided adequate level of this micronutrient in the soil (Table 4) and in leaves (Table 5).

Studies performed in *Medicago sativa* by Chen et al. (2006, 2008) reported that Ni and V supply through petroleum coke ashes was not phytotoxic, even after several successive cropping cycles. According to these authors, application of such ashes in agricultural soils after 30 months did not increase the content of these metals to a level that would impair their application in agriculture. In addition, since Ni availability is reduced with an increase of soil pH (Berbecea et al., 2011; Macedo et al., 2015), Ni application with soil acidity amendments, such as the BL, would guarantee non-phytotoxic levels for this metal.

The available content of Ni and V in ashes was directly related to speciation of these metals, and thus, their availability in the studied soils (Table 3). According to Jia et al. (2002), the main V form in ashes is calcium vanadium oxide hydrate ($Ca_2V_2O_7 \cdot 2H_2O$), with negligible solubility in water, releasing only 0.013% of total V for soil solution. Considering this value, in our study only 0.27 mg kg^{-1} of V would be available to maize and soybean plants (Table 3), and thus, BL application in agricultural soil would not result in negative environmental impact. The predominant Ni form in the ashes was $NiSO_4 \cdot nH_2O$, with a smaller occurrence as Ni_xS_y (Fig. 5), as verified by Pattanaik et al. (2007) and Silva et al. (2013). According to Linak et al. (2000), 85 to 90% of Ni in these ashes is water soluble, making it completely available to plants. Less soluble and less expressive forms, such as Ni ferrite ($NiFe_2O_4$) and Ni oxides are also reported (Pattanaik et al., 2007; Shah et al., 2009).

The presence of oxides and other non-identifiable forms of Ni were also verified in this study (Fig. 5). The occurrence of such forms in BL when compared with EL, which has nickel sulfate (very soluble) as the single form of Ni, may justify the higher leaf Ni content in soybean plants promoted by EL (Table 5), as well as the higher urease activity (Fig. 6k and 6l) and a greater soil Ni available content (Table 4).

Although leaf N content was not altered with the treatments (Table 5), we assume that Ni supply promoted N metabolism in maize and soybean plants, due to the higher urease activity verified in our study (Fig. 6e, 6f, 6k, and 6l). This enzyme acts in N assimilation, hydrolyzing urea ($CO[NH_2]_2$) into ammonia (NH_3) and carbon dioxide (CO_2) (Witte, 2011; Polacco et al., 2013). Nickel effect on N metabolism was also evidenced by the higher photosynthetic rates (Fig. 6a, 6b, 6g, and 6h) and the higher chlorophyll content (Fig. 6c, 6d, 6i, and 6j) in plants

fertilized with this micronutrient (BL and EL). Similar results reporting comparable Ni effects were recently published by Freitas et al. (2018), evidencing the importance of Ni in fertilization programs. According to these authors, an improved N metabolism and a better physiologic apparatus indicate the occurrence of hidden Ni deficiency in common soybean genotypes.

The product tested, BL, was more responsive in leguminous plants (Fig. 6k and 6l), suggesting that it occurs because of Ni effects on biological fixation of nitrogen (BNF). According to Collier and Tegeder (2012), leguminous plants as soybean have higher urease activity in comparison to other plant species since this enzyme participates in assimilation of ureides, a form of N translocated after fixation. In addition, the BL can also provide small amounts of Mo and Co (Table 2), elements that are directly related with BNF (Campo et al., 2002).

The predominant metals in both ashes, Al and Fe (Table 3), due to their naturally high levels in the clay fraction of Brazilian Oxisols (Schaefer et al., 2008), are not seen as an environmental hazard.

Even though the plant shoot dry weight did not increase under greenhouse conditions following the application of BL (Table 5), the improvement observed in many soil properties (increasing V%, pH, Ca, Mg, S, and Ni content; reducing Al) (Table 4), as well as in plant nutritional status (Table 5) and physiology (Fig. 6), ensure the promising use of BL in agriculture. In addition, the by-product also allows for the association of three important soil management practices in tropical agroecosystems, i.e., liming (to correct soil surface acidity), application of gypsum (to alleviate subsurface acidity), and mineral fertilization, thus promoting reduction in costs and application time. It is also a sustainable environmental destination for petroleum coke ashes. Notwithstanding, is it necessary to evaluate yet the effects of this by-product in field conditions, mainly on plant grain yield and on its residual effects in multi-cropping systems.

5 Conclusion

A novel product – blended limestone (BL) – was formulated, according to the current Brazilian regulation for liming materials, from petroleum coke ashes, consisting of 46.7% of fly ash, 20% of bottom ash, and 33.3% of a commercial limestone. This new source was efficient in neutralizing soil acidity in Oxisols, increasing V% and supplying Ca, Mg, S, and Ni to maize and soybean plants. Focusing on Ni fertilization, the BL increased the available content of this micronutrient in soils up to 5-fold (reaching up to 0.42 mg kg^{-1} in DTPA, 0.54 mg

kg^{-1} in citric acid, and 0.85 mg kg^{-1} in Mehlich-1). In maize leaves, Ni content also increased by 5 times (reaching 1.26 mg kg^{-1}), whereas in soybean leaves Ni levels reached 1.64 mg kg^{-1}, a 4-fold increase, positively affecting N metabolism in plants. Plant shoot dry weight did not change following BL application, yet the improvement of many soil properties, along with plant nutritional status and physiology ensure that BL is a feasible and sustainable technology for application in agriculture. In this way, it could be an alternative for the disposal of the by-products derived from petroleum coke combustion, besides attending a current market demand for Ni-based fertilizers. Notwithstanding, monitoring programs should be adopted to: 1) verify the dispersion of some metals in the BL, since the bottom ash has a considerably high variation in the content of some elements; and, 2) assess the potential residual effect of the new product under field conditions.

Acknowledgements

References

Anthony, E.J., Jia, L., Burwell, S.M., 2003. Petroleum coke FBC ash: a detailed look at calcium in the ash. ASME FBC2003-172, 613-620. doi:10.1115/FBC2003-172

Anthony, E.J., Jia, L., Burwell, S.M., Najman, J., Bulewicz, E.M., 2006. Understanding the behavior of calcium compounds in petroleum coke fluidized bed combustion (FBC) ash. J. Energy Resour. Technol. 128, 290-299. doi:10.1115/1.2358144

Anthony, E.J., Talbot, R.E., Jia, L., Granatstein, D.L., 2000. Agglomeration and fouling in three industrial petroleum coke-fired CFBC boilers due to carbonation and sulfation. Energy Fuels 14, 1021-1027. doi:10.1021/ef000024r

Basu, M., Pande, M., Bhadoria, P.B.S., Mahapatra, S.C., 2009. Potential fly-ash utilization in agriculture: a global review. Prog. Nat. Sci. 19, 1173-1186. doi:10.1016/j.pnsc.2008.12.006

Berbecea, A.A., Radulov, I., Sala, F., Crista, F., Lato, A., 2011. Interrelation between metal availability, soil pH and mineral fertilization. Res. J. Agric. Sci. 43, 19-22.

Brazil, 2017. Legislação fertilizantes. http://www.agricultura.gov.br/vegetal/fertilizantes/legislacao (access 18.04.17).

Broadley, M., Brown, P., Cakmak, I., Rengel, Z., Zhao, F., 2012. Function of nutrients: micronutrients, in: Marschner, P. (Ed), Mineral nutrition of higher plants. Elsevier, London, pp. 191-248.

Brown, P.H., Welch, R.M., Cary, E.E., 1987. Nickel: a micronutrient essential for higher plants. Plant Physiol. 85, 801-803. doi:10.1104/pp.85.3.801

Caires, E.F., Joris, H.A.W., Churka, S., 2011. Long-term effects of lime and gypsum additions on no-till corn and soybean yield and soil chemical properties in southern Brazil: liming and gypsum in no-till farming. Soil Use Manag. 27, 45-53. doi:10.1111/j.1475-2743.2010.00310.x

Campo, R.J., Albino, U.B., Hungria, M., 2002. Importance of molybdenum and cobalt to the biological nitrogen fixation, in: Pedrosa, F.O., Hungria, M., Yates, G., Newton, W.E. (Eds.), Nitrogen fixation: from molecules to crop productivity. Kluwer Academic Publishers, Dordrecht, pp. 597-598.

Chen, J., Lu, X., 2007. Progress of petroleum coke combusting in circulating fluidized bed boilers - a review and future perspectives. Resour. Conserv. Recycl. 49, 203-216. doi:10.1016/j.resconrec.2006.03.012

Chen, L., Dick, W.A., Kost, D., 2006. Circulating fluidized bed combustion product addition to acid soil: alfalfa (*Medicago sativa* L.) composition and environmental quality. J. Agric. Food Chem. 54, 4758-4765. doi:10.1021/jf0603275

Chen, L., Kost, D., Dick, W.A., 2010. Petroleum coke circulating fluidized bed combustion product effects on soil and water quality. Soil Sci. 175, 270-277. doi:10.1097/SS.0b013e3181e284c0

Chen, L., Kost, D., Dick, W.A., 2008. Petroleum coke circulating fluidized bed combustion product as a sulfur source for alfalfa. Commun. Soil Sci. Plant Anal. 39, 1993-2008. doi:10.1080/00103620802134826

Collier, R., Tegeder, M., 2012. Soybean ureide transporters play a critical role in nodule development, function and nitrogen export: nitrogen transport in soybean nodules. Plant J. 72, 355-367. doi:10.1111/j.1365-313X.2012.05086.x

CONAMA - Conselho Nacional do Meio Ambiente, 2009. Resolução Nº 420 de 28 de dezembro de 2009. Resolução CONAMA No 420/2009 - "Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas." - Data da legislação: 28/12/2009 -

Publicação DOU no 249, de 30/12/2009. Diário Oficial da União, Poder Executivo, Brasília, pp. 81-84.

Costa, E.T.S., Guilherme, L.R.G., Lopes, G., Curi, N., 2012. Mono- and multielement sorption of trace metals on oxidic industrial by-products. Water Air Soil Pollut. 223, 1661-1670. doi: 10.1007/s11270-011-0973-8

Duan, L.B., Chen, X.P., Li, Y.J., Liang, C., Zhao, C.S., 2010. Investigation on SO_2 emission from 410 t/h circulating fluidized bed boiler burning petroleum coke and coal. Asia-Pac. J. Chem. Eng. 5, 274-280. doi:10.1002/apj.258

Embrapa Solos, 2013. Sistema brasileiro de classificação de solos, 3 ed. Embrapa, Brasília.

Embrapa Solos, 2011. Manual de métodos de análise de solo. Embrapa Solos, Rio de Janeiro.

Embrapa Solos, 2000. Métodos de análise de tecidos vegetais utilizados na Embrapa Solos. Embrapa Solos, Rio de Janeiro.

Eskew, D.L., Welch, R.M., Cary, E.E., 1983. Nickel: an essential micronutrient for legumes and possibly all higher-plants. Science 222, 621-623. doi:10.1126/science.222.4624.621

Eskew, D.L., Welch, R.M., Norvell, W.A., 1984. Nickel in higher plants: further evidence for an essential role. Plant Physiol. 76, 691-693.

Ettler, V., Kvapil, J., Šebek, O., Johan, Z., Mihaljevič, M., Ratié, G., Garnier, J., Quantin, C., 2016. Leaching behaviour of slag and fly ash from laterite nickel ore smelting (Niquelândia, Brazil). Appl. Geochem. 64, 118-127. doi:10.1016/j.apgeochem.2015.09.019

Fageria, N.K., Baligar, V.C., 2008. Ameliorating soil acidity of tropical Oxisols by liming for sustainable crop production. Adv. Agro. 99, 345-399. doi:org/10.1016/S0065-2113(08)00407-0

Fageria, N.K., Nascente, A.S., 2014. Management of soil acidity of South American soils for sustainable crop production. Adv. Agron. 128, 221-275. doi:10.1016/B978-0-12-802139-2.00006-8

Fehr, W.R., Caviness, C.E., 1977. Stages of soybean development. Iowa State University Cooperative Extension Service, Iowa.

Font, O., Querol, X., Huggins, F., Chimenos, J., Fernandez, A., Burgos, S., Pena, F., 2005. Speciation of major and selected trace elements in IGCC fly ash. Fuel 84, 1364-1371. doi:10.1016/j.fuel.2004.06.039

Freitas, D.S., Rodak, B.W., Reis, A.R., Reis, F.B., Carvalho, T.S., Schulze, J., Carneiro, M.A.C., Guilherme, L.R.G., 2018. Hidden nickel deficiency? Nickel fertilization via soil improves nitrogen metabolism and grain yield in soybean genotypes. Front. Plant Sci. 9:614, 1-16. doi:10.3389/fpls.2018.00614

González, A., Moreno, N., Navia, R., Querol, X., 2010. Study of a Chilean petroleum coke fluidized bed combustion fly ash and its potential

application in copper, lead and hexavalent chromium removal. Fuel 89, 3012-3021. doi:10.1016/j.fuel.2010.04.032

Gonzalez, A., Navia, R., Moreno, N., 2009. Fly ashes from coal and petroleum coke combustion: current and innovative potential applications. Waste Manag. Res. 27, 976-987. doi:10.1177/0734242X09103190

Hill, J.M., Karimi, A., Malekshahian, M., 2014. Characterization, gasification, activation, and potential uses for the millions of tonnes of petroleum coke produced in Canada each year. Can. J. Chem. Eng. 92, 1618-1626. doi:10.1002/cjce.22020

Hogan, M.E., Swift, I.E., Done, J., 1983. Urease assay and ammonia release from leaf tissues. Phytochemistry 22, 663-667. doi:10.1016/S0031-9422(00)86958-7

Hower, J.C., Thomas, G.A., Mardon, S.M., Trimble, A.S., 2005. Impact of co-combustion of petroleum coke and coal on fly ash quality: case study of a Western Kentucky power plant. Appl. Geochem. 20, 1309-1319. doi:10.1016/j.apgeochem.2005.02.010

Izquierdo, M., Font, O., Moreno, N., Querol, X., Huggins, F.E., Alvarez, E., Diez, S., Otero, P., Ballesteros, J.C., Gimenez, A., 2007. Influence of a modification of the petcoke/coal ratio on the leachability of fly ash and slag produced from a large PCC power plant. Environ. Sci. Technol. 41, 5330-5335. doi:10.1021/es063002d

Jia, L., Anthony, E.J., Charland, J.P., 2002. Investigation of vanadium compounds in ashes from a CFBC firing 100 petroleum coke. Energy Fuels 16, 397-403. doi:10.1021/ef010238o

Li, F., Zhai, J., Fu, X., Sheng, G., 2006. Characterization of fly ashes from circulating fluidized bed combustion (CFBC) boilers co-firing coal and petroleum coke. Energy Fuels 20, 1411-1417. doi:10.1021/ef050377w

Linak, W.P., Miller, C.A., Wendt, J.O.L., 2000. Comparison of particle size distributions and elemental partitioning from the combustion of pulverized coal and residual fuel oil. J. Air Waste Manag. Assoc. 50, 1532-1544. doi:10.1080/10473289.2000.10464171

Liu, G., Simonne, E.H., Li, Y., 2011. Nickel nutrition in plants. Hortic. Sci. 1191, 1-5.

Lopes, A.S., Guilherme, L.R.G., 2016. A career perspective on soil management in the Cerrado region of Brazil. Adv. Agron. 137, 1-72. doi:10.1016/bs.agron.2015.12.004

Macedo, F.G., Bresolin, J.D., Santos, E.F., Furlan, F., Silva, W.T.L., Polacco, J.C., Lavres, J., 2015. Nickel availability in soil as influenced by liming and its role in soybean nitrogen metabolism. Front. Plant. Sci. 6, 1-4. doi:10.3389/fpls.2015.00754

McCullough, H., 1967. The determination of ammonia in whole blood by a direct colorimetric method. Clínica Chim. Acta 17, 297-304. doi:10.1016/0009-8981(67)90133-7

Milenkova, K., Borrego, A., Alvarez, D., Xiberta, J., Menéndez, R., 2003. Devolatilisation behaviour of petroleum coke under pulverised fuel combustion conditions. Fuel 82, 1883-1891. doi:10.1016/S0016-2361(03)00191-1

Murthy, B.N., Sawarkar, A.N., Deshmukh, N.A., Mathew, T., Joshi, J.B., 2014. Petroleum coke gasification: a review. Can. J. Chem. Eng. 92, 441-468. doi:10.1002/cjce.21908

Olmeda, J., Rojas, M.I.S., Frias, M., Donatello, S., Cheeseman, C.R., 2013. Effect of petroleum (pet) coke addition on the density and thermal conductivity of cement pastes and mortars. Fuel 107, 138-146. doi:10.1016/j.fuel.2013.01.074

Pandey, V.C., Singh, N., 2010. Impact of fly ash incorporation in soil systems. Agric. Ecosyst. Environ. 136, 16-27. doi:10.1016/j.agee.2009.11.013

Park, J.H., Edraki, M., Mulligan, D., Jang, H.S., 2014. The application of coal combustion by-products in mine site rehabilitation. J. Clean Prod. 84, 761-772. doi:10.1016/j.jclepro.2014.01.049

Pattanaik, S., Huggins, F.E., Huffman, G.P., Linak, W.P., Miller, C.A., 2007. XAFS studies of nickel and sulfur speciation in residual oil fly-ash particulate matters (ROFA PM). Environ. Sci. Technol. 41, 1104-1110. doi:10.1021/es061635m

Pearcy, R.W., Schulze, E.D., Zimmermann, R., 2000. Measurement of transpiration and leaf conductance, in: Pearcy, R.W., Ehleringer, J.R., Mooney, H.A., Rundel, P.W. (Eds.), Plant Physiological Ecology: Field Methods and Instrumentation. Springer Netherlands, Dordrecht, pp. 137-160. doi:10.1007/978-94-010-9013-1_8

Polacco, J.C., Mazzafera, P., Tezotto, T., 2013. Opinion - nickel and urease in plants: still many knowledge gaps. Plant Sci. 199-200, 79-90. doi:10.1016/j.plantsci.2012.10.010

Primavesi, A.C., 2004. Características de corretivos agrícolas. Embrapa Pecuária Sudeste, São Carlos.

Ram, L.C., Masto, R.E., 2014. Fly ash for soil amelioration: a review on the influence of ash blending with inorganic and organic amendments. Earth-Sci. Rev. 128, 52-74. doi:10.1016/j.earscirev.2013.10.003

Ritchie, S.W., Hanway, J.J., Benson, G.O., 1993. How a corn plant develops. Ames, Iowa State University of Science and Technology.

Rodak, B.W., Moraes, M.F., Pascoalino, J.A.L., Oliveira Junior, A., Castro, C., Pauletti, V., 2015. Methods to quantify nickel in soils and plant tissues. Rev. Bras. Ciênc. Solo 39, 788-793. doi:10.1590/01000683rbcs20140542

Schaefer, C.E.G.R., Fabris, J.D., Ker, J.C., 2008. Minerals in the clay fraction of Brazilian Latosols (Oxisols): a review. Clay Miner. 43, 137-154. doi:10.1180/claymin.2008.043.1.11

Shah, P., Strezov, V., Nelson, P.F., 2009. X-ray absorption near edge structure spectrometry study of nickel and lead speciation in coals and coal combustion products. Energy Fuels 23, 1518-1525. doi:10.1021/ef800824d

Shaheen, S.M., Hooda, P.S., Tsadilas, C.D., 2014. Opportunities and challenges in the use of coal fly ash for soil improvements - a review. J. Environ. Manage. 145, 249-267. doi:10.1016/j.jenvman.2014.07.005

Sheng, G., Li, Q., Zhai, J., 2012. Investigation on the hydration of CFBC fly ash. Fuel 98, 61-66. doi:10.1016/j.fuel.2012.02.008

Sheng, G., Zhai, J., Li, Q., Li, F., 2007. Utilization of fly ash coming from a CFBC boiler co-firing coal and petroleum coke in Portland cement. Fuel 86, 2625-2631. doi:10.1016/j.fuel.2007.02.018

Silva, L.F.O., Oliveira, M.L.S., Kautzmann, R.M., Ramos, C.G., Izquierdo, M., Dai, S., Wilcox, J., Hoffman, J., Hower, J.C., 2014. Geochemistry and mineralogy of coal-fired circulating fluidized bed combustion fly ashes. *CCGP Journal 6, 6-28. doi:10.4177/CCGP-D-14-00005.1*

Silva, L.F.O., Oliveira, M.L.S., Sampaio, C.H., Brum, I.A.S., Hower, J.C., 2013. Vanadium and nickel speciation in pulverized coal and petroleum coke co-combustion. Energy Fuels 27, 1194-1203. doi:10.1021/ef4000038

Singh, R.P., Gupta, A.K., Ibrahim, M.H., Mittal, A.K., 2010. Coal fly ash utilization in agriculture: its potential benefits and risks. Rev. Environ. Sci. Biotechnol. 9, 345-358. doi:10.1007/s11157-010-9218-3

Skousen, J., Yang, J.E., Lee, J.S., Ziemkiewicz, P., 2013. Review of fly ash as a soil amendment. Geosyst. Eng. 16, 249-256. doi:10.1080/12269328.2013.832403

Stankovic, D., Knezevic, M., Krstic, B., Sijacic-Nikolic, M., Vilotic, D., 2011. Nickel content in plants and soil in the area of the protected natural resource "Avala" - Belgrade. Glas. Umarskog Fak. 103, 131-146. doi:10.2298/GSF1103131S

Uchida, R., Hue, N.V., 2000. Soil acidity and liming, in: Silva, J.A., Uchida, R. (Eds), Plant nutrient management in Hawaii's soils, approaches for tropical and subtropical agriculture. College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa, Hawaii, pp. 101-111.

Uren, N.C., 1992. Forms, reactions, and availability of nickel in soils. Adv. Agron. 48, 141-203. doi:org/10.1016/S0065-2113(08)60937-2

Valle, L.A.R., Rodrigues, S.L., Ramos, S.J., Pereira, H.S., Amaral, D.C., Siqueira, J.O., Guilherme, L.R.G., 2016. Beneficial use of a by-product from the phosphate fertilizer industry in tropical soils: effects on soil properties and

maize and soybean growth. J. Clean Prod. 112, 113-120. doi:10.1016/j.jclepro.2015.07.037

Wang, J., Anthony, E.J., Abanades, J.C., 2004. Clean and efficient use of petroleum coke for combustion and power generation. Fuel 83, 1341-1348. doi:10.1016/j.fuel.2004.01.002

Witte, C.P., 2011. Urea metabolism in plants. Plant Sci. 180, 431-438. doi:10.1016/j.plantsci.2010.11.010
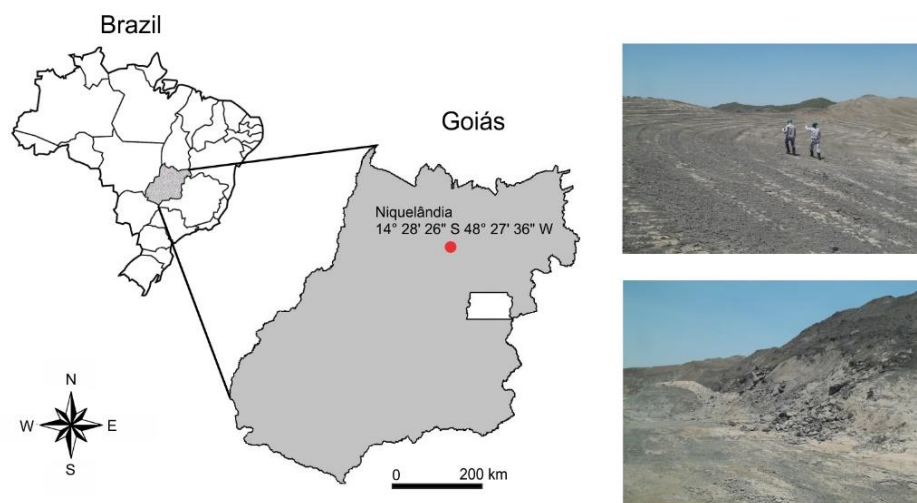
Fig. 1. Large amounts of petroleum coke ashes stored in open field piles in Votorantim Metais (red dot), a Ni exploration company.
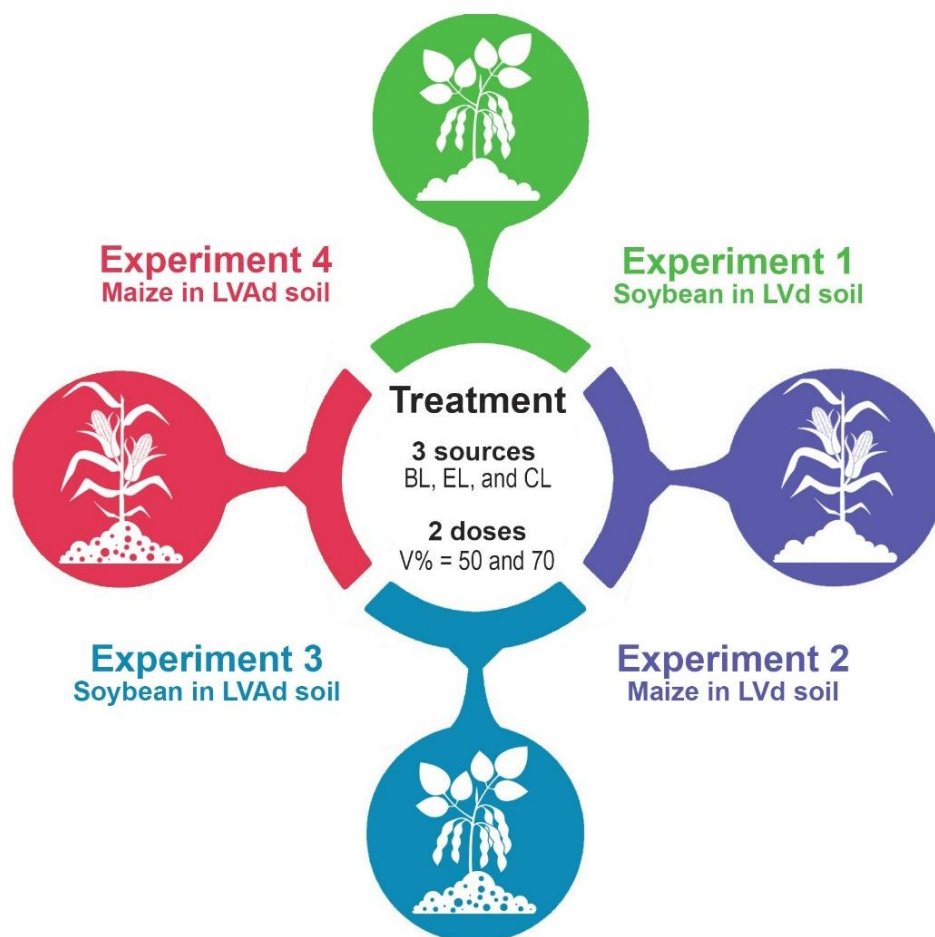
Fig. 2. Scheme of the four experiments used to access the agricultural and environmental feasibility of the new tested product, blended limestone (BL). V% - base saturation; EL - Enriched limestone; CL - Commercial limestone; LVd - Typical Red Dystrophic Latosol; LVAd - Typical Red-Yellow Dystrophic Latosol.
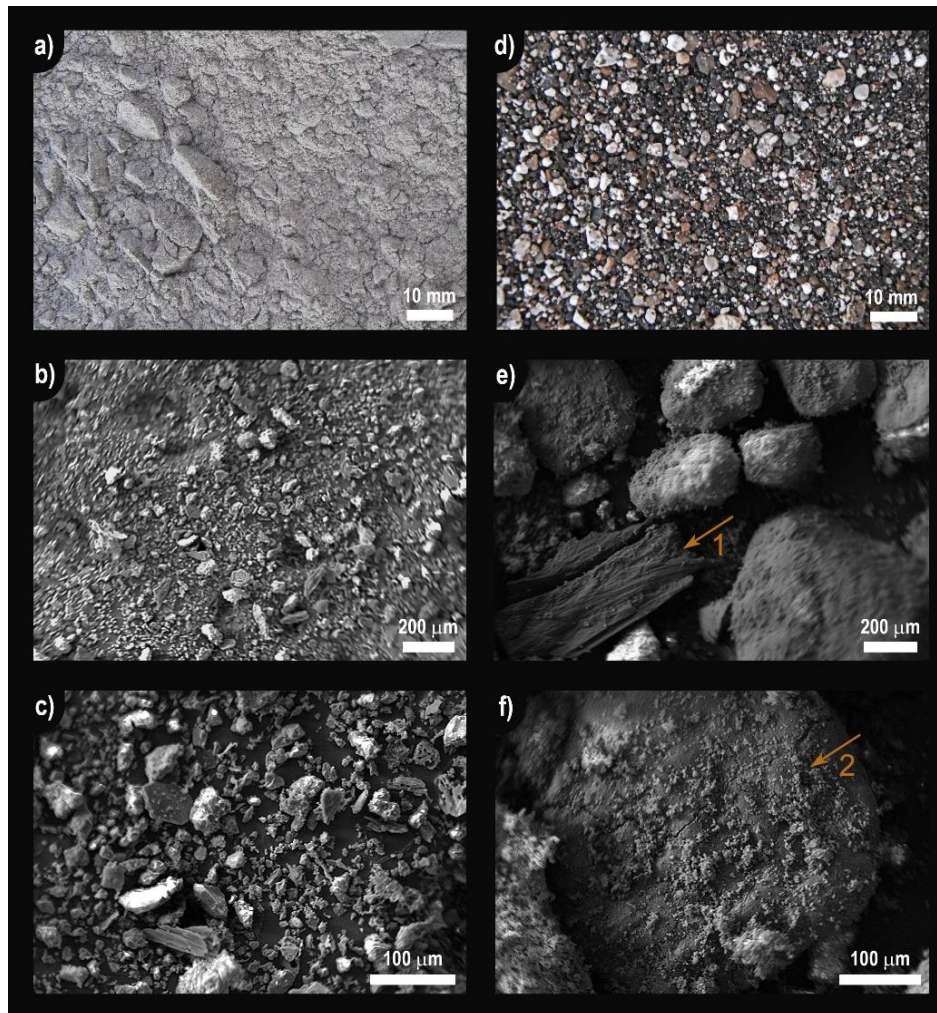
Fig. 3. Scanning electronic microscopy for fly ash in a) 5x, b) 100x, and c) 300x magnification, as well as bottom ash in d) 5x, e) 100x, and f) 300x magnification. Fly ash had finer granulometry and lighter color than bottom ash. In the bottom ash, was verified the presence of large pieces of petroleum coke (1) and a fine material sprayed over the particles (2).
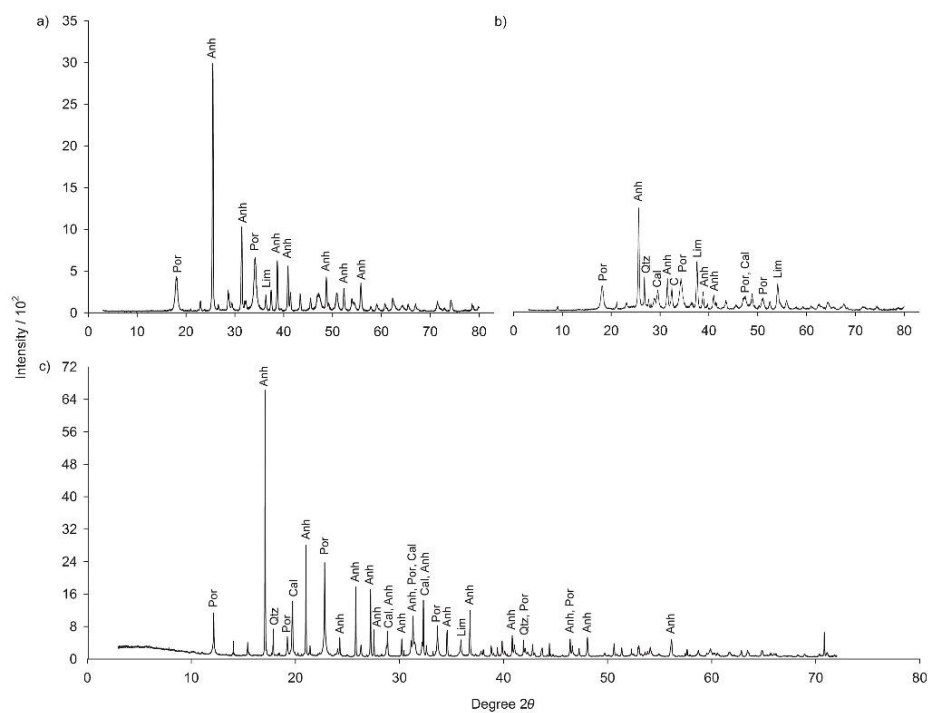
Fig. 4. X-ray diffractogram (Cu kα radiation) of a) fly ash and b) bottom ash, and synchrotron X-ray diffraction diffractogram (Au kα radiation) of a c) mixture of 50% fly ash and 50% bottom ash. Anh - anhydrite (CaSO$_4$); Cal - calcite (CaCO$_3$); Lim - lime (CaO); Por - portlandite [Ca(OH)$_2$]; Qtz - quartz (SiO$_2$).
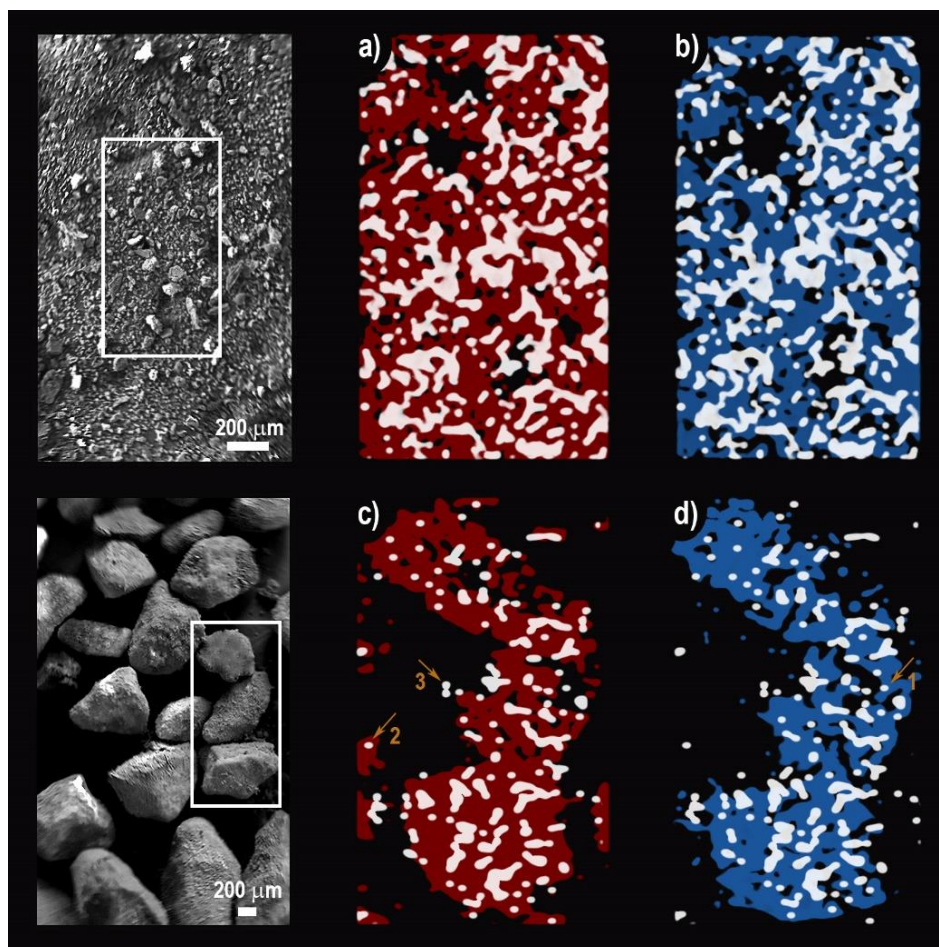
Fig. 5. Energy-dispersive X-ray spectroscopy with 100x magnification a-b) fly ash and c-d) bottom ash. This mapping shows a predominant occurrence of nickel sulfate ($NiSO_4 \cdot nH_2O$), and smaller occurrences of nickel oxide forms (Ni_xO_y) (1), nickel sulfide (Ni_xS_y) (2), and non-identifiable (3). Colors: Ni - white; S - red; O - blue.
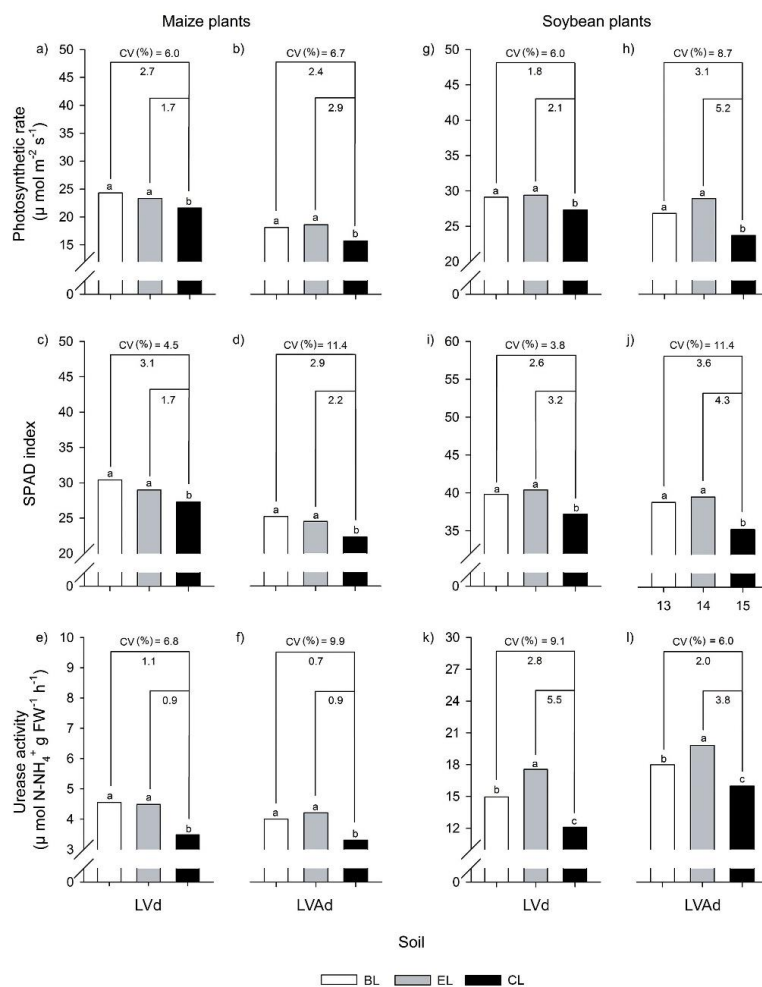
Fig. 6. Physiological responses from maize and soybean plants cultivated in LVd and LVAd soils, with application of blended limestone (BL), enriched limestone (EL), and commercial limestone (CL). Averages followed by the same letter did not differed among sources by Tukey test at $p < 0.05$. Doses (50% and 70% soil base saturation) did not differ for these variables. The value shown in upper part of each graphic represents the difference among the treatments (BL and EL) and the negative control (CL). CV - coefficient of variation; LVd - Typical Red Dystrophic Latosol; LVAd - Typical Red-Yellow Dystrophic Latosol.

Table 1

Chemical and physical (granulometry) characterization of two Oxisol, Typical Dystrophic Red Latosol (LVd) and Typical Dystrophic Red-Yellow Latosol (LVAd).

Properties	Units	LVd	LVAd
Sand	g kg^{-1}	40	850
Silt	g kg^{-1}	300	50
Clay	g kg^{-1}	660	100
SOM	g kg^{-1}	18.2	11.0
pH (CaCl$_2$)	-	4.3	4.2
pH (Water)	-	5.2	5.0
Al	cmol$_c$ kg^{-1}	0.2	0.1
Al + H	cmol$_c$ kg^{-1}	3.8	3.3
P	mg kg^{-1}	2.9	1.7
K	cmol$_c$ kg^{-1}	0.2	0.1
Ca	cmol$_c$ kg^{-1}	0.2	0.2
Mg	cmol$_c$ kg^{-1}	0.0	0.1
S	mg kg^{-1}	4.4	1.2
B	mg kg^{-1}	0.4	0.1
Cu	mg kg^{-1}	1.3	0.5
Fe	mg kg^{-1}	69.0	107.1
Mn	mg kg^{-1}	10.1	30.0
Zn	mg kg^{-1}	9.2	5.8
Available Ni (citric acid 2%)	mg kg^{-1}	< 0.005	< 0.005
Available Ni (DTPA)	mg kg^{-1}	< 0.05	< 0.05
Available Ni (Mehlich-1)	mg kg^{-1}	< 0.1	< 0.1
Total Ni (USEPA Method 3050-B)	mg kg^{-1}	< 0.005	< 0.005
V	%	10.0	9.5

SOM - soil organic matter; V - base saturation.

Table 2

Chemical composition (macronutrients, micronutrients, and beneficial elements), physical properties (fineness) of the fly ash, bottom ash, and the new product, blended limestone (BL), formulated by a mixture of ashes with commercial limestone (CL), fulfilling Brazilian legislation parameters.

Properties	Units	Fly ash			Bottom ash			CL	BL	Legislation [a]
		Range of content	Mean ± S	CV (%)	Range of content	Mean ± S	CV (%)	Mean ± S	Mean ± S	
					Chemical properties					
Ca	%	30.2 - 32.3	31.3 ± 0.7	2.2	21.2 - 33.9	24.9 ± 4.6	18.6	21.6 ± 0.1	26.8 ± 0.9	-
CaO	%	42.5 - 45.3	43.9 ± 0.9	2.2	29.6 - 47.6	34.8 ± 6.4	18.6	30.2 ± 0.2	37.6 ± 1.3	-
Mg	%	0.4 - 0.5	0.4 ± 0.1	5.5	0.2 - 0.4	0.3 ± 0.1	18.2	13.9 ± 2.7	4.9 ± 0.2	-
MgO	%	0.6 - 0.8	0.7 ± 0.1	6.0	0.3 - 0.7	0.6 ± 0.1	18.2	23.2 ± 1.8	8.1 ± 0.3	-
S	%	5.3 - 8.1	7.3 ± 1.0	13.9	11.4 - 14.1	12.1 ± 0.8	7.3	-	5.8 ± 0.7	-
Ni	mg kg^{-1}	497.1 - 565.7	525.9 ± 24.1	4.5	421.6 - 1,105.9	769.9 ± 216.9	28.1	1.5 ± 0.5	400.1 ± 87	-
Mo	mg kg^{-1}	32.7 - 38.5	35.6 ± 2.0	5.6	23.2 - 32.6	27.9 ± 2.9	10.5	-	-	-
Co	mg kg^{-1}	17.6 - 23.6	20.2 ± 1.8	9.3	11.4 - 30.1	20.5 ± 5.5	25.6	-	-	-
Si	%	0.7 - 1.0	0.9 ± 0.1	9.0	1.3 - 2.1	1.8 ± 0.2	14.2	-	-	-
CaO + MgO	%	43.2 - 46.0	44.6 ± 0.9	2.2	30.2 - 48.1	35.5 ± 6.3	18.0	53.6 ± 1.9	45.7 ± 1.2	38
NP	% CaCO$_3$eq	56.7 - 67.8	64.3 ± 3.1	4.8	29.0 - 64.7	42.2 ± 12.9	30.5	97.4 ± 1.2	70.9 ± 0.6	67
ENP	% CaCO$_3$eq	56.7 - 67.7	64.3 ± 3.1	4.8	19.0 - 45.3	28.6 ± 8.9	31.1	87.4 ± 0.6	64.8 ± 0.9	45
Moisture	%	0.1 - 2.9	1.1 ± 1.1	97.8	1.0 - 2.7	1.7 ± 0.5	33.5	0.1 ± 0.0	-	-
					Physical properties – TFE					
10-mesh sieve	%	100.0 - 100.0	100.0 ± 0.0	-	97.8 - 99.9	98.8 ± 0.6	0.6	99.9 ± 0.0	100.0 ± 0.1	100
20-mesh sieve	%	99.9 - 100.0	99.9 ± 0.1	0.1	86.4 - 98.2	91.1 ± 4.2	4.6	95.9 ± 0.5	96.9 ± 0.8	70
50-mesh sieve	%	99.4 - 99.9	99.8 ± 0.2	0.2	16.5 - 37.5	28.6 ± 6.0	21.1	74.3 ± 1.5	77.1 ± 1.3	50

[a] Law 35 from July 4th 2006 (Brazil, 2017); S - standard deviation; CV - coefficient of variation; NP - neutralization power; ENP - effective neutralizing; TFE - total fineness efficiency.

Table 3

Content of potentially hazardous elements in fly ash and bottom ash compared with safe levels in fertilizers and liming materials and quality guidelines in agricultural soils ruled by the Brazilian legislation.

Properties	Unit	Fly ash			Bottom ash			Legislation for fertilizers and liming material [a]	Quality guidelines in agricultural soils [b]
		Range of content	Mean ± S	CV (%)	Range of content	Mean ± S	CV (%)		
Ag	mg kg^{-1}	< 1.0	< 1.0	-	< 1.0	< 1.0	-	-	25.0
Al	mg kg^{-1}	3,366.0 - 3,763.0	3,545.3 ± 201.3	5.7	4,864.0 - 5,046.0	4,971.0 ± 95.1	1.9	-	-
As	mg kg^{-1}	0.7 - 0.9	0.8 ± 0.1	7.8	0.9 - 1.1	1.0 ± 0.1	7.5	2.0 - 4,000.0	35.0
B	mg kg^{-1}	12.0 - 13.6	12.8 ± 0.8	6.3	4.0 - 5.0	4.5 ± 0.5	11.1	-	-
Ba	mg kg^{-1}	22.6 - 25.4	24.0 ± 1.4	5.8	12.7 - 14.9	13.7 ± 1.1	8.1	-	300.0
Be	mg kg^{-1}	< 0.4	< 0.4	-	< 0.4	< 0.4	-	-	-
Cd	mg kg^{-1}	< 0.2	< 0.2	-	< 0.2	< 0.2	-	20.0 [c]	3.0
Cu	mg kg^{-1}	75.1 - 81.8	77.6 ± 3.7	4.7	59.2 - 65.2	62.5 ± 3.0	4.9	-	200.0
Cr	mg kg^{-1}	13.0 - 13.9	13.3 ± 0.5	3.7	9.1 -10.9	10.2 ± 0.9	9.3	40.0 - 500.0	150.0
Fe	mg kg^{-1}	3,311.0 - 3,880.0	3,594.3 ± 284.5	7.9	2,899.0 - 3,370.0	3,089.0 ± 248.3	8.0	-	-
Hg	mg kg^{-1}	< 0.5	< 0.5	-	< 0.5	< 0.5	-	0.05 - 2.5	12.0
Mn	mg kg^{-1}	97.8 - 110.2	102.5 ± 6.7	6.6	65.4 - 72.5	69.0 ± 3.6	5.2	-	-
Pb	mg kg^{-1}	< 0.2	< 0.2	-	< 0.2	< 0.2	-	1,000.0 [c]	180.0
Sb	mg kg^{-1}	< 1.0	< 1.0	-	< 1.0	< 1.0	-	-	5.0
Sr	mg kg^{-1}	1,163.3 - 1,229.3	1,190.0 ± 34.8	2.9	639.7 - 760.9	697.0 ± 60.9	8.7	-	-
Se	mg kg^{-1}	< 0.5	< 0.5	-	< 0.5	< 0.5	-	80.0	-
V	mg kg^{-1}	2,225.5 - 2,743.0	2,487.8 ± 156.4	6.2	2,208.0 - 6,548.0	4,543.9 ± 1,361.2	29.9	-	-
Zn	mg kg^{-1}	5.2 - 5.5	5.3 ± 0.2	2.9	1.3 - 1.7	1.5 ± 0.2	13.6	-	450.0

[a] Law 27 from June 5th 2006 (Brazil, 2017); [b] Law 420 from December 28th 2009 (CONAMA, 2009); [c] Maximum values allowed for soil acidity amendments; S - standard deviation; CV - coefficient of variation.

Table 4
Chemical properties of Typical Red Dystrophic Latosol (LVd) and Typical Red-Yellow Dystrophic Latosol (LVAd) soils after cultivation of maize and soybean plants with application of the blended limestone (BL), enriched limestone (EL), and commercial limestone (CL) in doses to reach 50% and 70% of soil base saturation (V%).

Treatments		pH		H + Al	Al	Ca	Mg	S	V	Ni (mg kg^{-1})		
Liming source	Doses	Water	CaCl$_2$	cmolc kg^{-1}				mg kg^{-1}	%	DTPA	Citric acid	Mehlich-1
								Maize plants				
								LVd				
BL	50%	5.4 B	4.9 B	3.3 A		1.8 aB	0.5 bB	10.3 aB	42 B	0.22 bB	0.47 bB	0.88 bB
EL	50%	5.5 B	4.9 B	3.8 A		1.6 bB	0.9 aB	7.2 abB	41 B	0.29 aB	0.56 aB	1.13 aB
CL	50%	5.5 B	4.9 B	3.8 A	0.0	1.4 bB	0.7 aB	3.0 bA	37 B	0.09 cB	0.10 cB	0.26 cA
BL	70%	5.6 A	5.2 A	2.6 B		2.5 aA	0.6 bA	17.1 aA	55 A	0.54 bA	0.51 bA	1.00 bA
EL	70%	5.7 A	5.3 A	3.2 B		2.0 bA	1.2 aA	11.7 aA	50 A	0.59 aA	0.63 aA	1.45 aA
CL	70%	5.8 A	5.3 A	2.7 B		1.7 bA	1.1 aA	3.7 bA	51 A	0.10 cA	0.13 cA	0.20 cA
CV (%)		1.2	1.1	12.1	-	10.9	7.4	19.3	8.7	5.9	10.8	12.6
								LVAd				
BL	50%	5.1 B	4.8 B			1.8 aB	0.5 bB	17.4 aB	50 B	0.29 aB	0.36 aB	0.55 bB
EL	50%	5.1 B	4.7 B			1.7 bB	0.7 aB	17.6 aB	52 B	0.35 aB	0.38 aB	0.72 aB
CL	50%	5.2 B	4.8 B	2.2	0.0	1.6 bB	0.6 aB	8.3 bA	49 B	0.09 bA	0.17 bA	0.20 cB
BL	70%	5.4 A	5.0 A			2.5 aA	0.7 bA	23.8 aA	61 A	0.47 aA	0.53 aA	0.62 bA
EL	70%	5.4 A	5.2 A			1.9 bA	0.9 aA	20.5 aA	57 A	0.50 aA	0.60 aA	0.97 aA
CL	70%	5.4 A	5.0 A			1.8 bA	0.8 aA	10.5 bA	58 A	0.09 bA	0.15 bA	0.22 cA
CV (%)		1.8	1.5	15.6	-	11.6	14.1	8.8	8.1	11.0	15.4	17.0
								Soybean plants				
								LVd				
BL	50%	5.4 B	4.8 B	3.6 A		1.6 aB	0.5 bA	8.8 aB	38 B	0.26 aB	0.49 aB	0.90 aB
EL	50%	5.4 B	4.7 B	3.8 A		1.5 abB	0.9 aB	6.3 aB	36 B	0.32 aB	0.43 aB	0.90 aB
CL	50%	5.5 B	4.8 B	3.2 A	0.0	1.3 bB	0.7 aB	2.9 bA	40 B	0.10 bA	0.16 bA	0.18 bB
BL	70%	5.6 A	5.0 A	3.0 B		2.5 aA	0.6 bA	14.8 aA	51 A	0.56 aA	0.66 aA	1.13 aA
EL	70%	5.7 A	5.1 A	3.1 B		1.9 bA	1.2 aA	10.7 aA	50 A	0.50 aA	0.66 aA	1.00 aA
CL	70%	5.7 A	5.0 A	3.1 B		1.7 cA	1.1 aA	2.7 bA	47 A	0.09 bA	0.12 bA	0.20 bA
CV (%)		1.9	2.7	8.6	-	5.5	7.4	17.3	8.3	13.0	19.1	13.3
								LVAd				
BL	50%	5.1 B	4.4 B	2.6 A		1.8 aB	0.6 b	12.5 aB	50 B	0.37 aB	0.44 bB	0.48 aB
EL	50%	5.1 B	4.3 B	2.7 A		1.5 bB	0.9 a	10.0 aB	47 B	0.34 aB	0.56 aB	0.50 aB
CL	50%	5.1 B	4.3 B	2.6 A	0.0	1.4 bB	0.8 a	3.1 bA	46 B	0.07 bA	0.09 cB	0.18 bA
BL	70%	5.4 A	4.9 A	2.2 B		2.2 aA	0.7 b	28.2 aA	58 A	0.52 aA	0.61 bA	0.73 aA
EL	70%	5.2 A	4.7 A	2.5 B		1.6 bA	0.9 a	22.0 aA	51 A	0.55 aA	0.67 aA	0.65 aA
CL	70%	5.5 A	4.6 A	2.3 B		1.5 bA	1.0 a	4.0 bA	53 A	0.11 cA	0.13 cA	0.15 bA
CV (%)		3.2	3.8	9.4	-	11.0	15.6	29.3	7.0	12.8	12.2	14.9

Averages were presented for non-significant treatments; Averages followed by the same letter do not differ among themselves by Tukey test at $p < 0.05$; Lowercase letters compare liming sources in the same dose and capital letters compare doses in the same liming source; CV - coefficient of variation.

Table 5

Calcium, Mg, S, N, and Ni leaf content and shoot dry weight in maize and soybean plants cultivated in Typical Red Dystrophic Latosol (LVd) and Typical Red-Yellow Dystrophic Latosol (LVAd) soils, after application of the blended limestone (BL), enriched limestone (EL), and commercial limestone (CL), in doses equivalent to reach 50% and 70% of soil base saturation (V%).

Treatments		Leaf content					Shoot dry weight
Liming source	Doses	Ca	Mg	S	N	Ni	g per plant
		g kg⁻¹				mg kg⁻¹	
				Maize plants			
				LVd			
BL	50%	3.0 a	2.9 B	1.6 a		1.0 aB	
EL	50%	1.5 b	2.3 B	1.4 a		1.1 aB	
CL	50%	1.8 b	2.9 B	1.0 b	24.4	0.2 bB	20.5
BL	70%	3.0 a	3.8 A	2.1 a		1.3 aA	
EL	70%	2.0 b	3.3 A	1.8 a		1.2 aA	
CL	70%	1.8 b	3.5 A	1.1 b		0.5 bA	
CV (%)		19.9	26.7	19.9	10.9	12.5	11.2
				LVAd			
BL	50%	2.2 a	2.6 B	1.9 a		1.1 aB	
EL	50%	1.7 b	2.9 B	2.0 a		1.2 aB	
CL	50%	1.6 b	3.7 B	1.5 b	24.2	0.1 bB	23.8
BL	70%	2.4 a	3.1 A	2.5 a		1.6 aA	
EL	70%	1.8 b	4.2 A	2.5 a		1.6 aA	
CL	70%	1.7 b	4.0 A	1.3 b		0.2 bA	
CV (%)		21.1	23.1	19.3	8.3	16.4	10.8
				Soybean plants			
				LVd			
BL	50%	12.0 aB	2.9 bB	2.3 a		1.3 bB	
EL	50%	9.0 bB	4.0 aB	2.0 a		1.7 aB	
CL	50%	9.5 bB	3.7 aB	1.8 b	50.6	0.4 cB	13.1
BL	70%	15.5 aA	3.9 bA	2.3 a		1.6 bA	
EL	70%	11.6 bA	4.7 aA	2.2 a		1.8 aA	
CL	70%	9.8 bA	4.3 aA	1.9 b		0.6 cA	
CV (%)		12.6	14.2	8.5	7.6	17.8	17.8
				LVAd			
BL	50%	12.6 a	4.9 b	2.4 a		1.5 aB	
EL	50%	10.8 b	5.6 a	2.4 a		1.6 aB	
CL	50%	10.7 b	6.2 a	2.1 b	55.9	0.1 bB	19.9
BL	70%	14.5 a	4.5 b	2.5 a		1.8 aA	
EL	70%	11.7 b	5.3 a	2.5 a		1.8 aA	
CL	70%	9.6 b	6.0 a	1.8 b		0.3 bA	
CV (%)		13.4	14.5	18.1	6.9	18.6	14.6

Averages were presented for non-significant treatments; Averages followed by the same letter do no differ among themselves by Tukey test at p < 0.05; Lowercase letters compare liming source in the same doses and capital letters compare doses in the same liming source; CV - coefficient of variation.

Highlights

- Feasible and sustainable technology for use of petroleum coke combustion ashes.
- New use of by-product in agriculture.
- Positive effects on soil properties and plant physiology.
- Supply of Ni micronutrient to plants, which improves N metabolism.

Artigo redigido conforme a norma do periódico científico *Journal of Cleaner Production* (versão submetida)

ARTIGO 2 – Short-term nickel residual effect in cultivated fields: Ni-enriched soil acidity amendments promote soybean plants growth and safe soil-Ni levels

Bruna Wurr Rodak [a], Douglas Siqueira Freitas [a], Leonardo Franco Bernardes [a], Geraldo Jânio Eugênio de Oliveira Lima [b], Guilherme Lopes [a], André Rodrigues dos Reis [c], Joachim Schulze [d], Luiz Roberto Guimarães Guilherme [a, *]

[a] Department of Soil Science, Federal University of Lavras, 3037, Lavras, Minas Gerais, CEP 37200-000, Brazil
[b] Agriculture and Environmental Technology Center, Alto do Córrego, Lindolfo Garcia St., 1,000, Paracatu, Minas Gerais, CEP 38600-000, Brazil
[c] School of Sciences and Engineering, São Paulo State University, Tupã, São Paulo, CEP 7602-496, Brazil
[d] Department of Crop Science, University of Goettingen, Carl-Sprengel-Weg 1, 37075, Goettingen, Germany
* Corresponding author. guilherm@dcs.ufla.br

Abstract

Nickel (Ni) fertilization is emerging in agriculture and has shown many beneficial effects on plant growth and yield. Taking into account that soil acidity amendments (SAA) are commonly used in tropical soils to adjust pH and that Ni availability in these soils is usually low, enriching SAAs with Ni may be advantageous not only in neutralizing soil acidity but also in providing uniform distribution of Ni in soils. Crops fertilization with this element has been performed without scientific criteria, which increases the risk of negative environmental impacts due to the uncertainty of safe levels. This study evaluated the short-term effects of Ni-application on soybean growth and on soil attributes, in field studies using three sources of SAAs – two enriched with Ni (Ni-rich mining by-product and Ni-salt) and a commercial SAA. Besides neutralizing soil acidity and increasing soil base saturation, the tested Ni-enriched sources were effective in providing Ni to the soil as well as safe Ni levels in soybean plants. A one-time Ni application resulted in Ni optimal levels in the first cropping season, enhancing grain yield by up to 658 kg ha^{-1}, while also improving N metabolism in soybean plants. Small residual effects of Ni levels were observed in the second year, yet yield gains were no longer observed, as soil available Ni concentrations decreased

to sub-optimal levels. Nickel-levels in the soil and in soybean grains were far below the safe guidelines for agricultural soils worldwide and for human intake. Thus, the application of Ni-enriched SAAs is a viable and sustainable technology that caused no negative impacts for the environment, bringing benefits for both, agricultural and mining sectors. Our findings also suggest that this micronutrient may require a year-to-year adjustment via Ni-fertilization, while total Ni concentration in the soil should be monitored over the cropping seasons.

Keywords: liming, Ni-fertilizer, petroleum coke ash, by-product, SDG12, plant-available Ni, tropical soil.

1 Introduction

'Ensure sustainable consumption and production patterns' is a key goal (SDG12) of the 2030 Agenda for Sustainable Development that aims to promote resource and energy use efficiency. This is especially relevant in agriculture, as substantial environmental impacts may occur during the food production process (United Nations, 2018). In order to reduce possible impacts that agricultural practices may offer to the environment, the development of new technologies for better soil/plant management, combining different management practices (e.g., reuse of by-products) is of great concern (Tilman et al., 2002; McBratney et al., 2005; Vanlauwe et al., 2010). In this scenario, plant nutrition and soil fertility have experienced a great progress, especially concerning the management of micronutrients in agricultural systems (Gupta and Gupta, 2005; Westfall et al., 2005; Brown, 2008). The recognition of nickel (Ni) as a micronutrient for crop plants was one of these important advances (Wood and Reilly, 2007). Adding Ni in fertilization programs may increase yield per unit time and land, minimizing expansion of cultivated area by intensification of agricultural systems (Sengar et al., 2008; Liu et al., 2011; Yusuf et al., 2011), thus increasing sustainability.

The evidence of Ni role in plants was first reported by Dixon et al. (1975), who demonstrated that this element was present in the urease active site. Nickel essentiality was further evidenced years later, when leguminous plants were cultivated under Ni depletion and had a toxic accumulation of urea on leaflet tips (Eskew et al., 1983, 1984). Then, Brown et al. (1987) demonstrated the Ni essentiality to non-leguminous plants. Growing these plants with varying N sources, they showed that no viable seeds were produced under Ni absence after three generations. Beside its function as a urease activator, promoting the

hydrolysis of urea into ammonia and carbon dioxide (Witte, 2011; Polacco et al., 2013), Ni is also a constituent of NiFe-hydrogenase, an enzyme that catalyzes the oxidation of molecular hydrogen in protons and electrons during the biological N_2 fixation in leguminous plants (Shafaat et al., 2013; Bagyinka, 2014). The oxidation of hydrogen gas recycles energy for nitrogenase, potentiating the N_2-fixation process as a whole (Ruiz-Argüeso et al., 2001). Therefore, Ni has essential role in N metabolism, which results in beneficial effects on plant growth and yield (Gerendas and Sattelmacher, 1997; Nyczepir and Wood, 2012; Kutman et al., 2014; Uruç Parlak, 2016).

In agriculture, Ni has been successfully applied as a mineral fertilizer in pecan (*Carya illinoinensis* [Wangenh.] K. Koch) and river birch (*Betula nigra* L.) (Wood et al., 2004a, 2004b, 2006; Ruter, 2005; Wood and Reilly, 2007; Nyczepir and Wood, 2012; Ojeda-Barrios et al., 2016). In these orchards, annual doses of 10 to 100 mg of Ni L^{-1} have been applied via leaf sprays. However, in other crop species, as soybean (*Glycine Max* [L.] Merrill) – one of world's major crops – studies evaluating Ni fertilization strategies are still incipient. In fact, for this crop plant, due to the lack of data associated with Ni benefits for plant growth and yield, farmers have been applying this micronutrient without scientific criteria, i.e., neither accurate nor safe doses are always employed. Such application may increase the risks of negative environmental impacts for both, the development of plants and human intake of Ni-rich food.

Nickel fertilization is used and required to increase Ni available concentrations in the soil, which are usually low, ranging from 0.1 to 1.0 mg kg^{-1} in natural and agricultural soils, with the exception of ultramafic regions and contaminated sites (Gil et al., 2004; Cancela et al., 2005; Jaworska et al., 2013; Dąbkowska-Naskręt et al., 2014; Rodak et al., 2015). According to Freitas et al. (2018), sub-optimal levels of this micronutrient in soils impose Ni-deficiency in soybean genotypes, even with no occurrence of visual deficiency symptoms. Also, special attention must be given to the fate of Ni in tropical soils, which are acidic and frequently Ni-deficient (Rodak et al., 2015).

Liming is a crucial soil management strategy for tropical soils, still it may decrease even more the Ni availability of soils (Ma et al., 2013; Zhang et al., 2015). In this scenario, the application of soil acidity amendments (SAA) that could correct soil acidity while at the same time provide adequate Ni amounts may be an interesting and advantageous approach in tropical agroecosystems. Combining liming with Ni fertilization using only one agricultural product is relevant to save time and reduce costs (Rodak et al., 2018). In addition to that,

taking into account that SAAs are usually required in high doses, the distribution of Ni coming from these products would result in a more homogeneous and uniform application of this micronutrient in all agricultural areas, thus improving crop yields and nutrient use efficiency (Fageria and Nascente, 2014; Lopes and Guilherme, 2016).

New emerging alternative Ni sources, especially by-products, seem to fit best for the tropics. In reality, Rodak et al. (2018) have recently shown that petroleum coke ashes – by-products of mining industries – could be perfectly suitable for such circsumstances, as they have a great capacity in reducing soil acidity and in providing Ni to plants. Yet, these authors emphasized that a relevant step concerning studies assessing the application of Ni in agriculture is not only the definition of ideal Ni sources, but also the evaluation of their residual effects, in order to maximize their benefits to soils, plants and the environment.

This study aimed to evaluate short-term effects of Ni-application on soils and on field-grown soybean plants, focusing on environmental and human-intake safety by using different sources of Ni-rich SAAs. With that we hope to foster the optimization of management practices while at the same time developing adequate Ni-fertilization, thus improving sustainability in agriculture, an action in accordance with SDG12 (Ensure sustainable consumption and production patterns) of the 2030 Agenda for Sustainable Development.

2 Material and methods

2.1 Experimental design and treatments

In order to evaluate the impact of applying SAAs enriched with Ni in providing this micronutrient to plants, as well as their residual effects, we carried out studies in soybean cultivated under field conditions in two cropping seasons.

The first crop took place from November 2015 till May 2016. The plots were of 15 m^2 (6 lines of 6.25 m, equally spaced by 0.4 m), set in a randomized blocks design and distributed in a factorial scheme with 3 sources x 2 doses, in four replicates. The sources of Ni were: 1) crushed limestone enriched with a Ni-rich by-product coming from a mining industry (hereafter called L+B); 2) crushed limestone enriched with a Ni salt (L+S); and, 3) crushed limestone alone, i.e., no Ni supplementation, used as a control (L) (Table 1). Since availability of nutrients is directly affected by soil pH, the sources were applied before soybean cultivation in two doses, aiming to increase the soil base saturation (V) to 1) 50% (low) and

2) 70% (high). These two levels of liming provided 2 and 3 kg of Ni ha^{-1}, respectively, for treatments where Ni was present.

The second crop was took place from November 2016 till May 2017, right after a half-year period as a fallow field. Although the experimental design was the same as mentioned for the first cropping season, in this second year no treatment was added to the system. This experiment was carried out to verify residual effects of the Ni previously applied.

2.2 Description of the experimental site

Field trials were conducted in a farm located in Coromandel, Brazil (Figure 1), at an altitude of 1,152 m. The region's climate, according to the Köppen-Geiger classification, is described as tropical wet and dry (Aw), with an average temperature of 25.8°C (highest temperature of 33.9°C and lowest temperature of 17.8°C) and an average annual precipitation of 1,458 mm.

The soil where the experiments were located was classified as Typical Red Dystrophic Latosol (Embrapa Solos, 2013), which corresponds to an Oxisol, according to the Soil Taxonomy (Soil Survey Staff, 1999). This area was left unplowed and unseeded for 10 years before the experiment implementation, being considered a fallow field. Physicochemical properties of soil before treatments application are shown in Table 2.

2.3 Soil fertilization and pH adjustment

To correct the soil acidity (soil pH) before the first crop, SAAs used in this study were manually incorporated down to a 20-cm depth. No lime was applied in the second crop. The treatment with Ni salt was enriched with 400 mg kg^{-1} of Ni in the form of $NiSO_4.6H_2O$ (L+S) to match the same Ni amount applied in the SAA with the by-product (L+B). Details regarding the Ni-enriched by-product can be found in Rodak et al. (2018).

In both soybean cropping seasons, soil fertilization was performed by application of 120 kg ha^{-1} of P_2O_5 ($NH_4H_2PO_4$), 72 kg ha^{-1} of K_2O (KCl), 6 kg ha^{-1} of Mn ($MnCl_2.4H_2O$), 4 kg ha^{-1} of Zn ($Zn[NO_3]_2.6H_2O$), 1.5 kg ha^{-1} of B (H_3BO_3), 0.5 kg ha^{-1} of Cu ($CuSO_4.5H_2O$), 25 g ha^{-1} of Mo ($[NH_4]_6Mo_7O_{24}.4H_2O$) (via seed), and 3 g ha^{-1} of Co ($CoN_2O_6.6H_2O$) (via seed). Additional application of 30 kg ha^{-1} of S ($CaSO_4.2H_2O$) was performed only for treatments L+S and L, since the treatment L+B already contained 6% of S coming from the by-product. Calcium

and Mg were supplied by the limestone in all treatments (Table 1). For N supply, soybean seeds (cultivar M8210 IPRO) were inoculated with N_2-fixing bacteria (*Bradyrhizobium japonicum* – SEMIA 5079 and 5080 strains, containing 10^9 mL^{-1} colony-forming units).

2.4 Plant analyses

To assess the effect of Ni provided by SAAs in plant nutritional status and N metabolism, the leaves and nodules of five soybean plants per plot were collected at the flowering stage (R1-R2) in both agricultural years. Plant samples, inside each year, were pooled and divided into homogenous sub-samples for analysis. The nutritional status of grains and soybean yield was assessed by harvesting the two central lines of soybean in each plot, excluding 0.5 m the end of each line, when pods have reached full maturity (R8). Phenological stages were defined according to Fehr and Caviness (1977).

2.4.1 Assessment of Ni concentration

Nickel concentration was determined in the third fully expanded leaf (from top to bottom), in the medium-large size nodules (> 3.5 mm^2), and in soybean grains. Samples were dried at 60 °C for 48 h. Afterwards, 0.3 g of dried samples were digested in a closed-vessel microwave system (CEM Mars 5, USA) using 65% nitric acid and 30% hydrogen peroxide prior to analysis. The Ni determination in samples was performed in an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Spectro Cirus, Germany). Certified reference materials were used for quality assurance (QA) and quality control (QC) protocols. The detection limit for Ni measurements was 0.15 mg kg^{-1}, thus, Ni concentrations below this value were considered as not detectable and so not used.

2.4.2 Estimation of N-urea metabolism

In order to access the main steps of N-urea metabolism – a pathway very affected by Ni in plants – urease activity, urea concentration, and ammonia concentration were evaluated in soybean plants by analyzing the fourth fully expanded leaf (from top to bottom).

For determining the leaf urease activity, 0.2 g of fresh weight (FW) was processed as previously described by Hogan et al. (1983). The enzyme activity

was estimated in a benchtop spectrophotometer (Shimadzu UV-1280, Japan) at 625 nm absorbance.

Leaf urea concentration was measured in 0.5 g of FW following the procedure proposed by Kyllingsbæk (1975). Urea was quantified by colorimetry (color intensity) at 540 nm absorbance.

Leaf ammonia concentration was determined in an extract obtained by centrifugation of 1 g of FW in 10 mL of MCW solution (60% [v/v] methanol, 25% [v/v] chloroform, and 15% [v/v] water) according to McCullough (1967). The ammonia quantification was performed by colorimetry at 630 nm absorbance.

2.4.3 Determination of biological N_2 fixation

Effects of Ni fertilization in N_2-fixation process were assessed by quantifying the concentration of ureides (allantoin and allantoic acid) in soybean leaves – which are the main forms of N transportation from the nodules to plant shoot – and by measuring the nitrogenase activity in the root nodules.

Total ureide concentrations were estimated in the fourth fully expanded leaf (from top to bottom) according the methodology described by Vogels and Van Der Drift (1970). The extract was obtained from 1 g of FW in MCW solution, as presented to leaf ammonia. Leaf ureides were determined by colorimetry at 535 nm absorbance.

Nitrogenase activity was determined in root nodules using the acetylene reduction assay adapted by Hardy et al. (1968). The enzyme activity calculation was performed by quantifying the production of ethylene by nodules in sealed vials using a gas chromatographer (Shimadzu GC-2010 Plus, Japan) equipped with an 80/100 Porapak N (Supelco, USA).

2.4.4 Grain yield evaluation

After harvesting, soybean grains were weighted for determining the grain yield. The grain moisture was determined with an automatic measuring device (Gehaka G650i, Brazil), and grain yield was normalized to 13% moisture.

2.5 Soil analyses

To assess the effect of applying the treatments on soil properties in both cropping years, just after soybean harvesting, soil samples were taken from the

two central lines from the 0-20 and 20-40 cm depths. For that, six subsamples were collected in each plot, then, homogenized, obtaining one sample per plot, which was submitted to soil testing analysis.

2.5.1 Determination of pH and base saturation

The effectiveness of the SAA sources to correct soil acidity was analyzed by measuring pH and base saturation of the soil.

Measurements of pH were performed in an extract containing 10 g of air-dried soil in 25 mL of water, after 5 min shaking and 30 min resting. Measuring was carried out by glass-electrode method using a benchtop pH meter (Hanna HI 2221, Brazil).

Soil base saturation (V) was calculated dividing the sum of basis (Ca^{2+}, Mg^{2+}, and K^+) by the cation exchange capacity (sum of basis + potential acidity [H + Al]), according to Embrapa Solos (2011). Calcium and Mg were extracted using 1 mol L^{-1} KCl solution and measured by an atomic absorption spectrometer. Potassium was extracted with a Mehlich-1 solution (0.05 M HCl and 0.0125 M H_2SO_4) and analyzed by flame photometry. Potential acidity was measured by titration using $Ca(C_2H_3O_2)_2$ pH 7.0 solution. All soil attributes were determined following the standard methodology recommended by Embrapa Solos (2011).

2.5.2 Determination of total and available Ni concentration

Total Ni concentration was determined following soil digestion in a closed-vessel microwave system using nitric acid and hydrogen peroxide, according to the USEPA Method 3050-B (USEPA, 1996). For quantifying the available Ni concentration, 5 g of grinded-dried soil were added to vessels containing 50 mL of Mehlich-1 solution. Samples were shaken for 10 min at 200 RPM, and after 16-h resting, the extract was collected for Ni measurements (Mehlich, 1953).

Nickel concentration in both cases (total and available) was determined using ICP-OES. Certified reference materials were used for QA and QC protocols. Measurements below 0.1 mg kg^{-1} of Ni were considered as not detectable and so not used.

2.6 Statistical analysis

Statistical analysis was performed through a two-way analysis of variance (F-test). When significant, means were compared by the Tukey´s test ($p < 0.05$). Statistical analyses were performed separately for each cropping season.

3 Results

3.1 Soybean grain yield

After application of the SAAs into soil in the first cropping season, the Ni-enriched sources, L+B and L+S, increased soybean grain yield in comparison with the control (L). Although the higher dose (V = 70%) reached greater yields, gains due to Ni supply were higher when the lower dose (V = 50%) was applied. In this scenario, L+B increased soybean yield by 658 kg ha^{-1} (~ 11 bags per hectare, considering a 60-kg bag of soybean) and L+S resulted in additional 391 kg ha^{-1} (~ 7 bags per hectare), both in comparison with control. This increase in grain yield was no longer observed in the second cropping season, irrespectively of the applied doses and sources (Fig. 2).

From the first to the second agricultural year, average values of soybean yield were slightly different. Considering the average values obtained from all treatments, when the lower dose was applied, the grain yield was 3,932 in the first and 4,166 kg ha^{-1} in the second year. On the other hand, when the higher dose was applied, yield decreased from the first to the second agricultural year, from 4,543 to 4,227 kg ha^{-1}, respectively (Fig. 2).

3.2 Nitrogen metabolism in soybean plants

In the first crop, N metabolism was enhanced in soybean plants in response to Ni exposure in both doses. The Ni-enriched SAAs increased urease activity by 43% and also improved the concentration of compounds involved in the N-urea metabolism, increasing ammonia by 31% and decreasing urea by 36%, when compared with the pure limestone. Moreover, the N_2-fixation process was intensified when Ni sources were applied in the soil, with an increase of 133% in nitrogenase activity and of 23% in ureide concentration (Table 3). Because the grain yield did not change in the second cropping season, N metabolism was not

evaluated, since the main goal of these measurements was to explain the Ni effects in soybean yield.

3.3 Nickel concentration in plant tissues

Irrespectively of the applied doses, the application of Ni-enriched SAAs resulted in a higher Ni concentration in soybean leaves when compared with the control. The plants cultivated under one-time application of SAAs, in the first cropping season, showed an increase of 223% in leaf Ni concentration, considering an average of 0.47 mg kg^{-1} in the control and 1.52 mg kg^{-1} in the Ni-enriched SAAs treated plants. In the second cropping season, the leaf Ni concentration increased by 163%, with an average of 0.19 mg kg^{-1} of Ni in the control and 0.50 mg kg^{-1} of Ni in treatments with the enriched SAAs. Although Ni effect has been kept in both agricultural years, Ni concentration in leaf was notably reduced from the first to the second year by 193% (average value, irrespectively of treatments) (Table 4).

For the first cropping season, Ni concentration in soybean grains followed the same trend reported for Ni concentration in leaves, being 17% higher in grains treated with Ni-enriched sources compared with the control (average values, 0.94 and 1.10 mg kg^{-1}, respectively). However, differences for grain Ni concentrations were not detected in the second cropping season, presenting an average value of 0.52 mg of Ni kg^{-1} in grains. Such value is approximately half of the average Ni concentration found in the grains of the first cropping season (disregarding the effect of the treatments) (Table 4).

Among the different plant tissues evaluated, Ni concentration in root nodules was considerably more affected following the application of this micronutrient via SAAs. When the products were applied in the lower dose, the nodule Ni concentration increased by 144% (from 0.39 mg kg^{-1} in the control to an average of 0.95 mg kg^{-1} in the Ni-enriched SAAs), while in the higher dose, an increasing of 332% was verified (from 0.41 mg kg^{-1} in the control to an average of 1.77 mg kg^{-1} of Ni in the enriched sources). In the second year, the effect of treatments was no longer observed (Table 4).

3.4 Changes in soil acidity and soil chemical properties

The tested SAAs were equally efficient in increasing soil pH, in both soil depths, i.e., 0-20 cm and 20-40 cm. Following soybean harvest in the first year,

the high dose resulted in an average pH of 6.0 in the soil upper layer and 5.9 in the lower layer, while the low dose had an average pH of 5.6 in both depths. After the second crop, there was no longer a difference between the doses, with an average pH of 5.9 in the upper layer and 5.8 in the lower layer. Chronologically, it is noteworthy that the lower dose was not sufficient to correct the soil acidity completely in the first cropping year, so that it demanded one year more to match the pH observed in the higher dose (Table 5).

Soil base saturation followed the same trend observed for soil pH values, i.e., the application of treatments increased soil base saturation, reaching values close to the expected (50 and 70% in the lower and higher doses) (Table 5).

It has to be mentioned that, macro- and micronutrient amounts applied into the soil were enough to attend e the soybean plants demand, thus there were not evidences of deficiencies to affect plant development (data not shown).

3.5 Total and available Ni concentration in the soil

During the harvest of soybean in the first year, available concentration of Ni in the soil increased following the application of Ni-enriched SAAs. Available concentration of Ni found for treatments L+B, L+S, and control were up to 0.45, 0.65, and 0.31 mg of Ni kg^{-1}, respectively. This effect was more prominent in the higher dose and very similar among the soil depths. The Ni concentration was significantly decreased in the second agricultural year – stating a weak residual effect of Ni, in the upper soil layer – reaching values close to 0.36 mg kg^{-1} in Ni enriched SAAs, in comparison with 0.24 mg kg^{-1} in the control, irrespectively of the applied doses. For soil samples collected from 20-40 cm depth, where Ni residual effects were not verified, the average value for available Ni concentration was 0.22 mg kg^{-1} (Fig. 3).

Considering all cropping seasons, sources, doses, and depths, the minimum (0.19 mg kg^{-1}) and maximum (0.65 mg kg^{-1}) values of available Ni in the soil did not range far apart from the initial value reported before cultivation (0.24 mg kg^{-1}) (Fig. 3).

As reported for available Ni, total Ni concentrations also increased in the first cropping season. In this year, irrespectively of the soil depth, the Ni-enriched SAAs resulted in a total Ni concentration up to 5.7 mg kg^{-1} in comparison with up to 3.9 mg kg^{-1} in the control. This effect was more pronounced in the higher dose. In the second soybean crop, the total concentration of this micronutrient had an opposite behavior from the Ni available, i.e., increasing from the first to the

second year. Therefore, the residual application increased the total concentration of Ni up to 6.5 mg kg^{-1} in enriched SAAs, in comparison with 4.0 mg kg^{-1} in the control. In this case, an effect of the doses was no longer observed (Fig. 4). It should be emphasized, however, that the slight increase of total Ni concentration in the soil in the second crop season can be due to the natural variability of the method of determination.

4 Discussion

The application of SAAs caused changes in some soil properties in both cropping seasons, mainly by increasing soil pH and base saturation through the soil profile, irrespectively of the applied doses (Table 5). Joris et al. (2013) and Crusciol et al. (2016) observed that the application of acidity amendments is able to neutralize the soil acidity, besides adding Ca and Mg and reducing exchangeable Al in soil surface. These effects evidence the importance of SAAs in creating a fertile environment for the proper growth and development of soybean plants. The residual effect observed in soil pH may be caused by the effective neutralizing power of the SAAs tested, in average equal to 79% (Table 1). We believe that the slower reactive parts in the limestone continued naturally reacting in the soil, even after the harvest of the first crop.

Nickel supply, associated with the capacity of SAAs in stabilizing soil acidity, brought even more benefits. The first effect of Ni fertilization in the soybean plants was observed during first cropping season, when the SAAs application significantly promoted the concentration of Ni readily available to plants. In addition, soybean plants had an increased concentration of this micronutrient in leaves and grains (Table 4), thus indicating that free Ni in the soil pool was absorbed strictly following its availability (Fig. 3). Using isotopic exchange kinetics, Echevarria et al. (2006) corroborated our data, showing the importance of creating a pool of exchangeable forms of this micronutrient in the soil for adequate mineral nutrition of plants.

After absorption, Ni was readily assimilated into plant metabolic processes, especially in some pathways related with N metabolism. In this study, urease, a key-enzyme of N-urea metabolism, had its activity increased by 43% in soybean leaves under Ni-enriched SAA treatments (Table 3). As observed by Kutman et al. (2013), soybean seeds enriched with Ni, as well as the external supply of this micronutrient, influenced leaf urease activity, which was progressively enhanced by higher Ni levels. In our study, the improved urease

activity allowed soybean plants to metabolize efficiently a high fraction of leaf urea, thus increasing the ammonia pool up to 31%, which is readily available for the metabolism in leaf tissues (Table 3). Recently, Freitas et al. (2018) also observed the beneficial effect of Ni fertilization in the ammonia synthesis, so that, Ni fertilized field-grown soybean genotypes had a higher production of this metabolic compound. Bai et al. (2006, 2007), studying the effect of Ni in the synthesis of amino acids originated by ammonia degradation, verified that Ni fertilization avoided the blocking of N assimilation routes in Ni deficient pecan plants. This happens due to the disruption of free amino acids conversion to other N compounds, i.e., glycine, valine, isoleucine, tyrosine, tryptophan, arginine, histidine, and glutamic acid. In addition to these gains in N-urea pathway, our data also have showed that Ni supply affected the biological N_2-fixation process. With the application of this micronutrient, the enzyme responsible for processing atmospheric N_2 into assimilation forms, the nitrogenase, had its activity increased by 133%, while the intermediate metabolite from this process, the ureides, also increased by 23% (Table 3). According to Lavres et al. (2016), soybean plants have a boost in N_2-fixation process when they are fertilized with Ni, probably due to a higher activity of NiFe-hydrogenase.

Associated with this boost in many N metabolism steps, it was observed that Ni fertilization promoted grain yield up to 658 kg ha^{-1}, which is equivalent to ~ 11 bags (1 bag equivalent to 60 kg) of soybean grains (Fig. 2). Freitas et al. (2018), studying a wide range of soybean genotypes, reported that yield gains due to Ni fertilization can be expected only when N assimilation is potentialized as a whole, when ammonia and urease activity in leaf are increased, associated with a decrease in leaf urea concentration. Kutman et al. (2013) also reported a boost in urea metabolism due to Ni application, resulting in a better soybean growth and production. According to Lavres et al. (2016), gains in grain yield are strictly related to the highest efficiency of N_2-fixation process. Data from the present study suggest that the higher N metabolism activation can explain the higher soybean yield.

Still discussing the gains in production of grains due to Ni fertilization, an interesting point was verified under application of the low dose of SAAs in the first crop. In this case, the Ni supply allowed soybean plants to overcome, at least in part, the very restrictive initial yield limitation imposed by incomplete correction of the soil acidity and the concentration of bases (Ca and Mg) lower than ideal. This fact can be clearly verified by the higher yield of soybean plants that have received Ni fertilization in contrast with non-fertilized ones (Fig. 2 and

Table 5). Under this condition, besides the N metabolism, Ni may have promoted some biotic/abiotic stress regulators during the development of plants. Fabiano et al. (2015) have pointed out that Ni plays an important role in plant antioxidant metabolism, performing an important step in the degradation of cytotoxic compounds that are naturally produced during abiotic stress conditions, such as nutritional limitations. Moreover, even though few studies have been performed using agricultural crops, positive effects of Ni on plant-biotic interactions for hyperaccumulator plants are well described elsewhere (Poschenrieder et al., 2006), and it may be contributing to yield responses of Ni fertilization in soybean as well. Even when proper growth conditions were reached by application of the high SAAs dose, a smaller, but clear, effect of the Ni in soybean plants was still found (Fig. 2 and Table 5). Similar results were reported by Macedo et al. (2016), assessing the effect of soil base saturation and Ni amendments in greenhouse-grown soybean plants. These authors verified that soybean plants showed a better physiological performance when growing in higher base saturation associated with an extra supply of Ni. These results reveal that the base saturation of soil is a key point to be established in order to reach the optimal Ni supplementation for plants.

Despite these considerable effects in grain yield and N metabolism (Fig. 2 and Table 3), our data revealed that the residual effect of the applied Ni does not last for a long time, irrespectively of the tested Ni source. Nickel remained available in the soil solely during the first year of cultivation, i.e., after soybean harvest in the first cropping season the available Ni pool was gradually turned into non-assimilative forms by plants (Fig. 3). Previous studies regarding Ni aging may help to understand the Ni behavior in soil (Ponizovsky et al., 2008; Rajaie et al., 2008; Smolders et al., 2009; Ma et al., 2013; Zhang et al., 2015). These previous works reported an initial reaction, when part of the Ni is rapidly exchanged between soil solution and soil solid phases, followed by slow decreases in availability due to Ni changing into less labile forms. According to Eick et al. (2001), this fast-initial reaction can be attributed to precipitation and chemisorption phenomena, whereas the slow reaction is more related with micropore diffusion process and surface precipitation of a Ni-Al layered double-hydroxide (LDH). As observed by Fischer et al. (2007) and Arai (2008), the iron oxyhydroxides (goethite, hematite, and ferrihydrite) can readily sequester Ni(II) dissolved in the soil solution and reduce its activity, especially due to their large surface areas and abundance of metal-binding sites. In addition to that, Axe and Trivedi (2002) and Ponizovsky et al. (2008) have pointed out that these processes

are gradually intensified with Ni aging, being attributed mainly due to intraparticle surface diffusion. A significant fraction of the Ni may be incorporated into the crystalline structure of iron (hydr)oxides over time, forming very stable sorption sites via inner-sphere complexes by monodentate and bidentate mononuclear linkages (Ford et al., 1999; Arai, 2008). According to Ma et al. (2013), the extent and rate of Ni sorption onto soil compounds is strictly controlled by soil acidity, so that, increasing pH increases aging reactions. Reduction in Ni bioavailability with aging was also reported by Buekers et al. (2008). Moreover, these authors described that aging processes are intensified when small Ni amounts are applied to soils, such as the doses tested in our study. Taking into account that tropical soils contain substantial amounts of Fe and Al oxyhydroxides (Schaefer et al., 2008), these soils can immobilize a high quantity of Ni easily. Moreover, tropical soils are also rich in low-activity 1:1 clay minerals as kaolinite (Schaefer et al., 2008), which can further intensify Ni retention processes, decreasing its activity. This is because Ni sequestration can also occur by the formation of secondary precipitates in aluminosilicate minerals (Eick et al., 2001; Arai, 2008). As reported by Nachtegaal and Sparks (2003) and McNear et al. (2007) in field soils, Ni can form both Ni-Al LDH surface precipitates and bidentate surface complexes on these minerals, becoming more recalcitrant over time. According to the previous discussion, it is clear that the residual effect of Ni in soils is low and this may indicate that an annual Ni fertilization should be considered.

Considering the residual amount of total Ni in the soil, i.e., Ni occupying the non-labile fractions of soil, no short-term ecotoxicological risks are expected. The maximum Ni concentration verified in this study was 6.5 mg kg^{-1} (Fig. 4), which is below the agricultural soil quality guideline of 30 mg kg^{-1} of Ni set by Brazilian regulations (CONAMA, 2009), and far below the values (mg of Ni kg^{-1}) established in China (40), Canada (45), and the European Union (50) for agricultural soils (Canadian Council of Ministers of the Environment, 2015; Tóth et al., 2016; Chen et al., 2018). Thus, the application of the tested doses, 2 and 3 kg ha^{-1} of Ni via SAAs cannot result in short-term ecotoxicological risks and can be considered environmentally safe. However, a long-term Ni fertilization study is required to verify its potentially accumulation to toxic levels in the soil profile.

With respect to Ni concentration in plant tissues, the maximum Ni concentration found in leaves, grains, and nodules were 1.55, 1.11, and 1.98 mg kg^{-1}, respectively (Table 4). Chen et al. (2009), Yusuf et al. (2011), and Sreekanth et al. (2013) reported values much higher in plant tissues to be considered as toxic for plants. For sensitive species, it is expected that only leaf Ni concentrations

higher than 10 mg kg^{-1} can cause toxicity, while for moderately tolerant species, this value can reach up to 50 mg kg^{-1}. Freitas et al. (2018), studying different soybean genotypes, have shown Ni concentrations ranging from 0.31 to 2.26 mg kg^{-1} in leaves and from 1.20 to 3.07 mg kg^{-1} in grains. These authors also reported the food safety of Ni fertilization. Simulating a restrictive scenario, a child would be able to have a daily intake higher than 100 g of soybean *in natura*, with no health risk. In our study, Ni values in grains were 2.8-fold lower than that observed by Freitas et al. (2018). Therefore, the daily intake of soybean grains could be even higher, 1,200 g of soybean grains (dry weight) per day for an adult (66.6 kg) and 280 g per day for children (15.4 kg) (for estimates using a reference dose for Ni of 0.02 mg kg^{-1} per day, calculated from a no-observed-adverse-effect level of 5.0 mg of Ni kg^{-1} per day). According to Do et al. (2007), the daily intake of *in natura* soybean grains is 2.5 ± 4.9 g (n = 708). In Asian countries – the largest soybean consumers – the daily intake of soybean and soy-related foods is 23.0 ± 18.2 g (Toyomura and Kono, 2002; Do et al., 2007; Katsuyama et al., 2009). These values confirm that Ni concentrations found for soybean grains in this study do not pose a threat to human health for direct consumption of grains.

Lastly, from an environmental point of view, achieving efficient and productive agricultural land use while conserving biodiversity is a global challenge (Tscharntke et al., 2012), which was reached in our study by applying Ni to soybean plants via the SAAs. The higher grain yield (Fig. 2) verified when Ni-enriched sources were applied may improve the soybean production chain as a whole, lowering production costs (Chen et al., 2014) and contributing to higher food security (FAO, 2006; Godfray et al., 2010; Curtis and Halford, 2014). Combining soil acidity correction with Ni fertilization in the same agricultural practice reduces the need of re-entering of machinery in crop fields due to a greater operational efficiency, resulting in time and money savings by farmers (Lopes and Guilherme, 2016). Moreover, this fact may also avoid a wasteful consumption of fossil fuels. Finally, using a by-product as a Ni-source with the same efficiency in adjusting soil pH and in supplying this micronutrient to plants is suggested to be a highly promising endeavor from an environmental perpective. The beneficial use of by-products in agriculture can substantially reduce waste generation and it is necessary to sustain the crop production in an eco-friendly way (Basu et al., 2009). In this way, our work can provide relevant and useful information for helping societies to achieve sustainable development in agriculture.

5 Conclusion

Nickel-enriched soil acidity amendments (SAA) – produced with a mining by-product or with a Ni salt – are a feasible and sustainable technology for application in agriculture, having the advantage of combining management practices such as neutralization of soil acidity and Ni supply to soybean plants. Still, due to benefits concerning sustainable consumption and production, we recommend the source derived from the by-product, since it is eco-friendly. Also, this source brings benefits for both, agricultural and mining sectors.

A one-time Ni application via SAAs in field-grown soybean plants reached optimal Ni levels in the first cropping season, resulting in higher grain yields and also improved N metabolism. Nickel had weak residual effect on the soil-plant system, no longer improving soybean productive in the second harvest. This fact was attributed to Ni sorption onto soil coloids, which renders Ni less available to plants over time. This fact suggest that Ni levels may demand a year-to-year adjustment via the addition of Ni-carrying fertilizers.

Regarding environmental safety, the Ni concentrations found in the soil and in soybean grains reached safe levels for agricultural soils and human ingestion. Yet, Ni-fertilization monitoring programs should be adopted to ensure the safe guidelines, mainly to evaluate the total levels of Ni in the soil.

Acknowledgements

References

Arai, Y., 2008. Spectroscopic evidence for Ni(II) surface speciation at the iron oxyhydroxides−water interface. Environ. Sci. Technol. 42, 1151–1156. doi:10.1021/es0719529

Axe, L., Trivedi, P., 2002. Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides. J. Colloid Interface Sci. 247, 259–265. doi:10.1006/jcis.2001.8125

Bagyinka, C., 2014. How does the ([NiFe]) hydrogenase enzyme work? Int. J. Hydrog. Energy 39, 18521–18532. doi:10.1016/j.ijhydene.2014.07.009

Bai, C., Reilly, C.C., Wood, B.W., 2007. Nickel deficiency affects nitrogenous forms and urease activity in spring xylem sap of pecan. J. Am. Soc. Hortic. Sci. 132, 302–309.

Bai, C., Reilly, C.C., Wood, B.W., 2006. Nickel deficiency disrupts metabolism of ureides, amino acids, and organic acids of young pecan foliage. Plant Physiol. 140, 433–443. doi:10.1104/pp.105.072983

Basu, M., Pande, M., Bhadoria, P.B.S., Mahapatra, S.C., 2009. Potential fly-ash utilization in agriculture: a global review. Prog. Nat. Sci. 19, 1173–1186. doi:10.1016/j.pnsc.2008.12.006

Brown, P.H., 2008. Micronutrient use in agriculture in the United States of America, in: Alloway, B.J. (Ed.), Micronutrient deficiencies in global crop production. Springer Netherlands, Dordrecht, pp. 267–286.

Brown, P.H., Welch, R.M., Cary, E.E., 1987. Nickel: a micronutrient essential for higher plants. Plant Physiol. 85, 801–803. doi:10.1104/pp.85.3.801

Buekers, J., Amery, F., Maes, A., Smolders, E., 2008. Long-term reactions of Ni, Zn and Cd with iron oxyhydroxides depend on crystallinity and structure and on metal concentrations. Eur. J. Soil Sci. 59, 706–715. doi:10.1111/j.1365-2389.2008.01028.x

Canadian Council of Ministers of the Environment. 2015. Canadian soil quality guidelines for the protection of environmental and human health: nickel (2015), in: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Cancela, R.C., González, A.P., Abreu, C.A., 2005. Total and extractable nickel and cadmium contents in natural soils. Commun. Soil Sci. Plant Anal. 36, 241–252. doi:10.1081/CSS-200043057

Chen, C., Huang, D., Liu, J., 2009. Functions and toxicity of nickel in plants: recent advances and future prospects. CLEAN - Soil Air Water 37, 304–313. doi:10.1002/clen.200800199

Chen, S., Wang, M., Li, S., Zhao, Z., Wen-di, E., 2018. Overview on current criteria for heavy metals and its hint for the revision of soil environmental quality standards in China. J. Integr. Agr. 17, 1–11. doi:10.1016/S2095-3119(17)61892-6

Chen, X., Cui, Z., Fan, M., Vitousek, P., Zhao, M., Ma, W., Wang, Z., Zhang, W., Yan, X., Yang, J., Deng, X., Gao, Q., Zhang, Q., Guo, S., Ren, J., Li, S., Ye, Y., Wang, Z., Huang, J., Tang, Q., Sun, Y., Peng, X., Zhang, J., He, M., Zhu, Y., Xue, J., Wang, G., Wu, L., An, N., Wu, L., Ma, L., Zhang, W., Zhang, F., 2014. Producing more grain with lower environmental costs. Nature 514, 486–489. doi:10.1038/nature13609

CONAMA - Conselho Nacional do Meio Ambiente, 2009. Resolução Nº 420 de 28 de dezembro de 2009. Resolução CONAMA Nº 420/2009 - "Dispõe

sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas." - Data da legislação: 28/12/2009 - Publicação DOU nº 249, de 30/12/2009. Diário Oficial da União, Poder Executivo, Brasília, pp. 81–84.

Crusciol, C.A.C., Artigiani, A.C.C.A., Arf, O., Carmeis Filho, A.C.A., Soratto, R.P., Nascente, A.S., Alvarez, R.C.F., 2016. Soil fertility, plant nutrition, and grain yield of upland rice affected by surface application of lime, silicate, and phosphogypsum in a tropical no-till system. Catena 137, 87–99. doi:10.1016/j.catena.2015.09.009

Curtis, T., Halford, N.G., 2014. Food security: the challenge of increasing wheat yield and the importance of not compromising food safety: wheat yield and food safety. Ann. Appl. Biol. 164, 354–372. doi:10.1111/aab.12108

Dąbkowska-Naskręt, H., Jaworska, H., Długosz, J., 2014. Assessment of the total nickel content and its available forms in the soils around cement plant Lafarge Poland. Int. J. Environ. Res. 8, 231–236. doi:10.22059/IJER.2014.712

Dixon, N.E., Gazzola, C., Blakeley, R.L., Zerner, B., 1975. Jack bean urease (EC 3.5.1.5). Metalloenzyme. Simple biological role for nickel. J. Am. Chem. Soc. 97, 4131–4133. doi:10.1021/ja00847a045

Do, M.H., Lee, S.S., Jung, P.J., Lee, M.H., 2007. Intake of fruits, vegetables, and soy foods in relation to breast cancer risk in Korean women: a case-control study. Nutr. Cancer 57, 20–27. doi: 10.1080/01635580701268063

Echevarria, G., Massoura, S.T., Sterckeman, T., Becquer, T., Schwartz, C., Morel, J.L., 2006. Assessment and control of the bioavailability of nickel in soils. Environ. Toxicol. Chem. 25, 643–651. doi:10.1897/05-051R.1

Eick, M.J., Naprstek, B.R., Brady, P.V., 2001. Kinetics of Ni (II) sorption and desorption on kaolinite: residence time effects. Soil Sci. 166, 11–17. doi:0038-075C/00/16601-11–17

Embrapa Solos, 2011. Manual de métodos de análise de solo, 2 ed. Embrapa Solos, Rio de Janeiro.

Embrapa Solos, 2013. Sistema brasileiro de classificação de solos, 3 ed. Embrapa, Brasília.

Eskew, D.L., Welch, R.M., Cary, E.E., 1983. Nickel: an essential micronutrient for legumes and possibly all higher plants. Science 222, 621–623. doi:10.1126/science.222.4624.621

Eskew, D.L., Welch, R.M., Norvell, W.A., 1984. Nickel in higher plants: further evidence for an essential role. Plant Physiol. 76, 691–693.

Fabiano, C.C., Tezotto, T., Favarin, J.L., Polacco, J.C., Mazzafera, P., 2015. Essentiality of nickel in plants: a role in plant stresses. Front. Plant Sci. 6, 1–4. doi:10.3389/fpls.2015.00754

Fageria, N.K., Nascente, A.S., 2014. Management of soil acidity of South American soils for sustainable crop production. Adv. Agron. 128, 221–275. doi:10.1016/B978-0-12-802139-2.00006-8

FAO - Food and Agriculture Organization, 2006. Plant nutrition for food security: a guide for integrated nutrient management, FAO fertilizer and plant nutrition bulletin. Food and Agriculture Organization of the United Nations, Rome.

Fehr, W.R., Caviness, C.E., 1977. Stages of soybean development. Iowa State University Cooperative Extension Service, Iowa.

Fischer, L., Brümmer, G.W., Barrow, N.J., 2007. Observations and modelling of the reactions of 10 metals with goethite: adsorption and diffusion processes. Eur. J. Soil Sci. 58, 1304–1315. doi:10.1111/j.1365-2389.2007.00924.x

Ford, R.G., Kemner, K.M., Bertsch, P.M., 1999. Influence of sorbate-sorbent interactions on the crystallization kinetics of nickel-and lead-ferrihydrite coprecipitates. Geochim. Cosmochim. Acta 63, 39–48. doi:10.1016/S0016-7037(99)00010-1

Freitas, D.S., Rodak, B.W., Reis, A.R., Reis, F.B., Carvalho, T.S., Schulze, J., Carneiro, M.A.C, Guilherme, L.R.G., 2018. Hidden nickel deficiency? Nickel fertilization via soil improves nitrogen metabolism and grain yield in soybean genotypes. Front. Plant Sci. 9. doi:10.3389/fpls.2018.00614

Gerendas, J., Sattelmacher, B., 1997. Significance of Ni supply for growth, urease activity and the concentrations of urea, amino acids and mineral nutrients of urea-grown plants. Plant Soil 190, 153–162. doi:10.1023/A:1004260730027

Gil, C., Boluda, R., Ramos, J., 2004. Determination and evaluation of cadmium, lead and nickel in greenhouse soils of Almería (Spain). Chemosphere 55, 1027–1034. doi:10.1016/j.chemosphere.2004.01.013

Godfray, H.C.J., Beddington, J.R., Crute, I.R., Haddad, L., Lawrence, D., Muir, J.F., Pretty, J., Robinson, S., Thomas, S.M., Toulmin, C., 2010. Food security: the challenge of feeding 9 billion people. Science 327, 812–818. doi:10.1126/science.1185383

Gupta, U.C., Gupta, S.C., 2005. Future trends and requirements in micronutrient research. Commun. Soil Sci. Plant Anal. 36, 33–45. doi:10.1081/CSS-200042962

Hardy, R.W.F., Holsten, R.D., Jackson, E.K., Burns, R.C., 1968. The acetylene-ethylene assay for N_2 fixation: laboratory and field evaluation. Plant Physiol. 43, 1185–1207. doi:10.1104/pp.43.8.1185

Hogan, M.E., Swift, I.E., Done, J., 1983. Urease assay and ammonia release from leaf tissues. Phytochemistry 22, 663–667. doi:10.1016/S0031-9422(00)86958-7

Jaworska, H., Bartkowiak, A., Różański, S., 2013. The influence of anthropogenically increased pH on the content and the mobility of nickel in arable soils in the surroundings of "Małogoszcz" cement plant. Soil Sci. Annu. 64, 15–19. doi:10.2478/ssa-2013-0003

Joris, H.A.W., Caires, E.F., Bini, A.R., Scharr, D.A., Haliski, A., 2013. Effects of soil acidity and water stress on corn and soybean performance under a no-till system. Plant Soil 365, 409–424. doi:10.1007/s11104-012-1413-2

Katsuyama, H., Arii, M., Tomita, M., Hidaka, K., Watanabe, Y., Tamechika, Y., Okuyama, T., Fushimi, S., Maeda, N., Higashimura, T., Fukunaga, M., Saijoh, K., 2009. Association between estrogen receptor α polymorphisms and equol production, and its relation to bone mass. Int. J. Mol. Med. 23, 793–798. doi:10.3892/ijmm_00000194

Kutman, B.Y., Kutman, U.B., Cakmak, I., 2014. Effects of seed nickel reserves or externally supplied nickel on the growth, nitrogen metabolites and nitrogen use efficiency of urea- or nitrate-fed soybean. Plant Soil 376, 261–276. doi:10.1007/s11104-013-1983-7

Kutman, B.Y., Kutman, U.B., Cakmak, I., 2013. Nickel-enriched seed and externally supplied nickel improve growth and alleviate foliar urea damage in soybean. Plant Soil 363, 61–75. doi:10.1007/s11104-012-1284-6

Kyllingsbæk, A., 1975. Extraction and colorimetric determination of urea in plants. Acta Agric. Scand. 25, 109–112. doi:10.1080/00015127509436239

Lavres, J., Franco, G.C., Câmara, G.M.S., 2016. Soybean seed treatment with nickel improves biological nitrogen fixation and urease activity. Front. Environ. Sci. 4, 1–11. doi:10.3389/fenvs.2016.00037

Liu, G., Simonne, E.H., Li, Y., 2011. Nickel nutrition in plants. Hortic. Sci. 1191, 1–5.

Lopes, A.S., Guilherme, L.R.G., 2016. A career perspective on soil management in the Cerrado region of Brazil. Adv. Agron. 137, 1–72. doi:10.1016/bs.agron.2015.12.004

Ma, Y., Lombi, E., McLaughlin, M.J., Oliver, I.W., Nolan, A.L., Oorts, K., Smolders, E., 2013. Aging of nickel added to soils as predicted by soil pH and time. Chemosphere 92, 962–968. doi:10.1016/j.chemosphere.2013.03.013

Macedo, F.G., Bresolin, J.D., Santos, E.F., Furlan, F., Silva, W.T.L., Polacco, J.C., Lavres, J., 2016. Nickel availability in soil as influenced by liming and its role in soybean nitrogen metabolism. Front. Plant Sci. 7, 1–12. doi:10.3389/fpls.2016.01358

McBratney, A., Whelan, B., Ancev, T., Bouma, J., 2005. Future directions of precision agriculture. Precis. Agric. 6, 7–23. doi:10.1007/s11119-005-0681-8

McCullough, H., 1967. The determination of ammonia in whole blood by a direct colorimetric method. Clin. Chim. Acta 17, 297–304. doi:10.1016/0009-8981(67)90133-7

McNear, D.H., Chaney, R.L., Sparks, D.L., 2007. The effects of soil type and chemical treatment on nickel speciation in refinery enriched soils: a multi-technique investigation. Geochim. Cosmochim. Acta 71, 2190–2208. doi:10.1016/j.gca.2007.02.006

Mehlich, A., 1953. Determination of P, Ca, Mg, K, Na, and NH_4. North Carolina Soil Test Division, Raleigh.

Nachtegaal, M., Sparks, D.L., 2003. Nickel sequestration in a kaolinite-humic acid complex. Environ. Sci. Technol. 37, 529–534. doi:10.1021/es025803w

Nyczepir, A.P., Wood, B.W., 2012. Foliar nickel application can increase the incidence of peach tree short life and consequent peach tree mortality. HortScience 47, 224–227.

Ojeda-Barrios, D.L., Sánchez-Chávez, E., Sida-Arreola, J.P., Valdez-Cepeda, R., Balandran-Valladares, M., 2016. The impact of foliar nickel fertilization on urease activity in pecan trees. J. Soil Sci. Plant Nutr. 16, 237–247. doi:10.4067/S0718-95162016005000019

Polacco, J.C., Mazzafera, P., Tezotto, T., 2013. Opinion – nickel and urease in plants: still many knowledge gaps. Plant Sci. 199–200, 79–90. doi:10.1016/j.plantsci.2012.10.010

Ponizovsky, A.A., Allen, H.E., Ackerman, A.J., 2008. Effect of field aging on nickel concentration in soil solutions. Commun. Soil Sci. Plant Anal. 39, 510–523. doi:10.1080/00103620701826746

Poschenrieder, C., Tolrà, R., Barceló, J., 2006. Can metals defend plants against biotic stress? Trends Plant Sci. 11, 288–295. doi:10.1016/j.tplants.2006.04.007

Rajaie, M., Karimian, N., Yasrebi, J., 2008. Nickel transformation in two calcareous soil textural classes as affected by applied nickel sulfate. Geoderma 144, 344–351. doi:10.1016/j.geoderma.2007.12.001

Rodak, B.W., Freitas, D.S., Lima, G.J.E.O., Reis, A.R., Schulze, J., Guilherme, L.R.G., 2018. Beneficial use of Ni-rich petroleum coke ashes: product characterization and effects on soil properties and plant growth. J. Clean. Prod. 198, 785–796. doi:10.1016/j.jclepro.2018.07.090

Rodak, B.W., Moraes, M.F., Pascoalino, J.A.L., Oliveira Junior, A., Castro, C., Pauletti, V., 2015. Methods to quantify nickel in soils and plant tissues. Rev. Bras. Ciênc. Solo 39, 788–793. doi:10.1590/01000683rbcs20140542

Ruiz-Argüeso, T., Palacios, J.M., Imperial, J., 2001. Regulation of the hydrogenase system in *Rhizobium leguminosarum*. Plant Soil 230, 49–57. doi:10.1023/A:1004578324977

Ruter, J.M., 2005. Effect of nickel applications for the control of mouse ear disorder on river birch. J. Environ. Hortic. 23, 17–20.

Schaefer, C.E.G.R., Fabris, J.D., Ker, J.C., 2008. Minerals in the clay fraction of Brazilian Latosols (Oxisols): a review. Clay Miner. 43, 137–154. doi:10.1180/claymin.2008.043.1.11

Sengar, R.S., Gupta, S., Gautam, M., Sharma, A., Sengar, K., 2008. Occurrence, uptake, accumulation and physiological responses of nickel in plants and its effects on environment. Res. J. Phytochemistry 2, 44–60. doi:10.3923/rjphyto.2008.44.60

Shafaat, H.S., Rüdiger, O., Ogata, H., Lubitz, W., 2013. [NiFe] hydrogenases: a common active site for hydrogen metabolism under diverse conditions. Biochim. Biophys. Acta BBA - Bioenerg. 1827, 986–1002. doi:10.1016/j.bbabio.2013.01.015

Smolders, E., Oorts, K., Van Sprang, P., Schoeters, I., Janssen, C.R., McGrath, S.P., McLaughlin, M.J., 2009. Toxicity of trace metals in soil as affected by soil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards. Environ. Toxicol. Chem. 28, 1633–1642. doi:10.1897/08-592.1

Soil Survey Staff, 1999. Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys, 2 ed. Natural Resources Conservation Service, U.S. Department of Agriculture, Washington.

Sreekanth, T.V.M., Nagajyothi, P.C., Lee, K.D., Prasad, T.N.V.K.V., 2013. Occurrence, physiological responses and toxicity of nickel in plants. Int. J. Environ. Sci. Technol. 10, 1129–1140. doi:10.1007/s13762-013-0245-9

Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S., 2002. Agricultural sustainability and intensive production practices. Nature 418, 671. doi:10.1038/nature01014

Tscharntke, T., Clough, Y., Wanger, T.C., Jackson, L., Motzke, I., Perfecto, I., Vandermeer, J., Whitbread, A., 2012. Global food security, biodiversity conservation and the future of agricultural intensification. Biol. Conserv. 151, 53–59. doi:10.1016/j.biocon.2012.01.068

Tóth, G., Hermann, T., Da Silva, M.R., Montanarella, L., 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. Environ. Int. 88, 299–309. doi:10.1016/j.envint.2015.12.017

Toyomura, K., Kono, S., 2002. Soybeans, soy foods, isoflavones and risk of colorectal cancer: a review of experimental and epidemiological data. Asian Pac. J. Cancer Prev. 3, 125–132.

United Nations, 2018. Sustainable development goals. https://www.un.org/sustainabledevelopment/sustainable-development-goals/ (access 18.04.18).

Uruç Parlak, K., 2016. Effect of nickel on growth and biochemical characteristics of wheat (*Triticum aestivum* L.) seedlings. NJAS - Wagening. J. Life Sci. 76, 1–5. doi:10.1016/j.njas.2012.07.001

USEPA - United States Environmental Protection Agency, 1996. Method 3050B: acid digestion of sediments, sludges, and soils. United States Environmental Protection Agency, Washington.

Vanlauwe, B., Bationo, A., Chianu, J., Giller, K.E., Merckx, R., Mokwunye, U., Ohiokpehai, O., Pypers, P., Tabo, R., Shepherd, K.D., Smaling, E.M.A., Woomer, P.L., Sanginga, N., 2010. Integrated soil fertility management: operational definition and consequences for implementation and dissemination. Outlook Agric. 39, 17–24. doi:10.5367/000000010791169998

Vogels, G.D., Van Der Drift, C., 1970. Differential analyses of glyoxylate derivatives. Anal. Biochem. 33, 143–157. doi:10.1016/0003-2697(70)90448-3

Westfall, D.G., Mortvedt, J.J., Peterson, G.A., Gangloff, W.J., 2005. Efficient and environmentally safe use of micronutrients in agriculture. Commun. Soil Sci. Plant Anal. 36, 169–182. doi:10.1081/CSS-200043024

Witte, C.P., 2011. Urea metabolism in plants. Plant Sci. 180, 431–438. doi:10.1016/j.plantsci.2010.11.010

Wood, B.W., Reilly, C.C., 2007. Nickel and plant disease, in: Datnoff, L.E., Elmer, W.H., Huber, D.M. (Eds.), Mineral nutritional and plant disease. The American Phytopathological Society, Minnesota, pp. 215–231.

Wood, B.W., Reilly, C.C., Nyczepir, A.P., 2006. Field deficiency of nickel in trees: symptoms and causes. Acta Hortic. 83–98. doi:10.17660/ActaHortic.2006.721.10

Wood, B.W., Reilly, C.C., Nyczepir, A.P., 2004a. Mouse-ear of pecan: I. Symptomatology and occurrence. HortScience 39, 95–100.

Wood, B.W., Reilly, C.C., Nyczepir, A.P., 2004b. Mouse-ear of pecan: II. Influence of nutrient applications. HortScience 39, 87–94.

Yusuf, M., Fariduddin, Q., Hayat, S., Ahmad, A., 2011. Nickel: an overview of uptake, essentiality and toxicity in plants. Bull. Environ. Contam. Toxicol. 86, 1–17. doi:10.1007/s00128-010-0171-1

Zhang, X., Li, J., Wei, D., Li, B., Ma, Y., 2015. Predicting soluble nickel in soils using soil properties and total nickel. PLOS ONE 10, e0133920. doi:10.1371/journal.pone.0133920
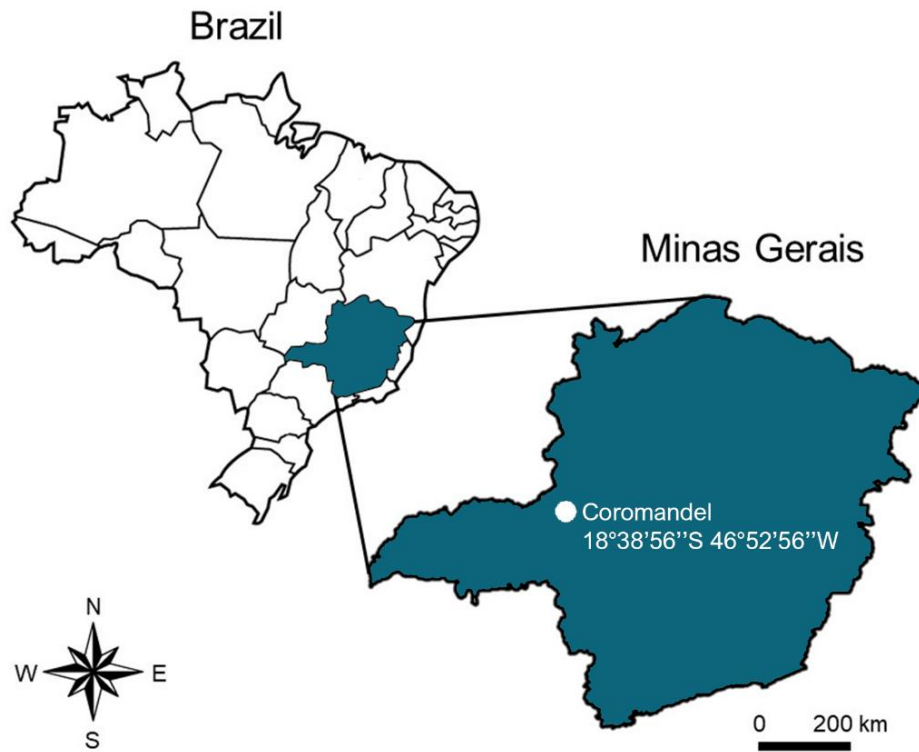
Fig. 1 Experimental site in the Southeast region of Brazil, state of Minas Gerais, city of Coromandel.

Fig. 2 Soybean yield chronology in two years of soybean cultivation under one-time application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation. n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; C.V., coefficient of variation; Bags shown on graph represent the difference among the treatments (L+B and L+S) and the control (L), being 1 bag equivalent to 60 kg.

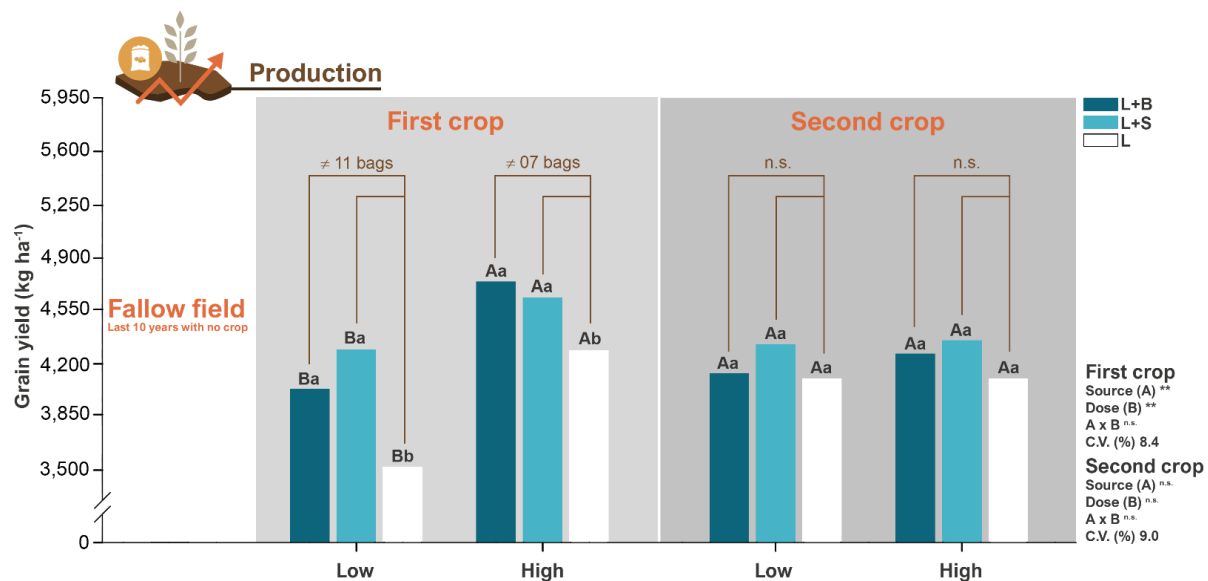**Fig. 3** Available Ni concentration chronology in two soil depths a) 0-20 cm and b) 20-40 cm in two years of soybean cultivation under one-time application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation. n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; C.V., coefficient of variation; Max, maximum; Min, minimum; Ni in Mehlich-1 extractant.
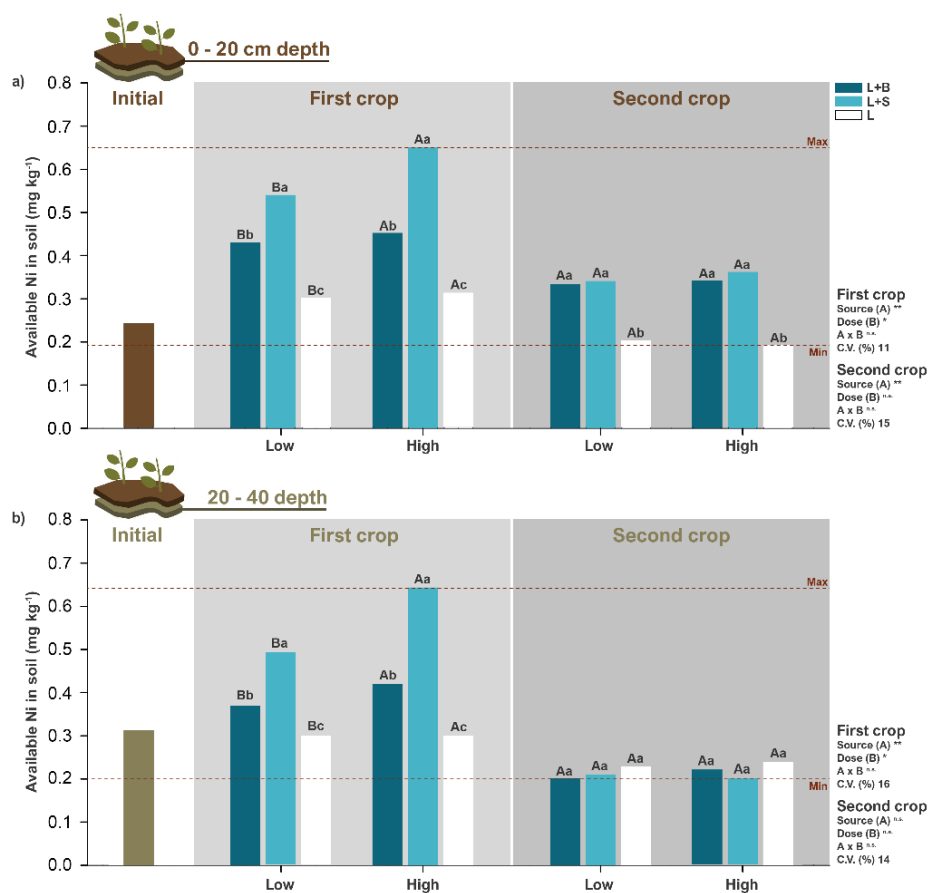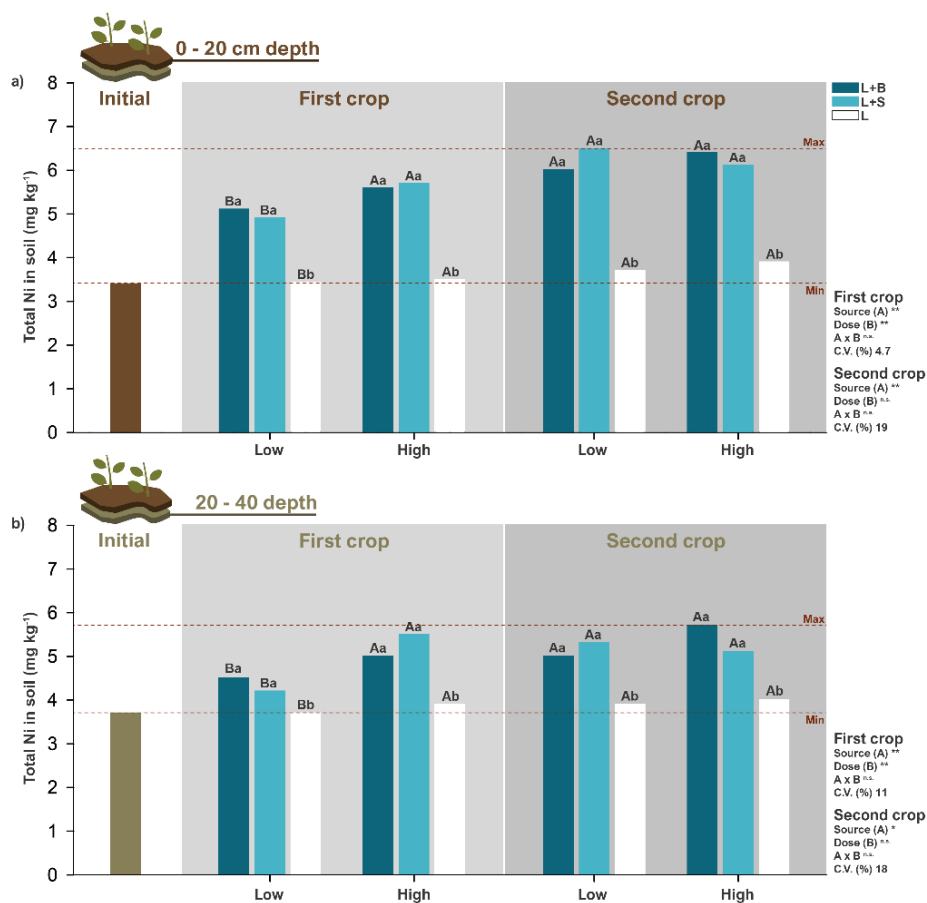
Fig. 4 Total Ni concentration chronology in two soil depths a) 0-20 cm and b) 20-40 cm in two years of soybean cultivation under one-time application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation. n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; C.V., coefficient of variation; Max, maximum; Min, minimum; Ni extracted using USEPA 3050-B method.

Table 1
Chemical properties of soil acidity amendments (SAA) enriched with Ni adopted in this study. The SAAs sources tested limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L) used as control.

Properties	Methods	Units	L+B	L+S	L
Ca	USEPA 3050-B	%	26	27	21
CaO	EDTA volumetric	%	37	30	30
Mg	USEPA 3050-B	%	5	13	13
MgO	EDTA volumetric	%	8	23	23
Ni	USEPA 3050-B	$mg\ kg^{-1}$	400	400	2
Neutralization power	Acid-base titration	% $CaCO_3$eq	70	97	97
Effective neutralizing power	[a]	% $CaCO_3$eq	64	87	87

[a] Product of total fineness efficiency and neutralization power, expressed as a percentage, with fineness obtained through granulometric analysis. Details on the characterization and formulation of the by-product can be found in Rodak et al. (2018).

Table 2

Physicochemical characteristics of the Typical Red Dystrophic Latosol (corresponding to Oxisol) used in this study.

Properties	Methods	Units	Depths	
			0-20 cm	20-40 cm
Chemical				
Organic matter	Colorimetric	g kg^{-1}	4.4	2.6
pH	Water	-	5.5	5.6
Al	KCl	cmol$_c$ kg^{-1}	0.1	0.0
Al + H	Ca(C$_2$H$_3$O$_2$)$_2$ pH 7.0	cmol$_c$ kg^{-1}	7.9	5.9
P	Mehlich-1	mg kg^{-1}	3.4	1.8
K	Mehlich-1	cmol$_c$ kg^{-1}	0.1	0.1
Ca	KCl	cmol$_c$ kg^{-1}	0.8	0.4
Mg	KCl	cmol$_c$ kg^{-1}	0.2	0.1
S	CaHPO$_4$	mg kg^{-1}	1.2	0.8
B	Hot water	mg kg^{-1}	0.2	0.2
Cu	Mehlich-1	mg kg^{-1}	1.5	1.1
Fe	Mehlich-1	mg kg^{-1}	214	93
Mn	Mehlich-1	mg kg^{-1}	3.2	2.3
Zn	Mehlich-1	mg kg^{-1}	1.9	1.3
Available Ni	Mehlich-1	mg kg^{-1}	0.24	0.31
Total Ni	USEPA 3050-B	mg kg^{-1}	3.41	3.72
Base saturation	[a]	%	13.0	9.0
Granulometry				
Sand	Hydrometer	g kg^{-1}	110	-
Silt	Hydrometer	g kg^{-1}	260	-
Clay	Hydrometer	g kg^{-1}	630	-

[a] Fraction of sum of basis (Ca^{2+}, Mg^{2+}, and K$^+$) and cation exchange capacity, expressed as a percentage; Soil classification according to Soil Survey Staff (1999) and Embrapa Solos (2013).

Table 3
Effect in N-urea metabolism and N_2 fixation in the first year of soybean cultivation with one-time in field application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation.

Treatments		N-urea metabolism			N_2 fixation	
		Urease activity	Urea concentration	Ammonia concentration	Nitrogenase activity	Ureide concentration
Source	Dose	(μmol g FW^{-1} h^{-1})	(μmol g FW^{-1})	(μmol g FW^{-1})	(pmol mg FW^{-1} min^{-1})	(μmol g FW^{-1})
L+B	Low	19 Aa	17 Ab	10 Aa	3.3 Aa	9.7 Aa
L+S	Low	21 Aa	17 Ab	9.5 Aa	3.6 Aa	9.5 Aa
L	Low	13 Ab	24 Aa	7.4 Ab	1.3 Ab	7.9 Ab
L+B	High	21 Aa	14 Ab	11 Aa	3.6 Aa	11 Aa
L+S	High	19 Aa	15 Ab	10 Aa	3.6 Aa	10 Aa
L	High	15 Ab	19 Aa	7.9 Ab	1.6 Ab	8.5 Ab
Source (A)		**	*	**	**	**
Dose (B)		n.s.	n.s.	n.s.	n.s.	n.s.
A x B		n.s.	n.s.	n.s.	n.s.	n.s.
C.V. (%)		16	24	13	14	12

n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; FW, fresh weight; C.V., coefficient of variation.

Table 4

Nickel concentration chronology in leaf, grain and nodule in two years of soybean cultivation with one-time in field application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation.

Treatments		First crop			Second crop		
		Ni concentration (mg kg^{-1})			Ni concentration (mg kg^{-1})		
Source	Dose	Leaf	Grain	Nodule	Leaf	Grain	Nodule
L+B	Low	1.49 Aa	1.11 Aa	0.95 Ba	0.49 Aa	0.53 Aa	n.d.
L+S	Low	1.50 Aa	1.10 Aa	0.95 Ba	0.50 Aa	0.55 Aa	n.d.
L	Low	0.64 Ab	0.94 Ab	0.39 Bb	0.18 Ab	0.41 Aa	n.d.
L+B	High	1.54 Aa	1.07 Aa	1.98 Aa	0.51 Aa	0.56 Aa	n.d.
L+S	High	1.55 Aa	1.10 Aa	1.56 Aa	0.50 Aa	0.57 Aa	n.d.
L	High	0.29 Ab	0.93 Ab	0.41 Ab	0.20 Ab	0.52 Aa	n.d.
Source (A)		**	**	*	**	n.s.	-
Dose (B)		n.s.	n.s.	*	n.s.	n.s.	-
A x B		n.s.	n.s.	n.s.	n.s.	n.s.	-
C.V. (%)		18	6.3	29	17	12	-

n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; Ni extracted using nitric-perchloric method; C.V., coefficient of variation; n.d., not detectable (< 0.15 mg kg^{-1}).

Table 5
Soil pH and soil base saturation (V) chronology in two years of soybean cultivation with one-time in field application of limestone mixed with a Ni-rich by-product (L+B), limestone enriched with a Ni salt (L+S) and pure limestone (L), in low and high doses based on soil base saturation.

Treatments		First crop		Second crop	
Source	Dose	pH	V (%)	pH	V (%)
0-20 cm depth					
L+B	Low	5.6 Ba	57 Ba	5.8 Aa	53 Ba
L+S	Low	5.6 Ba	51 Ba	5.9 Aa	53 Ba
L	Low	5.6 Ba	52 Ba	6.0 Aa	56 Ba
L+B	High	5.8 Aa	62 Aa	5.9 Aa	63 Aa
L+S	High	6.0 Aa	61 Aa	6.0 Aa	65 Aa
L	High	6.2 Aa	65 Aa	6.0 Aa	63 Aa
Source (A)		n.s.	n.s.	n.s.	n.s.
Dose (B)		**	**	n.s.	**
A x B		n.s.	n.s.	n.s.	n.s.
C.V. (%)		4.9	10	3.2	6.1
20-40 cm depth					
L+B	Low	5.6 Ba	48 Ba	5.9 Aa	32 Aa
L+S	Low	5.6 Ba	44 Ba	5.8 Aa	30 Aa
L	Low	5.7 Ba	41 Ba	5.9 Aa	30 Aa
L+B	High	5.8 Aa	51 Aa	5.7 Aa	34 Aa
L+S	High	5.9 Aa	59 Aa	5.7 Aa	32 Aa
L	High	5.9 Aa	48 Aa	5.8 Aa	29 Aa
Source (A)		n.s.	n.s.	n.s.	n.s.
Dose (B)		*	**	n.s.	n.s.
A x B		n.s.	n.s.	n.s.	n.s.
C.V. (%)		4.5	13	3.1	18

n.s., not significant; **, significant at $p < 0.01$; *, significant at $p < 0.05$ by F-test; Means followed by the same letter do not differ by Tukey´s test at $p < 0.05$; Unfolding the interaction, upper case letters are for doses while lower case letters are for Ni sources; pH, water; V, fraction of sum of basis (Ca^{2+}, Mg^{2+}, and K^+) and cation exchange capacity, expressed as a percentage; C.V., coefficient of variation.

Highlights

- The use of Ni-enriched soil acidity amendments is a feasible and sustainable technology in agriculture.
- Ni-fertilization enhanced soybean grain yield, associated with improved N metabolism.
- A weak residual effect of Ni in plant-soil system was observed, suggesting an annual fertilization.
- Nickel concentrations verified in the soil and in soybean grains were considered safe for humans and to the environment.