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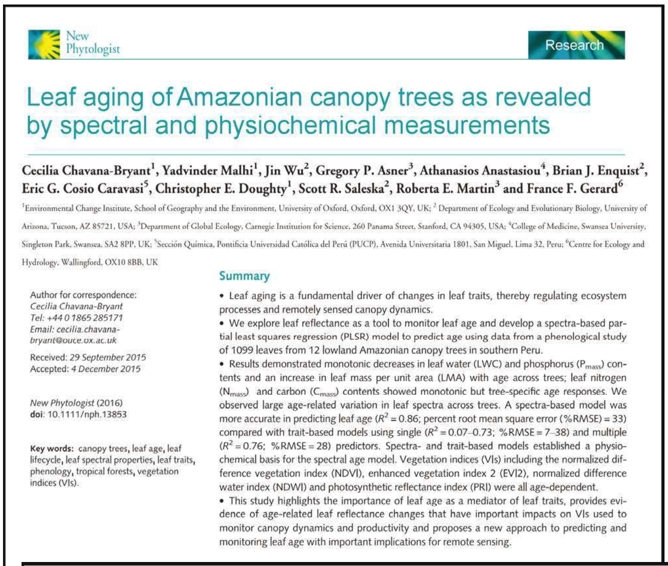

New Phytologist

Research

Leaf aging of Amazonian canopy trees as revealed by spectral and physiochemical measurements

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Key words: canopy trees, leaf age, leaf lifecycle, leaf spectral properties, leaf traits, phenology, tropical forests, vegetation indices (VIs).

Summary

- Leaf aging is a fundamental driver of changes in leaf traits, thereby regulating ecosystem processes and remotely sensed canopy dynamics.
- We explore leaf reflectance as a tool to monitor leaf age and develop a spectra-based partial least squares regression (PLSR) model to predict age using data from a phenological study of 1099 leaves from 12 lowland Amazonian canopy trees in southern Peru.
- Results demonstrated monotonic decreases in leaf water (LWC) and phosphorus (P_{mass}) contents and an increase in leaf mass per unit area (LMA) with age across trees; leaf nitrogen (N_{mass}) and carbon (C_{mass}) contents showed monotonic but tree-specific age responses. We observed large age-related variation in leaf spectra across trees. A spectra-based model was more accurate in predicting leaf age ($R^2 = 0.86$; percent root mean square error (%RMSE) = 33) compared with trait-based models using single ($R^2 = 0.07$–0.73; %RMSE = 7–38) and multiple ($R^2 = 0.76$; %RMSE = 28) predictors. Spectra- and trait-based models established a physiochemical basis for the spectral age model. Vegetation indices (VIs) including the normalized difference vegetation index (NDVI), enhanced vegetation index 2 (EVI2), normalized difference water index (NDWI) and photosynthetic reflectance index (PRI) were all age-dependent.
- This study highlights the importance of leaf age as a mediator of leaf traits, provides evidence of age-related leaf reflectance changes that have important impacts on VIs used to monitor canopy dynamics and productivity and proposes a new approach to predicting and monitoring leaf age with important implications for remote sensing.

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The potential use of chitosan as a biopolymer additive for enhanced mechanical properties and water resistance of earthen construction

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highlights

- Chitosan successfully improved the engineering behavior of earthen construction.
- Coating with 0.5% chitosan solution protected earthen materials from water erosion.
- Earthen material with 1%–3% chitosan admixture had high water erosion resistance.
- Samples with 3% chitosan admixture showed improved mechanical properties.

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abstract

The study investigates the feasibility of using chitosan biopolymer as an admixture, or as an external coating, for earthen constructions to improve their resistance in two components: water induced degradation and key mechanical properties. The resistance to water induced degradation was evaluated in terms of contact angle and drip erosion tests, while the influence on mechanical properties was measured through compressive, tensile and three-point bending tests. The results indicate that the use of low concentrations of chitosan can improve significantly the performance in the two components and therefore was found to be a promising treatment for new or existing construction.

1. Introduction

Earth has been used as a construction material since ancient times to build houses, archaeological, and historical monuments over the world. It is estimated that approximately 30% of the world population live in unreinforced earthen houses located principally in developing countries primarily due to economic considerations [1]. In recent years the use of earthen construction has seen an increase in popularity as an eco-friendly sustainable architectural approach. Its ability to be recycled indefinitely and aesthetic benefits have resulted in increased popularity of earth architecture with many museums, embassies, and other building types made of earth [2–4]. Additional benefits of building with earth, beyond economic considerations, include low ecological impact due to reduced greenhouse gas emissions during construction [2] as well as facilities with good thermal and acoustic behavior [5].

Different techniques have been reported for earthen construction primarily depending on the region of the world where it is used. According to [1], earthen construction techniques can be divided into three main groups: structure, monolithic and brickwork. Rammed earth walls (monolithic) and adobe masonry (brickwork) are the most widespread methods. As an example, in Peru, 34% of the houses are built with these two techniques [6].

Unfortunately earthen buildings can have some disadvantages. From a mechanical perspective, they are usually heavy, brittle, and present low tensile resistance which makes them especially vulnerable to seismic events [7]. For example, as shown in Fig. 1a, after the 2003 earthquake of Bam, Iran, historical earthen buildings were severely damaged [8]. Another negative aspect to consider

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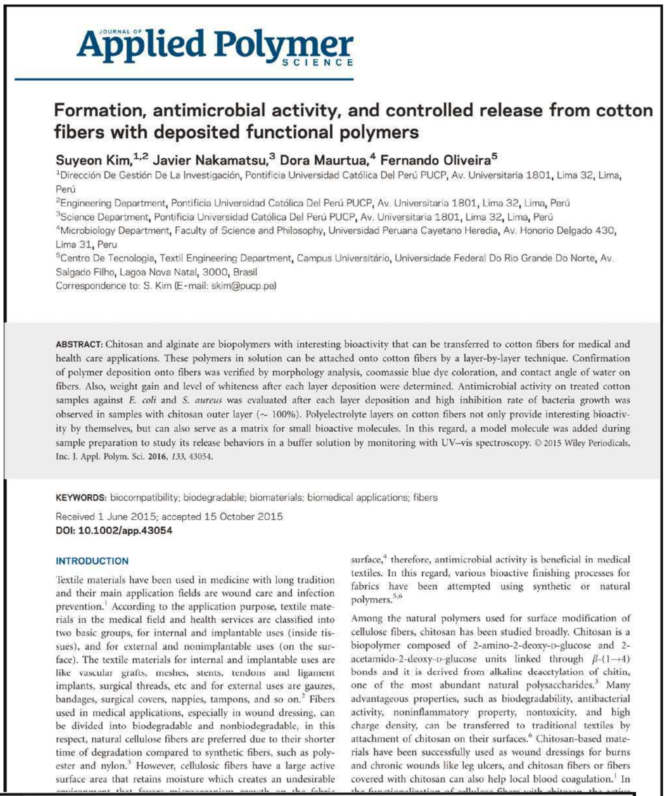

JOURNAL OF Applied Polymer SCIENCE

Formation, antimicrobial activity, and controlled release from cotton fibers with deposited functional polymers

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ABSTRACT: Chitosan and alginate are biopolymers with interesting bioactivity that can be transferred to cotton fibers for medical and health care applications. These polymers in solution can be attached onto cotton fibers by a layer-by-layer technique. Confirmation of polymer deposition onto fibers was verified by morphology analysis, coomassie blue dye coloration, and contact angle of water on fibers. Also, weight gain and level of whiteness after each layer deposition were determined. Antimicrobial activity on treated cotton samples against *E. coli* and *S. aureus* was evaluated after each layer deposition and high inhibition rate of bacteria growth was observed in samples with chitosan outer layer (~ 100%). Polyelectrolyte layers on cotton fibers not only provide interesting bioactivity by themselves, but can also serve as a matrix for small bioactive molecules. In this regard, a model molecule was added during sample preparation to study its release behaviors in a buffer solution by monitoring with UV–vis spectroscopy. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43054.

KEYWORDS: biocompatibility; biodegradable; biomaterials; biomedical applications; fibers

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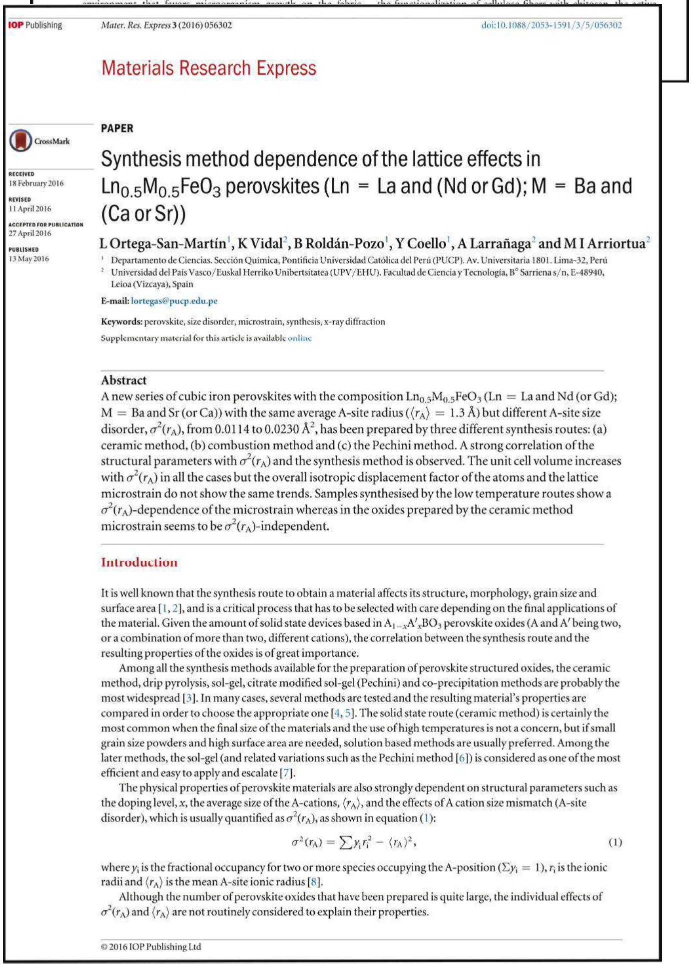
INTRODUCTION

Textile materials have been used in medicine with long tradition and their main application fields are wound care and infection prevention.[1] According to the application purpose, textile materials in the medical field and health services are classified into two basic groups, for internal and implantable uses (inside tissues), and for external and nonimplantable uses (on the surface). The textile materials for internal and implantable uses are like vascular grafts, meshes, stents, tendons and ligament implants, surgical threads, etc and for external uses are gauzes, bandages, surgical covers, nappies, tampons, and so on.[2] Fibers used in medical applications, especially in wound dressing, can be divided into biodegradable and nonbiodegradable, in this respect, natural cellulose fibers are preferred due to their shorter time of degradation compared to synthetic fibers, such as polyester and nylon.[3] However, cellulosic fibers have a large active surface area that retains moisture which creates an undesirable

surface,[4] therefore, antimicrobial activity is beneficial in medical textiles. In this regard, various bioactive finishing processes for fabrics have been attempted using synthetic or natural polymers.[5,6]

Among the natural polymers used for surface modification of cellulose fibers, chitosan has been studied broadly. Chitosan is a biopolymer composed of 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose units linked through β-(1→4) bonds and it is derived from alkaline deacetylation of chitin, one of the most abundant natural polysaccharides.[3] Many advantageous properties, such as biodegradability, antibacterial activity, noninflammatory property, nontoxicity, and high charge density, can be transferred to traditional textiles by attachment of chitosan on their surfaces.[6] Chitosan-based materials have been successfully used as wound dressings for burns and chronic wounds like leg ulcers, and chitosan fibers or fibers covered with chitosan can also help local blood coagulation.[1] In



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PAPER

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Synthesis method dependence of the lattice effects in $\mathrm{Ln_{0.5}M_{0.5}FeO_3}$ perovskites (Ln = La and (Nd or Gd); M = Ba and (Ca or Sr))

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Keywords: perovskite, size disorder, microstrain, synthesis, x-ray diffraction

Supplementary material for this article is available online

Abstract

A new series of cubic iron perovskites with the composition $\mathrm{Ln_{0.5}M_{0.5}FeO_3}$ (Ln = La and Nd (or Gd); M = Ba and Sr (or Ca)) with the same average A-site radius ($\langle r_A \rangle = 1.3$ Å) but different A-site size disorder, $\sigma^2(r_A)$, from 0.0114 to 0.0230 Å^2, has been prepared by three different synthesis routes: (a) ceramic method, (b) combustion method and (c) the Pechini method. A strong correlation of the structural parameters with $\sigma^2(r_A)$ and the synthesis method is observed. The unit cell volume increases with $\sigma^2(r_A)$ in all the cases but the overall isotropic displacement factor of the atoms and the lattice microstrain do not show the same trends. Samples synthesised by the low temperature routes show a $\sigma^2(r_A)$-dependence of the microstrain whereas in the oxides prepared by the ceramic method microstrain seems to be $\sigma^2(r_A)$-independent.

Introduction

It is well known that the synthesis route to obtain a material affects its structure, morphology, grain size and surface area [1, 2], and is a critical process that has to be selected with care depending on the final applications of the material. Given the amount of solid state devices based in $\mathrm{A_{1-x}A'_xBO_3}$ perovskite oxides (A and A′ being two, or a combination of more than two, different cations), the correlation between the synthesis route and the resulting properties of the oxides is of great importance.

Among all the synthesis methods available for the preparation of perovskite structured oxides, the ceramic method, drip pyrolysis, sol-gel, citrate modified sol-gel (Pechini) and co-precipitation methods are probably the most widespread [3]. In many cases, several methods are tested and the resulting material's properties are compared in order to choose the appropriate one [4, 5]. The solid state route (ceramic method) is certainly the most common when the final size of the materials and the use of high temperatures is not a concern, but if small grain size powders and high surface area are needed, solution based methods are usually preferred. Among the later methods, the sol-gel (and related variations such as the Pechini method [6]) is considered as one of the most efficient and easy to apply and escalate [7].

The physical properties of perovskite materials are also strongly dependent on structural parameters such as the doping level, x, the average size of the A-cations, $\langle r_A \rangle$, and the effects of A cation size mismatch (A-site disorder), which is usually quantified as $\sigma^2(r_A)$, as shown in equation (1):

$$\sigma^2(r_A) = \sum y_i r_i^2 - \langle r_A \rangle^2, \tag{1}$$

where y_i is the fractional occupancy for two or more species occupying the A-position ($\Sigma y_i = 1$), r_i is the ionic radii and $\langle r_A \rangle$ is the mean A-site ionic radius [8].

Although the number of perovskite oxides that have been prepared is quite large, the individual effects of $\sigma^2(r_A)$ and $\langle r_A \rangle$ are not routinely considered to explain their properties.

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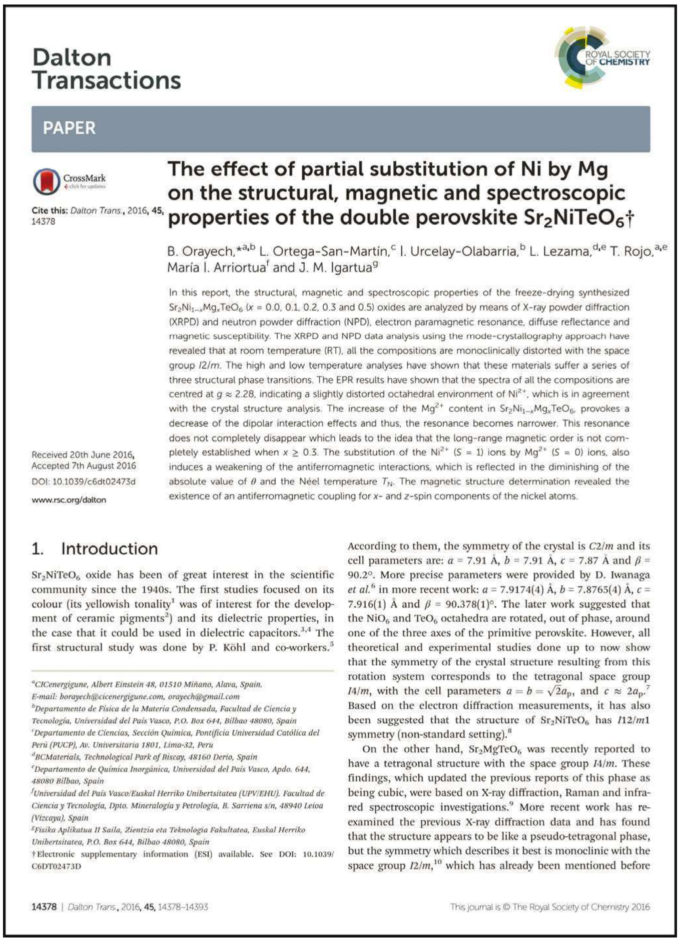
* *Solo se incluyen artículos de miembros de la Sección Química de la PUCP que aparezcan firmados con la afiliación a esta sección, independientemente de si los colaboradores son, o no, de la PUCP hasta el 30 de septiembre de 2016. El acceso al artículo depende de la suscripción del usuario a las editoriales correspondientes. Se han incluido solo revistas científicas que se encuentran indexadas en las bases de datos* ***Scopus*** *y* ***Web of Science****, de reconocido prestigio internacional.*



Dalton Transactions

PAPER

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The effect of partial substitution of Ni by Mg on the structural, magnetic and spectroscopic properties of the double perovskite Sr_2NiTeO_6†

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In this report, the structural, magnetic and spectroscopic properties of the freeze-drying synthesized $Sr_2Ni_{1-x}Mg_xTeO_6$ (x = 0.0, 0.1, 0.2, 0.3 and 0.5) oxides are analyzed by means of X-ray powder diffraction (XRPD) and neutron powder diffraction (NPD), electron paramagnetic resonance, diffuse reflectance and magnetic susceptibility. The XRPD and NPD data analysis using the mode-crystallography approach have revealed that at room temperature (RT), all the compositions are monoclinically distorted with the space group $I2/m$. The high and low temperature analyses have shown that these materials suffer a series of three structural phase transitions. The EPR results have shown that the spectra of all the compositions are centred at $g \approx 2.28$, indicating a slightly distorted octahedral environment of Ni^{2+}, which is in agreement with the crystal structure analysis. The increase of the Mg^{2+} content in $Sr_2Ni_{1-x}Mg_xTeO_6$, provokes a decrease of the dipolar interaction effects and thus, the resonance becomes narrower. This resonance does not completely disappear which leads to the idea that the long-range magnetic order is not completely established when $x \geq 0.3$. The substitution of the Ni^{2+} (S = 1) ions by Mg^{2+} (S = 0) ions, also induces a weakening of the antiferromagnetic interactions, which is reflected in the diminishing of the absolute value of θ and the Néel temperature T_N. The magnetic structure determination revealed the existence of an antiferromagnetic coupling for x- and z-spin components of the nickel atoms.

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1. Introduction

Sr_2NiTeO_6 oxide has been of great interest in the scientific community since the 1940s. The first studies focused on its colour (its yellowish tonality[1] was of interest for the development of ceramic pigments[2]) and its dielectric properties, in the case that it could be used in dielectric capacitors.[3,4] The first structural study was done by P. Köhl and co-workers.[5] According to them, the symmetry of the crystal is $C2/m$ and its cell parameters are: a = 7.91 Å, b = 7.91 Å, c = 7.87 Å and β = 90.2°. More precise parameters were provided by D. Iwanaga *et al.*[6] in more recent work: a = 7.9174(4) Å, b = 7.8765(4) Å, c = 7.916(1) Å and β = 90.378(1)°. The later work suggested that the NiO_6 and TeO_6 octahedra are rotated, out of phase, around one of the three axes of the primitive perovskite. However, all theoretical and experimental studies done up to now show that the symmetry of the crystal structure resulting from this rotation system corresponds to the tetragonal space group $I4/m$, with the cell parameters $a = b = \sqrt{2}a_p$, and $c \approx 2a_p$.[7] Based on the electron diffraction measurements, it has also been suggested that the structure of Sr_2NiTeO_6 has $I12/m1$ symmetry (non-standard setting).[8]

On the other hand, Sr_2MgTeO_6 was recently reported to have a tetragonal structure with the space group $I4/m$. These findings, which updated the previous reports of this phase as being cubic, were based on X-ray diffraction, Raman and infrared spectroscopic investigations.[9] More recent work has re-examined the previous X-ray diffraction data and has found that the structure appears to be like a pseudo-tetragonal phase, but the symmetry which describes it best is monoclinic with the space group $I2/m$,[10] which has already been mentioned before

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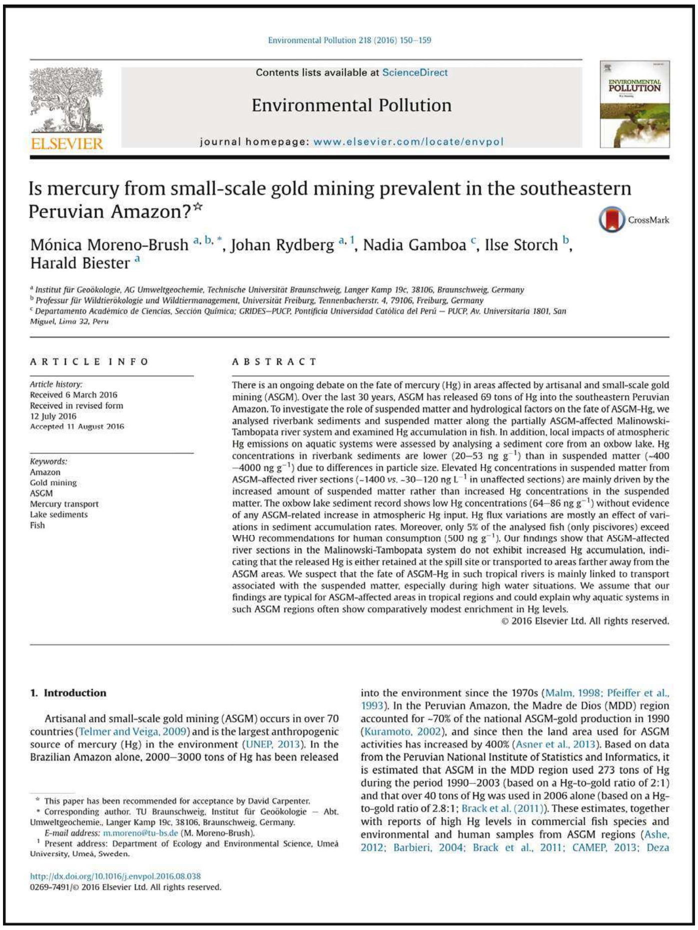

Environmental Pollution 218 (2016) 150–159

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ELSEVIER

Is mercury from small-scale gold mining prevalent in the southeastern Peruvian Amazon?☆

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A B S T R A C T

There is an ongoing debate on the fate of mercury (Hg) in areas affected by artisanal and small-scale gold mining (ASGM). Over the last 30 years, ASGM has released 69 tons of Hg into the southeastern Peruvian Amazon. To investigate the role of suspended matter and hydrological factors on the fate of ASGM-Hg, we analysed riverbank sediments and suspended matter along the partially ASGM-affected Malinowski-Tambopata river system and examined Hg accumulation in fish. In addition, local impacts of atmospheric Hg emissions on aquatic systems were assessed by analysing a sediment core from an oxbow lake. Hg concentrations in riverbank sediments are lower (20–53 ng g^{-1}) than in suspended matter (~400–4000 ng g^{-1}) due to differences in particle size. Elevated Hg concentrations in suspended matter from ASGM-affected river sections (~1400 *vs.* ~30–120 ng L^{-1} in unaffected sections) are mainly driven by the increased amount of suspended matter rather than increased Hg concentrations in the suspended matter. The oxbow lake sediment record shows low Hg concentrations (64–86 ng g^{-1}) without evidence of any ASGM-related increase in atmospheric Hg input. Hg flux variations are mostly an effect of variations in sediment accumulation rates. Moreover, only 5% of the analysed fish (only piscivores) exceed WHO recommendations for human consumption (500 ng g^{-1}). Our findings show that ASGM-affected river sections in the Malinowski-Tambopata system do not exhibit increased Hg accumulation, indicating that the released Hg is either retained at the spill site or transported to areas farther away from the ASGM areas. We suspect that the fate of ASGM-Hg in such tropical rivers is mainly linked to transport associated with the suspended matter, especially during high water situations. We assume that our findings are typical for ASGM-affected areas in tropical regions and could explain why aquatic systems in such ASGM regions often show comparatively modest enrichment in Hg levels.

1. Introduction

Artisanal and small-scale gold mining (ASGM) occurs in over 70 countries (Telmer and Veiga, 2009) and is the largest anthropogenic source of mercury (Hg) in the environment (UNEP, 2013). In the Brazilian Amazon alone, 2000–3000 tons of Hg has been released into the environment since the 1970s (Malm, 1998; Pfeiffer et al., 1993). In the Peruvian Amazon, the Madre de Dios (MDD) region accounted for ~70% of the national ASGM-gold production in 1990 (Kuramoto, 2002), and since then the land area used for ASGM activities has increased by 400% (Asner et al., 2013). Based on data from the Peruvian National Institute of Statistics and Informatics, it is estimated that ASGM in the MDD region used 273 tons of Hg during the period 1990–2003 (based on a Hg-to-gold ratio of 2:1) and that over 40 tons of Hg was used in 2006 alone (based on a Hg-to-gold ratio of 2.8:1; Brack et al. (2011)). These estimates, together with reports of high Hg levels in commercial fish species and environmental and human samples from ASGM regions (Ashe, 2012; Barbieri, 2004; Brack et al., 2011; CAMEP, 2013; Deza

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☆ This paper has been recommended for acceptance by David Carpenter.

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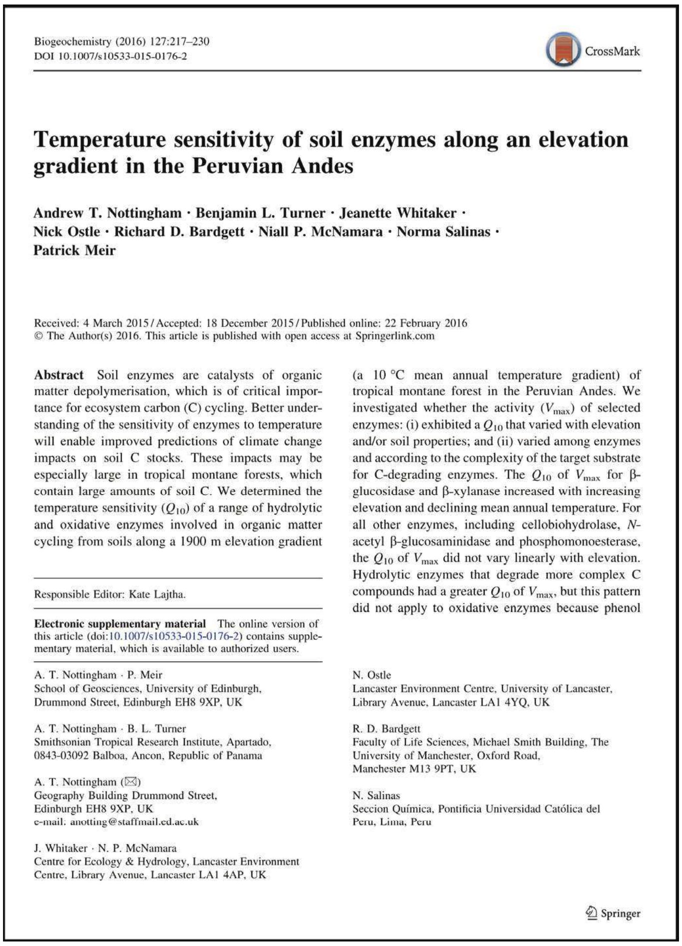

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Temperature sensitivity of soil enzymes along an elevation gradient in the Peruvian Andes

Andrew T. Nottingham · Benjamin L. Turner · Jeanette Whitaker · Nick Ostle · Richard D. Bardgett · Niall P. McNamara · Norma Salinas · Patrick Meir

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Abstract Soil enzymes are catalysts of organic matter depolymerisation, which is of critical importance for ecosystem carbon (C) cycling. Better understanding of the sensitivity of enzymes to temperature will enable improved predictions of climate change impacts on soil C stocks. These impacts may be especially large in tropical montane forests, which contain large amounts of soil C. We determined the temperature sensitivity (Q_{10}) of a range of hydrolytic and oxidative enzymes involved in organic matter cycling from soils along a 1900 m elevation gradient (a 10 °C mean annual temperature gradient) of tropical montane forest in the Peruvian Andes. We investigated whether the activity (V_{max}) of selected enzymes: (i) exhibited a Q_{10} that varied with elevation and/or soil properties; and (ii) varied among enzymes and according to the complexity of the target substrate for C-degrading enzymes. The Q_{10} of V_{max} for β-glucosidase and β-xylanase increased with increasing elevation and declining mean annual temperature. For all other enzymes, including cellobiohydrolase, *N*-acetyl β-glucosaminidase and phosphomonoesterase, the Q_{10} of V_{max} did not vary linearly with elevation. Hydrolytic enzymes that degrade more complex C compounds had a greater Q_{10} of V_{max}, but this pattern did not apply to oxidative enzymes because phenol

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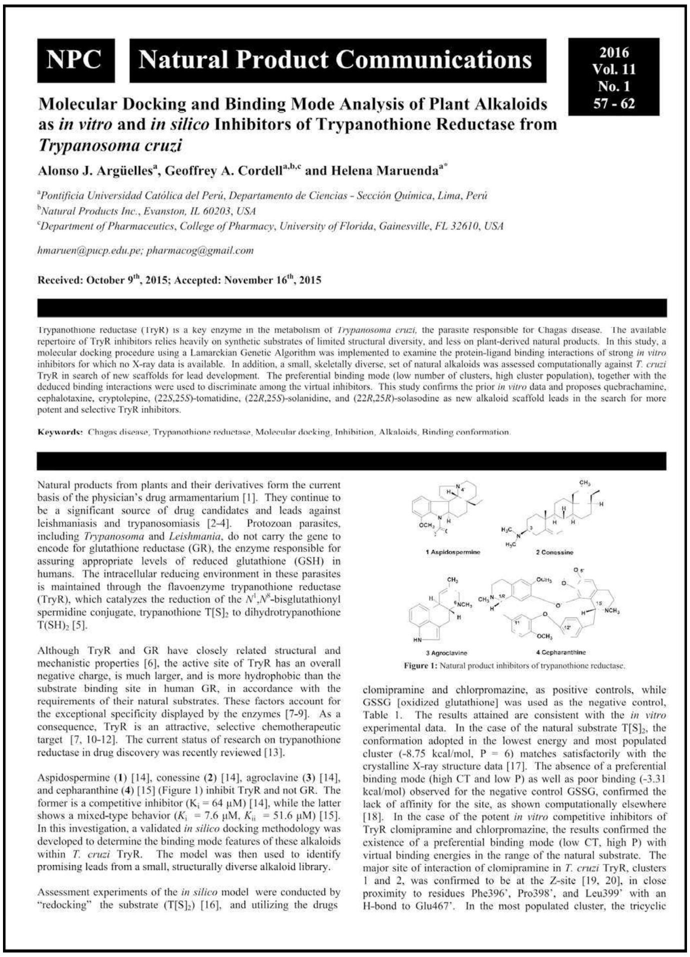

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Molecular Docking and Binding Mode Analysis of Plant Alkaloids as *in vitro* and *in silico* Inhibitors of Trypanothione Reductase from *Trypanosoma cruzi*

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Trypanothione reductase (TryR) is a key enzyme in the metabolism of *Trypanosoma cruzi*, the parasite responsible for Chagas disease. The available repertoire of TryR inhibitors relies heavily on synthetic substrates of limited structural diversity, and less on plant-derived natural products. In this study, a molecular docking procedure using a Lamarckian Genetic Algorithm was implemented to examine the protein-ligand binding interactions of strong *in vitro* inhibitors for which no X-ray data is available. In addition, a small, skeletally diverse, set of natural alkaloids was assessed computationally against *T. cruzi* TryR in search of new scaffolds for lead development. The preferential binding mode (low number of clusters, high cluster population), together with the deduced binding interactions were used to discriminate among the virtual inhibitors. This study confirms the prior *in vitro* data and proposes quebrachamine, cephalotaxine, cryptolepine, (22*S*,25*S*)-tomatidine, (22*R*,25*S*)-solanidine, and (22*R*,25*R*)-solasodine as new alkaloid scaffold leads in the search for more potent and selective TryR inhibitors.

Keywords: Chagas disease, Trypanothione reductase, Molecular docking, Inhibition, Alkaloids, Binding conformation.

Natural products from plants and their derivatives form the current basis of the physician's drug armamentarium [1]. They continue to be a significant source of drug candidates and leads against leishmaniasis and trypanosomiasis [2-4]. Protozoan parasites, including *Trypanosoma* and *Leishmania*, do not carry the gene to encode for glutathione reductase (GR), the enzyme responsible for assuring appropriate levels of reduced glutathione (GSH) in humans. The intracellular reducing environment in these parasites is maintained through the flavoenzyme trypanothione reductase (TryR), which catalyzes the reduction of the N^1,N^8-bisglutathionyl spermidine conjugate, trypanothione $T[S]_2$ to dihydrotrypanothione $T(SH)_2$ [5].

Although TryR and GR have closely related structural and mechanistic properties [6], the active site of TryR has an overall negative charge, is much larger, and is more hydrophobic than the substrate binding site in human GR, in accordance with the requirements of their natural substrates. These factors account for the exceptional specificity displayed by the enzymes [7-9]. As a consequence, TryR is an attractive, selective chemotherapeutic target [7, 10-12]. The current status of research on trypanothione reductase in drug discovery was recently reviewed [13].

Aspidospermine (**1**) [14], conessine (**2**) [14], agroclavine (**3**) [14], and cepharanthine (**4**) [15] (Figure 1) inhibit TryR and not GR. The former is a competitive inhibitor (K_i = 64 μM) [14], while the latter shows a mixed-type behavior (K_i = 7.6 μM, K_{ii} = 51.6 μM) [15]. In this investigation, a validated *in silico* docking methodology was developed to determine the binding mode features of these alkaloids within *T. cruzi* TryR. The model was then used to identify promising leads from a small, structurally diverse alkaloid library.

Assessment experiments of the *in silico* model were conducted by "redocking" the substrate ($T[S]_2$) [16], and utilizing the drugs clomipramine and chlorpromazine, as positive controls, while GSSG [oxidized glutathione] was used as the negative control, Table 1. The results attained are consistent with the *in vitro* experimental data. In the case of the natural substrate $T[S]_2$, the conformation adopted in the lowest energy and most populated cluster (-8.75 kcal/mol, P = 6) matches satisfactorily with the crystalline X-ray structure data [17]. The absence of a preferential binding mode (high CT and low P) as well as poor binding (-3.31 kcal/mol) observed for the negative control GSSG, confirmed the lack of affinity for the site, as shown computationally elsewhere [18]. In the case of the potent *in vitro* competitive inhibitors of TryR clomipramine and chlorpromazine, the results confirmed the existence of a preferential binding mode (low CT, high P) with virtual binding energies in the range of the natural substrate. The major site of interaction of clomipramine in *T. cruzi* TryR, clusters 1 and 2, was confirmed to be at the Z-site [19, 20], in close proximity to residues Phe396', Pro398', and Leu399' with an H-bond to Glu467'. In the most populated cluster, the tricyclic

1 Aspidospermine 2 Conessine 3 Agroclavine 4 Cepharanthine

Figure 1: Natural product inhibitors of trypanothione reductase.