LEONARDO TULLIO
(ORGANIZADOR)

PAUTA AMBIENTAL BRASILEIRA E A PROMOÇÃO DA SUSTENTABILIDADE

Atena
Editora
Ano 2022

LEONARDO TULLIO
(ORGANIZADOR)

PAUTA AMBIENTAL BRASILEIRA E A PROMOÇÃO DA SUSTENTABILIDADE

Atena
Editora
Ano 2022

Editora chefe
Profª Drª Antonella Carvalho de Oliveira
Editora executiva
Natalia Oliveira
Assistente editorial
Flávia Roberta Barão
Bibliotecária
Janaina Ramos
Projeto gráfico
Bruno Oliveira
Camila Alves de Cremo
Daphynny Pamplona
Luiza Alves Batista
Natália Sandrini de Azevedo
Imagens da capa
iStock
Edição de arte
Luiza Alves Batista

2022 *by* Atena Editora
Copyright © Atena Editora
Copyright do texto © 2022 Os autores
Copyright da edição © 2022 Atena Editora
Direitos para esta edição cedidos à Atena Editora pelos autores.
Open access publication by Atena Editora

Todo o conteúdo deste livro está licenciado sob uma Licença de Atribuição *Creative Commons*. Atribuição-Não-Comercial-NãoDerivativos 4.0 Internacional (CC BY-NC-ND 4.0).

O conteúdo dos artigos e seus dados em sua forma, correção e confiabilidade são de responsabilidade exclusiva dos autores, inclusive não representam necessariamente a posição oficial da Atena Editora. Permitido o *download* da obra e o compartilhamento desde que sejam atribuídos créditos aos autores, mas sem a possibilidade de alterá-la de nenhuma forma ou utilizá-la para fins comerciais.

Todos os manuscritos foram previamente submetidos à avaliação cega pelos pares, membros do Conselho Editorial desta Editora, tendo sido aprovados para a publicação com base em critérios de neutralidade e imparcialidade acadêmica.

A Atena Editora é comprometida em garantir a integridade editorial em todas as etapas do processo de publicação, evitando plágio, dados ou resultados fraudulentos e impedindo que interesses financeiros comprometam os padrões éticos da publicação. Situações suspeitas de má conduta científica serão investigadas sob o mais alto padrão de rigor acadêmico e ético.

Conselho Editorial
Ciências Agrárias e Multidisciplinar
Prof. Dr. Alexandre Igor Azevedo Pereira – Instituto Federal Goiano
Profª Drª Amanda Vasconcelos Guimarães – Universidade Federal de Lavras
Profª Drª Andrezza Miguel da Silva – Universidade do Estado de Mato Grosso
Prof. Dr. Arinaldo Pereira da Silva – Universidade Federal do Sul e Sudeste do Pará
Prof. Dr. Antonio Pasqualetto – Pontifícia Universidade Católica de Goiás
Profª Drª Carla Cristina Bauermann Brasil – Universidade Federal de Santa Maria

Prof. Dr. Cleberton Correia Santos – Universidade Federal da Grande Dourados
Profª Drª Diocléa Almeida Seabra Silva – Universidade Federal Rural da Amazônia
Prof. Dr. Écio Souza Diniz – Universidade Federal de Viçosa
Prof. Dr. Edevaldo de Castro Monteiro – Universidade Federal Rural do Rio de Janeiro
Prof. Dr. Fábio Steiner – Universidade Estadual de Mato Grosso do Sul
Prof. Dr. Fágner Cavalcante Patrocínio dos Santos – Universidade Federal do Ceará
Profª Drª Girlene Santos de Souza – Universidade Federal do Recôncavo da Bahia
Prof. Dr. Guilherme Renato Gomes – Universidade Norte do Paraná
Prof. Dr. Jael Soares Batista – Universidade Federal Rural do Semi-Árido
Prof. Dr. Jayme Augusto Peres – Universidade Estadual do Centro-Oeste
Prof. Dr. Júlio César Ribeiro – Universidade Federal Rural do Rio de Janeiro
Profª Drª Lina Raquel Santos Araújo – Universidade Estadual do Ceará
Prof. Dr. Pedro Manuel Villa – Universidade Federal de Viçosa
Profª Drª Raissa Rachel Salustriano da Silva Matos – Universidade Federal do Maranhão
Prof. Dr. Renato Jaqueto Goes – Universidade Federal de Goiás
Prof. Dr. Ronilson Freitas de Souza – Universidade do Estado do Pará
Profª Drª Talita de Santos Matos – Universidade Federal Rural do Rio de Janeiro
Prof. Dr. Tiago da Silva Teófilo – Universidade Federal Rural do Semi-Árido
Prof. Dr. Valdemar Antonio Paffaro Junior – Universidade Federal de Alfenas

Pauta ambiental brasileira e a promoção da sustentabilidade

Diagramação: Camila Alves de Cremo
Correção: Mariane Aparecida Freitas
Indexação: Amanda Kelly da Costa Veiga
Revisão: Os autores
Organizador: Leonardo Tullio

Dados Internacionais de Catalogação na Publicação (CIP)

P335 Pauta ambiental brasileira e a promoção da sustentabilidade / Organizador Leonardo Tullio. – Ponta Grossa - PR: Atena, 2022.

Formato: PDF
Requisitos de sistema: Adobe Acrobat Reader
Modo de acesso: World Wide Web
Inclui bibliografia
ISBN 978-65-258-0271-8
DOI: https://doi.org/10.22533/at.ed.718223005

1. Sustentabilidade e meio ambiente. I. Tullio, Leonardo (Organizador). II. Título.

CDD 333.72

Elaborado por Bibliotecária Janaina Ramos – CRB-8/9166

Atena Editora
Ponta Grossa – Paraná – Brasil
Telefone: +55 (42) 3323-5493
www.atenaeditora.com.br
contato@atenaeditora.com.br

Ano 2022

DECLARAÇÃO DOS AUTORES

Os autores desta obra: 1. Atestam não possuir qualquer interesse comercial que constitua um conflito de interesses em relação ao artigo científico publicado; 2. Declaram que participaram ativamente da construção dos respectivos manuscritos, preferencialmente na: a) Concepção do estudo, e/ou aquisição de dados, e/ou análise e interpretação de dados; b) Elaboração do artigo ou revisão com vistas a tornar o material intelectualmente relevante; c) Aprovação final do manuscrito para submissão.; 3. Certificam que os artigos científicos publicados estão completamente isentos de dados e/ou resultados fraudulentos; 4. Confirmam a citação e a referência correta de todos os dados e de interpretações de dados de outras pesquisas; 5. Reconhecem terem informado todas as fontes de financiamento recebidas para a consecução da pesquisa; 6. Autorizam a edição da obra, que incluem os registros de ficha catalográfica, ISBN, DOI e demais indexadores, projeto visual e criação de capa, diagramação de miolo, assim como lançamento e divulgação da mesma conforme critérios da Atena Editora.

DECLARAÇÃO DA EDITORA

A Atena Editora declara, para os devidos fins de direito, que: 1. A presente publicação constitui apenas transferência temporária dos direitos autorais, direito sobre a publicação, inclusive não constitui responsabilidade solidária na criação dos manuscritos publicados, nos termos previstos na Lei sobre direitos autorais (Lei 9610/98), no art. 184 do Código penal e no art. 927 do Código Civil; 2. Autoriza e incentiva os autores a assinarem contratos com repositórios institucionais, com fins exclusivos de divulgação da obra, desde que com o devido reconhecimento de autoria e edição e sem qualquer finalidade comercial; 3. Todos os e-book são *open access, desta forma* não os comercializa em seu site, sites parceiros, plataformas de *e-commerce,* ou qualquer outro meio virtual ou físico, portanto, está isenta de repasses de direitos autorais aos autores; 4. Todos os membros do conselho editorial são doutores e vinculados a instituições de ensino superior públicas, conforme recomendação da CAPES para obtenção do Qualis livro; 5. Não cede, comercializa ou autoriza a utilização dos nomes e e-mails dos autores, bem como nenhum outro dado dos mesmos, para qualquer finalidade que não o escopo da divulgação desta obra.

APRESENTAÇÃO

A obra “Pauta ambiental brasileira e a promoção da sustentabilidade” aborda uma apresentação de 11 capítulos envolvendo pesquisas que englobam educação, projetos e manejo sustentável no cenário ambiental.

Pesquisar sobre variáveis que pressupõem a sustentabilidade no meio, é assunto com ênfase no cenário nacional e mundial. Esclarecer relações entre ação humana e ambiente é o foco principal desta obra. Os autores trazem aspectos da sociedade em contribuição para um mundo mais sustentável.

O cenário das mudanças climáticas são preocupantes e exigem pesquisas que vão além, que definam estratégias de conservação, manejo e educação social. Pois a remediação de um problema nem sempre é uma tarefa fácil, mas tendo a percepção da realidade em que vivemos podemos traçar metas e rumos para novos caminhos.

Educação ambiental faz parte é se torna cada vez mais evidente como resultado primordial para a conscientização dos problemas ambientais e a promoção de virtudes que proponham a sustentabilidade do meio.

Na leitura dos capítulos, serão discutidos esses aspectos por pesquisadores preocupados em demostrar possibilidades para uma abordagem mais técnica e ao mesmo tempo refletiva sobre o tema ambiental.

Sustentabilidade é possível agirmos já?

A resposta para essa pergunta iremos descobrir a seguir. Boa leitura.

Leonardo Tullio

SUMÁRIO

CAPÍTULO 1 1

BIOMONITORING OF POTENTIALLY TOXIC ELEMENTS IN TWO POLLUTED AREAS FROM LURIGANCHO-CHOSICA USING THE GENUS *Tillandsia latifolia* AND *T. purpurea* AS BIOMONITOR

Alex Rubén Huamán de La Cruz
Adriana Gioda
Nancy Curasi Rafael
Mohamed Mehdi Hadi Mohamed
Andrés Camargo Caysahuana
Alberto Rivelino Patiño Rivera
Julio Ángeles Suazo

https://doi.org/10.22533/at.ed.7182230051

CAPÍTULO 2 16

CONSUMO, SUSTENTABILIDADE E SOCIEDADE: FATORES CLIMÁTICOS SOB A ÓTICA ECONÔMICO-ECOLÓGICA

Barbara Lúcia Guimarães Alves
Nathalia Guimarães Alves

https://doi.org/10.22533/at.ed.7182230052

CAPÍTULO 3 29

A EDUCAÇÃO NA PROMOÇÃO DA SUSTENTABILIDADE: CULTURA E NATUREZA COMO PATRIMÔNIOS DE PRESERVAÇÃO

Carlos César Leonardi

https://doi.org/10.22533/at.ed.7182230053

CAPÍTULO 4 44

INCENTIVOS PÚBLICOS A PRESERVAÇÃO E RECUPERAÇÃO DA VEGETAÇÃO NATIVA NA PROPRIEDADE FAMILIAR RURAL DO RS: PROPOSTAS PARA REGULAMENTAÇÃO DO CÓDIGO ESTADUAL DE MEIO AMBIENTE DE 2020

Domingos Benedetti Rodrigues
Cristian Maidana
Gabriela Colomé Moreira
Fabrício da Silva Aquino

https://doi.org/10.22533/at.ed.7182230054

CAPÍTULO 5 55

CONTRIBUIÇÃO DAS COOPERATIVAS DE CATADORES DE MATERIAIS RECICLÁVEIS PARA A REDUÇÃO DAS EMISSÕES DE GASES DE EFEITO ESTUFA

Jefferson Faria Dionisio de Oliveira
Emília Wanda Rutkowski

https://doi.org/10.22533/at.ed.7182230055

CAPÍTULO 6 63

BIOMONITORING OF TOXIC ELEMENTS IN PLANTS COLLECTED NEAR LEATHER

TANNING INDUSTRY
Alex Rubén Huamán de La Cruz
Adriana Gioda
Nancy Curasi Rafael
Mohamed Mehdi Hadi Mohamed
Andrés Camargo Caysahuana
Alberto Rivelino Patiño Rivera
Julio Ángeles Suazo
Ide Unchupaico Payano
https://doi.org/10.22533/at.ed.7182230056

CAPÍTULO 7..76

UM ESTUDO SOBRE RECICLAGEM E REUTILIZAÇÃO DE RESÍDUOS TÊXTEIS DESCARTADOS DA INDÚSTRIA DE VESTUÁRIO
Natalia Gonçalves dos Santos
https://doi.org/10.22533/at.ed.7182230057

CAPÍTULO 8..89

CONSERVAÇÃO DA NATUREZA E COEXISTÊNCIA DO RURAL NO URBANO NA APA BACIA DO RIO DO COBRE/SÃO BARTOLOMEU, SALVADOR-BA (BR)
Débora Carol Luz da Porciúncula
Cristina Maria Macêdo de Alencar
Manuel Vitor Portugal Gonçalves
Mariana Reis Santana
Vinnie Mayana Lima Ramos
André Augusto Araújo Oliveira
Gláucio Alã Vasconcelos Moreira
Thiago Guimarães Siqueira de Araújo
Fátima Carmelo Balthazar da Silveira Lima
Flávio Souza Batista
https://doi.org/10.22533/at.ed.7182230058

CAPÍTULO 9..113

PERCEPÇÃO SOBRE O PROJETO QUELÔNIOS DO ARAGUAIA NO MUNICIPIO DE SANTA MARIA DAS BARREIRAS, PARÁ, BRASIL
Vanessa Lima Araújo Luz
Adriana Malvasio
https://doi.org/10.22533/at.ed.7182230059

CAPÍTULO 10..127

TÉCNICAS MPPT: UMA ANÁLISE COMPARATIVA ENTRE OS PRINCIPAIS MÉTODOS E SUA INFLUÊNCIA NA EFICIÊNCIA DO SISTEMA FOTOVOLTAICO
José Ramon Nunes Ferreira
Alberto Grangeiro de Albuquerque Neto
Vinivios dos Santos Mangueira
https://doi.org/10.22533/at.ed.71822300510

CAPÍTULO 11 136

UMA VISÃO INTERDISCIPLINAR DOS EFEITOS DO MANEJO DO SOLO EM BACIAS HIDROGRÁFICAS

Mauricio Willians de Lima
Yasmin di Paula Teixeira Oliveira
Jaqueline Silva de Oliveira
Deimid Rodrigues da Silva
Maria Carolina Sarto Fernandes Rodrigues
João Elias Lopes Fernandes Rodrigues
Maria de Lourdes Souza Santos
Flávia Kelly Siqueira de Souza
Antonio Rodrigues Fernandes

https://doi.org/10.22533/at.ed.71822300511

SOBRE O ORGANIZADOR 160

ÍNDICE REMISSIVO 161

CAPÍTULO 6

BIOMONITORING OF TOXIC ELEMENTS IN PLANTS COLLECTED NEAR LEATHER TANNING INDUSTRY

Data de aceite: 02/05/2022

Alex Rubén Huamán de La Cruz
Escuela Profesional de Ingeniería Ambiental, Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa (UNISCJSA)
La Merced – Perú
https://orcid.org/0000-0003-4583-9136

Adriana Gioda
Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio)
Rio de Janeiro
http://lattes.cnpq.br/3948737758921845

Nancy Curasi Rafael
Escuela Profesional de Ingeniería Ambiental, Universidad Peruana Unión (UPeU)
Lima – Perú
https://orcid.org/0000-0001-8148-4366

Mohamed Mehdi Hadi Mohamed
Vicerrectorado de Investigación, Universidad Peruana Los Andes (UPLA)
Huancayo – Perú
https://orcid.org/0000-0003-1940-8383

Andrés Camargo Caysahuana
Escuela Profesional de Ingeniería Civil, Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa (UNISCJSA)
La Merced – Perú
https://orcid.org/0000-0003-3509-4919

Alberto Rivelino Patiño Rivera
Escuela Profesional de Administración de Negocios Internacionales, Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa (UNISCJSA)
La Merced – Perú
https://orcid.org/0000-0002-3783-9796

Julio Ángeles Suazo
Escuela Profesional de ingeniería Forestal y Ambiental, Universidad Nacional Autónoma de Tayacaja Daniel Hernández Morillo
Pampas – Perú
https://orcid.org/0000-0001-8327-9032

Ide Unchupaico Payano
Vicerrectorado de Investigación, Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa (UNISCJSA)
La Merced – Perú
https://orcid.org/0000-0002-6441-5016

ABSTRACT: The present work aimed the study of atmospheric deposition of toxic elements near to a tannery industry from black material deposited collected on leaf surfaces of cinnamon trees (*Cinnamomum zeylanicum*). Elements such as As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). For comparison purpose two sites with similar black particles deposited on leaves away from tannery industry were considered. Results showed that toxic elements measured in the black particles collected near tannery area were significantly higher than those in comparison sites. Enrichment factors (EF) of

As and Cr were markedly impacted by anthropogenic emissions, whereas the other elements were moderately/slightly enriched. Cluster analysis identified Cr element as anthropogenic source from leather industry, while As possibly attributed to wide use of pesticides and herbicides in agricultural practices. The results indicated that emissions from the leather industry and agricultural activities are the main source of pollution in this area.

KEYWORDS: Leather industry, ICP-MS, toxic elements, biomonitoring, atmospheric particles.

INTRODUCTION

Leather industry, an age-old activity, covers diverse products, industrial processes, and has significant economic influence. Leather tanning is the conversion of raw materials as hides and skins into leather, which can be used to manufacture a wide range of consumer products such as footwear, garment, furniture, automotive, clothes, and leather goods. Turning skin into leather requires of several stages (preparatory stage, tanning, and crusting) and use of massive amounts of hazardous chemicals such as chromium (Cr), synthetic tannins, oils, resins, biocide, detergents, among other reagents.

As content of pollutants depend on the nature of the source, environments that are not affected by contaminant sources from natural or anthropogenic activities will contain low levels of the analyte of interest. Usually, higher chromium levels in an environment (soil, air, or water) are resulted from improper discharge of solid waste, wastewater, and gaseous emission from anthropogenic activities such as leather tanning, steel alloys, stainless steel, chrome plating, paint pigments, wood preserving, textile, ceramic glazes, electroplating, and other activities (Sverre and Acosta 2007). The leather industry is considered as major source of environmental pollution of chromium because tanning process use significant amounts of chromium salts as dyeing (Ribeiro 2002).

Chromium is a hard steel-grey toxic metal element and may occur naturally as chromite ($FeCr_2O_4$) in the environment. This element is usually found in two oxidation states: trivalent chromium, Cr (III), and hexavalent chromium, Cr (VI). Other valence states (minus stable or short-lived) in biological materials can also occur. Trivalent form is more abundant and much less toxic and less mobile than Cr (VI). It acts as essential dietary nutrient to maintenance of normal glucose tolerance for human and animals in low doses, while Cr (VI) compounds are considered 1,000 times more toxic than Cr (III) (Kimbrough et al. 1999). Its toxicity is related to its high redox potential, mobility, and ability to penetrate biological membranes. Chromium (VI) is also known as carcinogenic and mutagenic agent (World Health Organization 2000) and can cause several hazardous.

Nova Esperança do Sul, a small city in the south of Brazil, named the capital of the boot, has a big tannery, whose main articles are semi-finished and finished full grain leather and splits for the furniture and the automotive industries (Giannetti et al. 2004; BRASIL 2016). These goods are mainly sold to the foreign market. In general, leather industries eliminate leftover materials and leather shaving through burning. As the industry is located in the center of the city, there are complaints from the population due to the constant atmospheric emissions (Joseph and Nithya 2009). The particles generated during the burning spread throughout the city, leaving the houses dirty, causing bad smell and health problems, although there is no official record. For this reason, the objective of this study was to verify if the particles deposited in the soil and on the surfaces of plants are from natural origin or related to tanning activities. The specific goals of this study were (1) to investigate the levels of toxic elements (As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn) present in the deposited material on the surface of the leaves of *Cinnamomum zeylanicum*, (2) to assess contamination levels, and (3) to identify the likely source(s) of the elements comparing to soil composition.

MATERIALS AND METHODS

Study area

This study was conducted in the city of Nova Esperança do Sul (S1) (29° 24′ 24″ S, 54° 49′ 50″ W), state of Rio Grande do Sul, Brazil (Fig. 1). It is located southernmost part of the country covering an area of about 190,85 km^2 of which 39,36 % is field, 27,15 % is used to agricultural activities, and 0.72 % is urban area with 5,087 inhabitants (IBGE 2016). The climate is subtropical with a variation of average temperature maximum of 38 °C, medium of 17,8 °C, and minimum of 3 °C. The average annual of precipitation is of 1.794,59 mm. The predominant wind direction is from the northwest. In this region, two sites were chosen: S1A-center that is located about 300 m far from the tannery and S1B-Planalto that is located about 5 km from the tannery.

The presence of fungi also causes deposits of black particles on the leaves of various types of plants. In order to evaluate if the particles deposited in the plants sampled in Nova Esperança do Sul are from natural or anthropogenic origin, a site located in Lumiar (S2) (22° 22′ 0.12″ S, 42° 12′ 0″ W, S2), district of Nova Friburgo, state of Rio de Janeiro, Brazil (Fig. 1), about 100 km from Rio de Janeiro city, was chosen. This site is placed in a mountainous region, in the Atlantic Forest covering an area of 7 km^2 and 5,000 inhabitants (IBGE 2016), without pollution of industries or traffic. Climate is warm and temperate with average annual precipitation and temperature of 1437 mm and 19.5 °C.

Sampling

A total of three periods, May 2016 (P1), September 2016 (P2) and October 2017 (P3), of sampling of leaves of cinnamon tree (*Cinnamomum zeylanicum*) was carried out at Nova Esperança do Sul, RS (S1). About 300 g of both leaves without particles on its surface (clean leaves, CLS1A and CLS1B) and leaves with particles for three periods at S1A (Fig. 1a) were collected (were no found leaves with particles at S1B). Additional dry leaves were collected at S1A (DLS1A). Soil samples (about 500 g) at surface and at 10 cm depth were also taken adjacent to the trees from which leaves samples were collected (SS1A and SS1B). For comparison purpose, clean leaves (CLS2) and leaves of lemon tree (*citrus limon*) covered with similar black particles (PS2) (Fig. 1b) were collected at Lumiar, RJ (S2) on February 2017. Sampling collection was at a height of 1.5-2 m above the ground, using gloves latex, stored in self-sealing plastic bags and posteriorly transported to the laboratory.

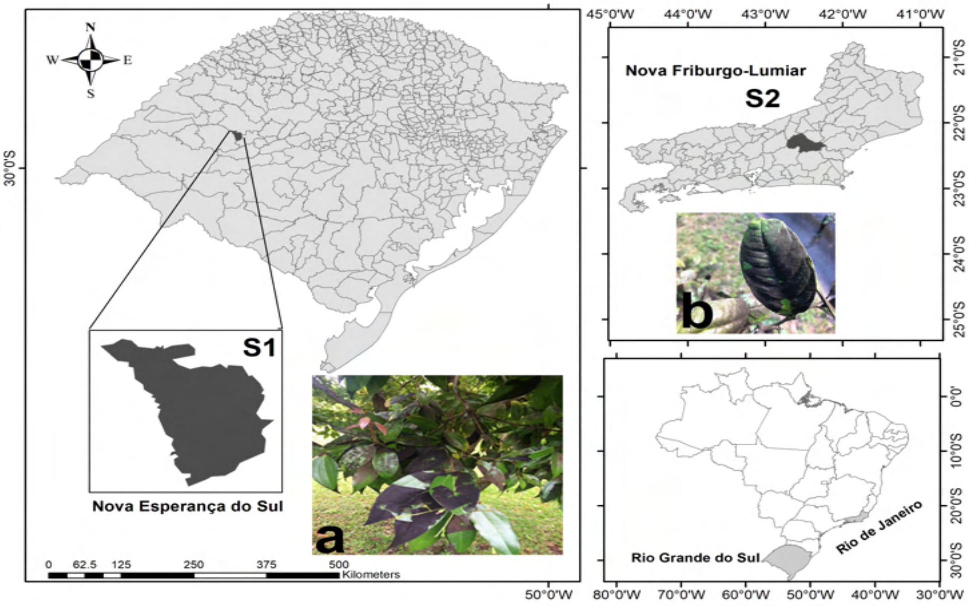

Fig. 1 Location of the study area and samples collected in Rio Grande do Sul (Nova Esperança do Sul, S1) and Rio de Janeiro states (Nova Friburgo-Lumiar, S2).

Sample preparation and chemical analysis

In the laboratory, the deposited material (black particles) on leaf surface was removed carefully using plastic knife and stored in Falcon tubes (50 mL). The black particles, leaves and soil samples were dried in an oven at 50 °C until completely dried. Dried samples were grounded in agate ceramic mortar. The elements were extracted from 0.25 g samples using mixed-acid digestion method into a Teflon bottle (savillex) on a hotplate for 4 h at 250 °C (Bing et al. 2016). After digestion, the samples were cooled to room temperature and transferred into a Falcon tube (15 mL) and diluted with deionized water. The concentration of As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn in the final solutions were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Elan DRC II mass spectrometer (PerkinElmer, USA). Blank and triplicate samples were analyzed to provide quality control. The sample digestion and analysis procedure were checked using Certified Reference Material (CRMs), NIST SRM 1648a - Urban Particulate Matter and NIST SRM 1515 - Apple Leaves. Table 1 shows the limits of detection (LOD) and limits of quantification (LOQ), and the extraction efficiencies of the CRMs used. As it is seen, extraction efficiencies higher than 80 % were obtained for most elements in both CRMs.

Elements	LOD	LOQ	CRM – Apple leaves			CRM – Urban particulate matter		
	(μg g^{-1})	(μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})	% Extracted	Certified value (μg g^{-1})	Found value (μg g^{-1})	% extracted
As	0.004	0.013	0.038±0.007	0.041±0.011	108	115.5 ± 3.9	94.13 ± 4.21	81.5
Ba	0.11	0.36	49±2	45.13 ± 1.22	77.9	-	-	-
Cr	0.02	0.07	0.30	0.34 ± 0.03	113	402 ± 13	347 ± 10	86.3
Cu	0.01	0.04	5.64 ± 0.24	4.94 ± 0.51	87.6	610 ± 70	616 ± 21	101
Fe	4.16	13.73	83 ± 5	76 ± 7	91.0	39200 ± 2100	35320 ± 256	90.0
Ni	0.02	0.06	0.91 ± 0.12	1.02 ± 0.05	112	81.1 ± 6.8	80.3 ± 5.2	99.0
Pb	0.09	0.30	0.470 ±0.024	0.44 ± 0.03	93.5	6550 ± 33	6173 ± 21	94.2
Sb	0.002	0.006	0.013	0.012 ± 0.004	90.9	45.4 ± 1.4	29.41 ± 3.12	64.8
V	0.02	0.08	0.26 ± 0.03	0.30 ± 0.04	115	127 ± 11	138 ± 8	109
Zn	0.15	0.49	12.5 ± 0.3	13.40 ± 1.30	107	4800 ± 270	4286 ± 167	89.2

- Non reported.

Table 1 Limits of detection (LOD) and limits of quantification (LOQ) by ICP-MS and concentration of Certified Reference Materials of leaves (NIST SRM 151 – apple leaves) and PM (NIST SRM 1648 – urban particulate matter) used to evaluate the extraction efficiencies.

Statistical Analysis

One-way ANOVA (with Tukey post hoc test) was used to assess the significant differences ($p<0.05$) between pairs of means concentration among different sampling periods and sampling sites.

Using the measured concentrations of the elements, the enrichment factors (EFs) of each element to evaluate the source contribution have been calculated, as follow:

$$EF_X = \frac{(C_X/C_n)_{sample}}{(C_X/C_n)_{background}} \tag{1}$$

where C$_x$ and C$_n$ are the concentration of the element X and *n* in the sample and in the background. The “sample” refers to the concentrations of the elements present in the black particles removed from the leaves at S1 and S2, while the “background” for S1 consist in the average soil composition value of both soils (superficial and deep) collected surrounding and for S2 was considered the composition given by Taylor and McLennan (1985). In this work, Fe was used as reference. If enrichment factor is < 1, the element is depleted in the environment and natural sources are predominant. If EF > 1 means that the element is relatively enrichment in the environment, while EF > 5 suggests that a large fraction of the element may be ascribed to anthropogenic sources (Wu et al. 2007; Enamorado-Báez et al. 2015).

Cluster analysis (CA) was used to identify and characterize the association of the group of elements as well as to have idea the probable source origin. Statistical analyses were performed using CRAN R (R Team Core 2015) free software through of the following packages: ggplot2 (Wickham 2016), dplyr (Wickham et al. 2017), and ClusterofVar (Chavent et al. 2012).

RESULTS

Descriptive statistics

Table 2 presents the elemental concentrations of As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn measured and ANOVA results among leaves collected from: CLS1A, DLS1A, CLS1B, and CLS2. We can see from the Table 2 that there is a statistically significant difference (except Sb ($p > 0.05$)) among the different sites of collection ($p < 0.05$) for most of the elements measured. Dead leaves (DLS1A) show more elevated concentration values for most of the elements than CLS1A. However, it is very immature attribute the dead of the leaves to these elements. Difference between the elements measured in the leaves from S2 and S1 may be ascribed to that are different species of tree and soil.

Table 3 shows the elemental concentrations of As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn analyzed and ANOVA results from black particles removed from the leaves collected at S1 (three periods, P1, P2, and P3) and S2 (PS2). All elements present higher concentration values at S1 than S2. Statistically significant differences were observed between the three periods and PS2 for most of the elements. Among periods was observed a similar tendency.

Soil samples analysis collected at 300 m and 5.0 km far from tannery area (S1) are showed in Table 4. Metal concentrations in the deep soil and superficial soil showed minimal variation between them at 300 m of tannery area. Both soil analyses at 300 m present higher concentration values for all toxic metals than deep soils analysed at 5.0 km.

Element	S1			S2	
	CLS1A, 300 m Mean ± S.D.	DLS1A, 300m Mean ± S.D.	CLS1B, 5 km Mean ± S.D.	CLS2 Mean ± S.D.	ANOVA
As	0.37 ± 0.06 b	0.44 ± 0.05 ab	0.49 ± 0.04 a	0.15 ± 0.04 c	***
Ba	64.61 ± 5.44 a	63.18 ± 2.79 a	69.58 ± 2.79 a	27.19 ± 3.38 b	***
Cr	0.28 ± 0.04 c	3.82 ± 0.88 a	0.78 ± 0.08 c	2.58 ± 0.20 b	***
Cu	3.96 ± 0.30 c	6.57 ± 0.39 b	8.40 ± 0.68 a	2.59 ± 0.29 d	***
Fe	113 ± 8 c	135 ± 19 c	180 ± 35 b	573 ± 18 a	***
Ni	1.27 ± 0.11 c	2.40 ± 0.53 b	5.65 ± 0.58 a	1.51 ± 0.27 c	***
Pb	0.12 ± 0.03 b	0.15 ± 0.02 b	0.26 ± 0.03 a	0.29 ± 0.04 a	***
Sb	0.05 ± 0.01 a	0.03 ± 0.02 ab	0.02 ± 0.01 b	0.03 ± 0.01 ab	0.1079
V	0.12 ± 0.03 b	0.51 ± 0.14 a	0.42 ± 0.07 a	0.42 ± 0.04 a	**
Zn	22.6 ± 1.3 b	21.3 ± 2.66 bc	18.4 ± 1.6 c	23.7 ± 1.4 b	**

^{p} Values on each horizontal line followed by the same letter do not differ significantly (p = 0.05). * Significance at 0.05 probability level. ** Significant at 0.01 probability level. *** Significant at 0.001 probability level.

Table 2 Mean values (± standard deviation, S.D.) and results of the analysis de variance (ANOVA) of the elements measured in leaves without material deposited on surface collected in different at Nova Esperança do Sul (S1) and Lumiar (S2).

Element	S1			S2	ANOVA
	P1 Mean ± S.D.	P2 Mean ± S.D.	P3 Mean ± S.D.	PS2 Mean ± S.D.	
As	3.75 ± 0.20 ab	4.12 ± 0.38 a	3.13 ± 0.62 b	0.34 ± 0.05 c	***
Ba	86.7 ± 2.6 ab	91.0 ± 3.0 a	82.8 ± 5.9 b	61.2 ± 1.8 c	***
Cr	68.7 ± 3.1 a	44.3 ± 1.9 b	51.7 ± 11.6 b	10.7 ± 1.0 c	***
Cu	18.41 ± 1.73 b	24.70 ± 2.47 a	26.48 ± 1.95 a	4.14 ± 0.46 c	***
Fe	7484 ± 189 a	7083 ± 259 a	7107 ± 825 a	4745 ± 123 b	***
Ni	4.01 ± 0.19 a	5.21 ± 0.19 b	5.31 ± 1.11 b	3.05 ± 0.32 b	***
Pb	5.10 ± 0.41 ab	7.40 ± 0.40 a	7.17 ± 2.43 a	2.97 ± 0.30 b	**
Sb	0.37 ± 0.04 a	0.54 ± 0.05 b	0.29 ± 0.02 c	0.05 ± 0.02 d	***
V	23.7 ± 2.5 b	31.6 ± 2.5 a	24.8 ± 1.9 b	6.2 ± 0.3 c	***
Zn	75.6 ± 1.7 b	83.8 ± 4.7 a	79.5 ± 2.1 ab	30.3 ± 3.9 c	***

^{p} Values on each horizontal line followed by the same letter do not differ significantly (p = 0.05). * Significance at 0.05 probability level. ** Significant at 0.01 probability level. *** Significant at 0.001 probability level.

Table 3 Mean values (± standard deviation, S.D.) and results of the analysis de variance (ANOVA) of the elements measured in black particles collected at Nova Esperança do Sul (S1) during the three periods (P1, P2, and P3) and Lumiar (PS2).

Elements	Deep soil 300 m Mean ± S.D.	Superficial Soil 300 m Mean ± S.D.	Deep Soil 5.0 km Mean ± S.D.	ANOVA
As	5.79 ± 1.20 a	5.92 ± 1.19 a	1.54 ± 0.34 b	**
Ba	421 ± 22 a	358 ± 86 a	47.6 ± 1.4 b	***
Cr	47.78 ± 2.24 b	60.93 ± 3.82 a	5.43 ± 0.14 c	***
Cu	83.01 ± 2.15 a	70.81 ± 6.13 b	5.35 ± 0.18 c	***
Fe	54496 ± 1427 a	54940 ± 1486 a	4582 ± 249 b	***
Ni	13.68 ± 1.50 a	9.93 ± 0.83 b	2.10 ± 0.03 c	***
Pb	35.87 ± 2.77 a	34.03 ± 1.48 a	4.93 ± 0.67 b	***
Sb	1.24 ± 0.79 a	0.45 ± 0.07 ab	0.09 ± 0.02 b	0.051
V	167 ± 27 a	183 ± 29 a	18.97 ± 1.11 b	***
Zn	197 ± 5 a	209 ± 9 b	14.73 ± 2.14 c	***

[p] Values on each horizontal line followed by the same letter do not differ significantly ($p = 0.05$). * Significance at 0.05 probability level. ** Significant at 0.01 probability level. *** Significant at 0.001 probability level.

Table 4 Mean values (±standard deviation, S.D.) and results of the analysis de variance (ANOVA) of the trace elements measured soil samples collected at 300 m and 5.0 km of distance from tannery area. All samples collected on October 2017.

Enrichment factor (EF)

The enrichment factors, for all elements in black particles for the three periods at site S1A (P1, P2, and P3) and S2 were calculated as described in statistical analysis, and is shown in Fig. 2. $EF > 5$, suggest anthropogenic influence, as it is seen here for Cr (all periods) and As (P1 and P2) in site SA1. Enrichment factors between 1 and 4 were found for the other elements, indicating slight enrichment of these elements in the environment. In site S2, $EF < 2$ was observed for most elements, except for Zn ($EF \approx 4$). In general, EF values were in the order Cr > As > Zn > Ni > Cu > Sb > Ba > V > Pb, with Cr exhibiting always highest levels during the three periods of sampling at S1A.

Cluster analysis (CA)

Cluster analysis (CA) was applied to the data of soils (superficial and deep) and black particles removed from leaves (three periods) collected at site S1A. Elements with $EF < 2$ were not considered in CA. The resulting dendrogram from these toxic elements revealed two main groups: Cr constitutes the Group I, while Sb (subgroup 2A), As, Ni, Cu, Zn (subgroup 2B) constitute the Group 2. These results suggest that Group I has anthropogenic origin, while Group 2 may have a mixture of anthropogenic sources (As, Ni, Cu, and Zn) and soil particles (Sb).

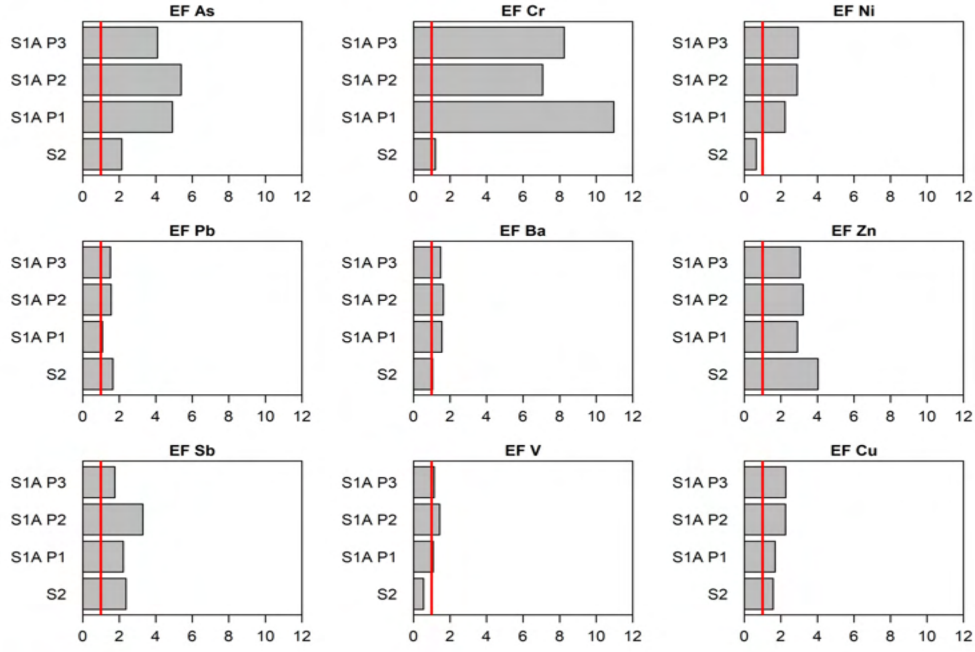

Fig. 2 Comparison among EFs of the elements measured on black particles removed from leaves in Nova Esperança do Sul, RS (S1) (three periods P1, P2, and P3) and Lumiar, RJ (S2). Fe is used as reference element.

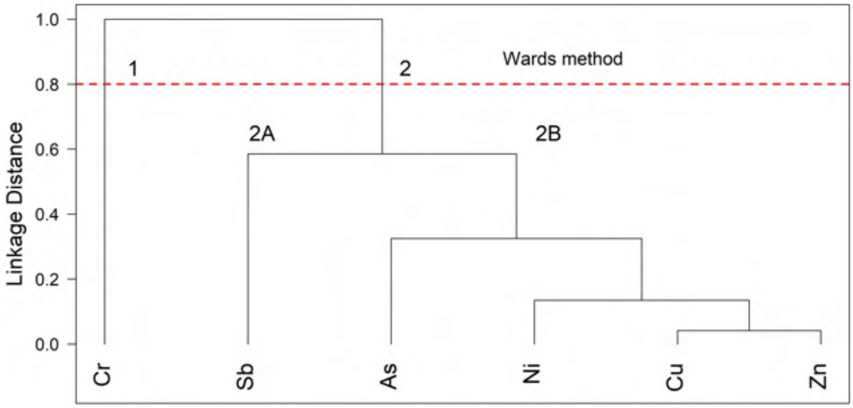

Fig. 3 Dendrogram representing the grouping of elements based on analysis of black particles removed from leaves of the three sampling periods and soil samples collected at Nova Esperança do Sul, RS (S1A).

DISCUSSION

Concentration levels of Cr obtained near tannery area for both soils and black particles were always higher than samples collected at 5.0 km and in Lumiar site. In terms of EFs, Cr and As total were clearly enriched in the three sampling periods at Rio Grande do Sul (site S1A), which are likely associated with anthropogenic activities. Leather industry is one of the industries considered as major source pollution of chromium because use significant amounts of chromium salt during tanning process (Kimbrough et al. 1999; Dixit et al. 2015). In the study area, chromium-tanned leather has been used for many decades to the manufacturing of a large variety of products; therefore the enrichment of this element may be attributed to tannery industry. Arsenic is a metalloid belongs to Group 15 of the periodic table and occurs naturally in the environment (Wilson et al. 2010). However, this element was recognized as a potentially harmful element (Morais et al. 2012). Arsenic is used in the manufacture of several products such as glass, ceramics, electronics, cosmetics, but also is used in agricultural activities through of pesticides, herbicides formulations (Zhou et al. 2018) and biocides that usually are used to wastewater treatment effluent (Bollmann et al. 2014). The land in the study area is used to produce a variety of products, such as corn, soy, tobacco, cassava, sugar cane and rice, where agrochemical are usually employed by farmers. Like other industries do not exist in this area, we may to affirm that a big part from As is related to agricultural activities. For instance, Zhou et al (2018) determined As concentrations in arable soils and found an increasing accumulation trend compared over past decades, which is related with the long-term application of phosphate fertilizers in agricultural practice.

In relation to the other elements Ni, Pb, Ba, Zn, Sb, V, and Cu was observed low enrichment of these metals in this area. These elements usually are related to vehicular sources (Akiyama 2006; Matti Maricq 2007; Amato et al. 2009; Kertész et al. 2010), and its low enrichment may be attributed to that this region is a rural area with reduced vehicular fleet.

The Group 1 of CA shows clearly Cr as a separate variable, which is consistent with the fact that chromium is a key element in tanning process to obtain leather. Sb is a metalloid occurring naturally in the environment as trace elements (Wilson et al. 2010). However in the last decades Sb is associated to traffic due to that several parts of vehicle contain Sb alloys and other Sb compounds (Fujiwara et al. 2011; Hu et al. 2015; Sanchez-Rodas et al. 2017). As it is seen in the subgroup 2B, arsenic is a little separated of the other elements, which may indicate that is released from anthropogenic sources but no necessarily of the same source of Ni, Cu and Zn. Arsenic also occurs naturally and it is noted their relation with Sb. Both elements were related to anthropogenic activities that can produce adverse effects to humans and the environment (Cooper and Harrison 2009).

CONCLUSIONS

This study evaluated the content of toxic elements in a region surrounding a large tannery area, located at Nova Esperanca do Sul, Rio Grande do Sul, Brazil. The results of the analysis of black particles collected near leather industry show higher concentration of all elements analyzed in the three sampling periods (approximately two years) compared to an area rural (Lumiar). In the same way, soil samples (both deep soil and surface soil) collected around tannery area shown higher concentration for all elements than deep soil collected to 5.0 km of distance. Enrichment factor higher than 5 were obtained for Cr (three periods) and As (two periods) suggesting anthropogenic influence of both elements. EF > 4 for Ni, Pb, Ba, Zn, Sb, and Cu were found. Cluster analysis related Cr to leather industry, whereas As was related to the use of pesticides or herbicides.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ACKNOWLEDGMENTS

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil).

REFERENCES

Akiyama K (2006) Gas chromatographic analysis and aerosol mass spectrometer measurement of diesel exhaust particles composition. Talanta 70:178–181. doi: 10.1016/j.talanta.2006.02.044

Amato F, Pandolfi M, Viana M, et al (2009) Spatial and chemical patterns of PM10 in road dust deposited in urban environment. Atmos Environ 43:1650–1659. doi: 10.1016/j.atmosenv.2008.12.009

Bing H, Wu Y, Zhou J, Sun H (2016) Biomonitoring trace metal contamination by seven sympatric alpine species in Eastern Tibetan Plateau. Chemosphere 165:388–398. doi: 10.1016/j.chemosphere.2016.09.042

Bollmann UE, Tang C, Eriksson E, et al (2014) Biocides in urban wastewater treatment plant influent at dry and wet weather: Concentrations, mass flows and possible sources. Water Res 60:64–74. doi: 10.1016/j.watres.2014.04.014

BRASIL CRDB (2016) AGRICULTORES FAMILIARES PLURIATIVOS NA REGIÃO DO VALE DO JAGUARI/RS: UM ESTUDO EM NOVA ESPERANÇA DO SUL. UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

Chavent M, Simonet VK, Liquet B, Kuentz-simonet V (2012) ClustOfVar : An R Package for the Clustering of Variables

Cooper RG, Harrison AP (2009) The exposure to and health effects of antimony - review article. Indian J Occup Environ Med 13:3–10. doi: 10.4103/0019-5278.50716

Dixit S, Yadav A, Dwivedi PD, Das M (2015) Toxic hazards of leather industry and technologies to combat threat: A review. J Clean Prod 87:39–49. doi: 10.1016/j.jclepro.2014.10.017

Enamorado-Báez SM, Gómez-Guzmán JM, Chamizo E, Abril JM (2015) Levels of 25 trace elements in high-volume air filter samples from Seville (2001–2002): Sources, enrichment factors and temporal variations. Atmos Res 155:118–129. doi: 10.1016/j.atmosres.2014.12.005

Fujiwara F, Rebagliati RJ, Marrero J, et al (2011) Antimony as a traffic-related element in size-fractionated road dust samples collected in Buenos Aires. Microchem J 97:62–67. doi: 10.1016/j.microc.2010.05.006

Giannetti BF, Bonilla SH, Almeida CMVB (2004) Developing eco-technologies: A possibility to minimize environmental impact in Southern Brazil. J Clean Prod 12:361–368. doi: 10.1016/S0959-6526(03)00033-7

Hu X, He M, Li S (2015) Antimony leaching release from brake pads: Effect of pH, temperature and organic acids. J Environ Sci (China) 29:11–17. doi: 10.1016/j.jes.2014.08.020

IBGE (2016) Estimativas da populacao residente no brasil e unidades da federacao com data de referencia em 1 julho de 2016

Joseph K, Nithya N (2009) Material flows in the life cycle of leather. J Clean Prod 17:676–682. doi: 10.1016/j.jclepro.2008.11.018

Kertész Z, Szoboszlai Z, Angyal A, et al (2010) Identification and characterization of fine and coarse particulate matter sources in a middle-European urban environment. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms 268:1924–1928. doi: 10.1016/j.nimb.2010.02.103

Kimbrough DE, Cohen Y, Winer AM, et al (1999) A critical assessment of chromium in the environment. Crit Rev Environ Sci Technol 29:1–46. doi: 10.1080/10643389991259164

Matti Maricq M (2007) Chemical characterization of particulate emissions from diesel engines: A review. J Aerosol Sci 38:1079–1118. doi: 10.1016/j.jaerosci.2007.08.001

Morais S, Garcia F, Pereira M de L (2012) Heavy Metals and Human Health. In: Environmental Health - Emerging Issues and Practice. pp 227–246

R Team Core (2015) A language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna Austria. R Foundation for Statistical Computing, Vienna, Austria

Ribeiro SH (2002) Determination of total chromium traces in tannery effluents by electrothermal atomic absorption spectrometry , flame atomic absorption spectrometry and UV Á v isible spectrophotometric methods. 58:629–633

Sanchez-Rodas D, Alsioufi L, Sanchez de la Campa AM, Gonzalez-Castanedo Y (2017) Antimony speciation as geochemical tracer for anthropogenic emissions of atmospheric particulate matter. J Hazard Mater 324:213–220. doi: 10.1016/j.jhazmat.2016.10.051

Sverre L, Acosta M (2007) Handbook on the Toxicology of Metals, Chapter 24, 3rd edn.

Taylor S, McLennan R (1985) Chemical Composition of Continental Crust and the Primitive Mantle. 136:. doi: 10.1007/978-4-431-53996-4

Wickham H, Francois R, Henry L, Müller K (2017) A Grammar of Data Manipulation. Cran

Wickham MH (2016) An Implementation of the Grammar of Graphics

Wilson SC, Lockwood P V., Ashley PM, Tighe M (2010) The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review. Environ Pollut 158:1169–1181. doi: 10.1016/j.envpol.2009.10.045

World Health Organization (2000) Chapter 6.4 Chromium. Air Qual Guidel - Second Ed 3:1–14. doi: 10.1016/S0959-6380(00)80018-5

Wu YS, Fang GC, Lee WJ, et al (2007) A review of atmospheric fine particulate matter and its associated trace metal pollutants in Asian countries during the period 1995-2005. J Hazard Mater 143:511–515. doi: 10.1016/j.jhazmat.2006.09.066

Zhou Y, Niu L, Liu K, et al (2018) Arsenic in agricultural soils across China : Distribution pattern, accumulation trend, influencing factors, and risk assessment. Sci Total Environ 616–617:156–163. doi: 10.1016/j.scitotenv.2017.10.232

ÍNDICE REMISSIVO

A

Atmospheric particles 64

B

Biomonitoring 1, 2, 3, 4, 12, 13, 14, 15, 63, 64, 73

C

Comércio ilegal 117, 119, 120, 121, 122

Consumo 16, 17, 19, 20, 21, 22, 23, 24, 25, 27, 28, 77, 80, 86, 113, 115, 119, 120, 122, 123, 124, 125, 127, 158

Cooperativa 55, 57, 60

Cultura 22, 28, 29, 31, 34, 36, 43, 47, 93, 97, 109, 110, 147, 152, 155

D

Dignidade humana 90, 93

E

Economia 16, 19, 20, 25, 47, 59, 77, 82, 84, 89, 103, 106, 121

Educação 29, 30, 31, 32, 33, 34, 36, 37, 41, 44, 50, 52, 54, 89, 91, 92, 97, 99, 103, 108, 109, 111, 113, 118, 120, 121, 123, 125, 149, 158

G

Gás de efeito estufa 55, 56

I

ICP-MS 1, 2, 5, 63, 64, 66, 67

Impactos aquático 136

Incentivos 44, 45, 46, 48, 50, 51, 53

L

Leather industry 64, 72, 73

M

Mata Atlântica 89, 90, 91, 94, 95, 96, 97, 98, 99, 101, 105, 106, 109

Materiais recicláveis 55, 57, 58, 59, 60, 61, 62

Metals 2, 3, 8, 13, 15, 68, 72, 74, 158, 159

Método P&O 127, 129, 130

Mínimo existencial ambiental 90, 93, 103

Mudança climática 55, 56, 57

N

Natureza 16, 17, 18, 19, 20, 23, 24, 26, 28, 29, 30, 31, 34, 36, 37, 41, 43, 46, 78, 89, 90, 91, 92, 93, 94, 95, 97, 99, 101, 103, 104, 108, 109, 110, 113, 114, 115, 116, 122, 123, 125, 138, 140

P

Patrimônio 29, 30, 31, 32, 34, 35, 36, 37, 38, 39, 41, 42, 43

Podocnemis 117, 125

Pollution 2, 3, 4, 12, 13, 14, 15, 64, 65, 72, 137, 156, 157, 158, 159

Preservação ambiental 45

Propriedade familiar 44, 45, 46, 47, 48, 49, 50, 51, 53

Q

Qualidade da água 56, 105, 115, 136, 141, 142, 144, 146, 147, 148, 149, 150, 156, 158

R

Reciclagem 55, 56, 57, 59, 60, 61, 76, 77, 78, 79, 80, 81, 82, 84, 85, 86, 87

Regulamentação 44, 45, 46, 48, 51, 53

Ruralidade metropolitana 89, 90, 94, 95

S

Sistemas fotovoltaicos 127, 134, 135

Sociedade 16, 20, 21, 22, 23, 27, 28, 31, 33, 34, 35, 37, 44, 46, 56, 89, 90, 91, 93, 94, 98, 99, 100, 103, 104, 105, 106, 109, 114, 125, 127, 147

Sustentabilidade 16, 17, 19, 20, 21, 23, 25, 27, 28, 29, 36, 37, 38, 41, 47, 50, 62, 76, 79, 90, 92, 97, 105, 110, 111, 112, 113, 122, 125, 128, 150

T

Técnicas MPPT 127, 135

Tillandsia genus 2

Toxic elements 1, 2, 9, 63, 64, 65, 70, 72

U

Uso do solo 136, 141, 142, 147, 151, 152, 156, 158

V

Vestuário 76, 77, 78, 80

www.atenaeditora.com.br
contato@atenaeditora.com.br
@atenaeditora
www.facebook.com/atenaeditora.com.br

PAUTA AMBIENTAL BRASILEIRA E A PROMOÇÃO DA SUSTENTABILIDADE

Atena
Editora
Ano 2022

www.atenaeditora.com.br
contato@atenaeditora.com.br
@atenaeditora
www.facebook.com/atenaeditora.com.br

PAUTA AMBIENTAL BRASILEIRA E A PROMOÇÃO DA SUSTENTABILIDADE

Atena
Editora
Ano 2022