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Vanadium Health Research Programme: Recent Published Literature

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Report to Vanitec

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This document is a report by IEH Consulting Ltd. for the Vanadium International Technical Committee (VANITEC).

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29th March 2020

Introduction

This report presents the bibliographic details of the 149 papers identified as being published during the period January 2020 to March 2020.

The papers were selected because they address research areas that are considered of direct relevance to the health and environmental effects of Vanadium. In order to aid review, the papers are presented under the following categories; it should be noted however, that when considered appropriate, some papers may appear in more than one section.

Section 1 – HUMAN EXPOSURE MEASUREMENT AND MODELLING: Papers relating to the measurement or modelling of environmental and occupational Vanadium exposure; the development of human biomarkers of exposure or effect.

Section 2 - HEALTH EFFECTS: Papers on the influence of Vanadium on health, disease and dysfunction; assessment of the influence of genetic and epigenetic factors on human susceptibility to the effects of Vanadium; development and implementation of new medical approaches to the treatment of excessive Vanadium exposure.

Section 3 – BIOLOGICAL MECHANISMS: Papers on the biochemical and toxicological mechanisms underlying the effects of Vanadium.

Section 4 – USES OF VANADIUM: Papers relating to the use of Vanadium in medical and dental devices, dietary supplements and as therapeutic agents.

Section 5 – ENVIRONMENTAL EFFECTS in PLANTS and SOIL: Papers relating to the effects following environmental exposure to Vanadium that are specific to plants and soil.

Section 6 – ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS: Papers relating to the effects following environmental exposure to Vanadium that are specific to terrestrial organisms.

Section 7 – ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS: Papers relating to the effects following environmental exposure to Vanadium that are specific to aquatic organisms.

Section 8 – MISCELLANEOUS: Other papers considered of general interest or potential relevance to the study of the health effects of Vanadium that do not relate to the above categories.

1. HUMAN EXPOSURE MEASUREMENT AND MODELLING

Alghamdi, M.A., Hassan, S.K., Alzahrani, N.A.*, et al.* (2019) Risk assessment and implications of schoolchildren exposure to classroom heavy metals particles in Jeddah, Saudi Arabia. *International Journal of Environmental Research and Public Health,* 16(24).
Available at: https://www.mdpi.com/1660-4601/16/24/5017/pdf
Keywords: Classrooms air conditioner filter particles; Contamination level; Health risk; Heavy metals; Indoor air quality; Schools; arsenic; cadmium; carcinogen; chromium; cobalt; copper; heavy metal; iron; lead; manganese; nickel; vanadium; zinc; air quality; cancer; indoor air; particulate matter; pollution exposure; public space; risk assessment; air conditioning; airborne particle; Article; cancer risk; child; controlled study; environmental enrichment; environmental exposure; health hazard; human; indoor air pollution; ingestion; inhalation; residential area; Saudi Arabia; school; school child; skin; suburban area; urban area; Jeddah; Makkah [Saudi Arabia]

Abstract:
Classrooms Air Conditioner Filter (CACF) particles represent all of the exposed particles that have migrated to the interior environment. This study was conducted to assess the heavy metals contamination in CACF particles from Jeddah primary schools located in urban, suburban and residential areas; and to evaluate their health risks of children exposure (non-carcinogenic and carcinogenic). Heavy metals levels in CACF particles of schools were in the following order: urban schools > suburban schools > residential schools. Fe, Mn and Zn were the dominant species. Geo-accumulation index (Igeo), contamination factor (CF) and pollution load index (PLI) values indicated that the contamination levels was in the following order Cd > Pb > Zn > As > Cu > Ni > Mn > Cr > Co >V > Fe. School CACF particles was moderately contaminated with As and Zn and moderately to heavily contaminated with Pb and Cd. Enrichment factors (EFs) indicated that Zn, Cd, Pb, As and Cu in CACF particles were severe enriched. The hazard quotient (HQs) and hazards index (HI) values for heavy metals were lower than the acceptable level of one. As, Pb, Cr and Mn were exhibited high non-cancer effects for children. The lifetime cancer risk (LCR) and total lifetime cancer risk (TLCR), HQs and HI values for the different exposure pathways of heavy metals decreased in the following order: ingestion > dermal contact > inhalation. Carcinogenic and non-carcinogenic risk rank order of schools were urban schools > suburban schools > residential schools. The LCR and TLCR of heavy metals was in the following order: Co > Ni >Cr > Cd > As > Pb. The ingestion lifetime cancer risk (LCRing) and TLCR values from exposure to Ni and Cr in urban and suburban schools, Cd in urban schools, and Co in all Jeddah schools only exceed the acceptable range (1 × 10−6–1 × 10−4) Only LCRing and TLCR values from exposure to∑ carcinogens exceed the acceptable level. © 2019 by the authors. Licensee MDPI, Basel, Switzerland. T.

Amato-Lourenco, L.F., Ranieri, G.R., de Oliveira Souza, V.C.*, et al.* (2020) Edible weeds: Are urban environments fit for foraging? *Science of the Total Environment,* 698.
Available at:
https://www.sciencedirect.com/science/article/pii/S0048969719339373/pdfft?md5=35170162ad92607fc150fa309e9a44a2&pid=1-s2.0-S0048969719339373-main.pdf
Keywords: Biomonitoring; Edible weeds; Foraging; Traffic pollution; Urban environment; Wild edible plants; Urban planning; Edible plants; Urban environments; Pollution; aluminum; arsenic; barium; cadmium; chromium; cobalt; lead; manganese; nickel; rubidium; vanadium; zinc; heavy metal; concentration (composition); edible species; traffic emission; urban pollution; weed; Amaranthus; Article; Brazil; concentration (parameter); controlled study; edible plant; edible weed; highway; nonhuman; Plantago; Plantago tomentosa; priority

journal; Taraxacum officinale; traffic; urban area; chemistry; city; dietary exposure; environmental monitoring; soil; soil pollutant; Sao Paulo [Brazil]; Cities; Metals, Heavy; Plant Weeds; Soil Pollutants

Abstract:
Foraging wild-growing edible plants (WEPs) is a re-emerging practice with increasing popularity worldwide, including in urban areas. However, in cities, this practice raises questions about the safety of foraging these plants for human consumption, due to the potential exposure of plants to higher levels of pollutants. In this study, the concentration of 12 elements (Al, V, Cr, Mn, Co, Ni, Zn, As, Rb, Cd, Ba and Pb) in three different WEPs (Amaranthus spp., Plantago tomentosa and Taraxacum officinale) were determined according to different traffic categories in the municipality of São Paulo. Additionally, plants were sampled within the inner areas of three municipal parks in the same study region. Different gradients of elemental concentrations were obtained according to the traffic categories. Freeways presented higher concentrations of several elements than local roads or parks. For the WEPs collected along freeways and some plants along arterial roads, the concentrations of Pb exceeded safety levels for human consumption. Our data suggest that foraging in large urban centres should be performed preferentially in low-traffic areas. © 2019 Elsevier B.V.

Ashrap, P., Watkins, D.J., Mukherjee, B.*, et al.* (2020) Predictors of urinary and blood Metal(loid) concentrations among pregnant women in Northern Puerto Rico. ***Environmental Research,*** **183: 109178.**
Keywords: Biomarkers; Blood; Exposure assessment; Metals; Pregnancy; Urine

Abstract:
Given the potential adverse health effects related to toxic trace metal exposure and insufficient or excessive levels of essential trace metals in pregnant women and their fetuses, the present study characterizes biomarkers of metal and metalloid exposure at repeated time points during pregnancy among women in Puerto Rico. We recruited 1040 pregnant women from prenatal clinics and collected urine, blood, and questionnaire data on demographics, product use, food consumption, and water usage at up to three visits. All samples were analyzed for 16 metal(loid)s: arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), titanium (Ti), uranium (U), vanadium (V), and zinc (Zn). Urine samples were additionally analyzed for molybdenum (Mo), platinum (Pt), antimony (Sb), tin (Sn), and tungsten (W). Mean concentrations of most metal(loid)s were higher among participants compared to the general US female population. We found weak to moderate correlations for inter-matrix comparisons, and moderate to strong correlations between several metal(loid)s measured within each biological matrix. Blood concentrations of Cu, Zn, Mn, Hg, and Pb were shown to reflect reliable biomarkers of exposure. For other metals, repeated samples are recommended for exposure assessment in epidemiology studies. Predictors of metal(loid) biomarkers included fish and rice consumption (urinary As), fish and canned food (blood Hg), drinking public water (blood Pb), smoking (blood Cd), and iron/folic acid supplement use (urinary Cs, Mo, and Sb). Characterization of metal(loid) biomarker variation over time and between matrices, and identification of important exposure sources, may inform future epidemiology studies and exposure reduction strategies.

Aullón Alcaine, A., Schulz, C., Bundschuh, J.*, et al.* (2020) Hydrogeochemical controls on the mobility of arsenic, fluoride and other geogenic co-contaminants in the shallow

aquifers of northeastern La Pampa Province in Argentina. ***Science of the Total Environment,*** **715: 136671.**
Keywords: Arsenic; Fluoride; Shallow groundwater; La Pampa; Loess sediments; Volcanic ash

Abstract:
Elevated Arsenic (As) and Fluoride (F) concentrations in groundwater have been studied in the shallow aquifers of northeastern of La Pampa province, in the Chaco-Pampean plain, Argentina. The source of As and co-contaminants is mainly geogenic, from the weathering of volcanic ash and loess (rhyolitic glass) that erupted from the Andean volcanic range. In this study we have assessed the groundwater quality in two semi-arid areas of La Pampa. We have also identified the spatial distribution of As and co-contaminants in groundwater and determined the major factors controlling the mobilization of As in the shallow aquifers. The groundwater samples were circum-neutral to alkaline (7.4 to 9.2), oxidizing (Eh ~0.24 V) and characterized by high salinity (EC = 456–11,400 μS/cm) and Na+–HCO3– water types in recharge areas. Carbonate concretions ("tosca") were abundant in the upper layers of the shallow aquifer. The concentration of total As (5.6 to 535 μg/L) and F (0.5 to 14.2 mg/L) were heterogeneous and exceeded the recommended WHO Guidelines and the Argentine Standards for drinking water. The predominant As species were arsenate As(V) oxyanions, determined by thermodynamic calculations. Arsenic was positively correlated with bicarbonate (HCO3−), fluoride (F), boron (B) and vanadium (V), but negatively correlated with iron (Fe), aluminium (Al), and manganese (Mn), which were present in low concentrations. The highest amount of As in sediments was from the surface of the dry lake. The mechanisms for As mobilization are associated with multiple factors: geochemical reactions, hydrogeological characteristics of the local aquifer and climatic factors. Desorption of As(V) at high pH, and ion competition for adsorption sites are considered the principal mechanisms for As mobilization in the shallow aquifers. In addition, the long-term consumption of the groundwater could pose a threat for the health of the local community and low cost remediation techniques are required to improve the drinking water quality. ".

Bena, A., Orengia, M., Gandini, M.*, et al.* (2020) Human biomonitoring of metals in workers at the waste-to-energy incinerator of Turin: An Italian longitudinal study. ***International Journal of Hygiene and Environmental Health,*** **225: 113454.**
Keywords: Human biomonitoring (HBM); Incinerator workers; Longitudinal study; Metals; Occupational exposure; Waste-to-energy (WTE) incinerator

Abstract:
Evidence of negative health effects of solid waste management is uncertain. Available reviews suggests the use of biomarkers in human biomonitoring (HBM) to detect low exposure levels. In September 2013, a waste-to-energy plant located in the Turin (Italy) went into operation. The SPoTT (acronym for Population health Surveillance in the Turin incinerator's area) monitoring program was set up to assess the potential health impact caused by the plant. The paper illustrates the results of HBM of metals in the workers before the plant went into operation and then at 1 year and 3 years. This study is one of the few focusing on workers with a longitudinal design (the first in Italy). Eighteen metals in urine and lead in blood were determined by sector field inductively coupled plasma mass spectrometry. Information on participant habits and other characteristics that could potentially affect metals concentrations were collected via a structured questionnaire. Subjects were classified according to their work role at the facility: administrative staff workers (AW); plant workers (PW). Nonparametric methods were used to evaluate the changes in metals concentration over time. Comparison of the metals concentration in the samples taken at baseline and at the following two-time points shows a general decrease in

levels: urinary concentration of beryllium (Be), cobalt (Co), mercury (Hg), Ir, nickel (Ni), tin (Sn), thallium (Tl), and blood level of lead (Pb) among the PW and Ir and Pd among the AW were significantly lower at T2 versus baseline. A decrease was also recorded in arsenic (As) among the PW and in cadmium (Cd), chromium (Cr), palladium (Pd), rhodium (Rh), and zinc (Zn) for both groups, whereas the levels of copper (Cu) and vanadium (V) remained unchanged over time. The downward trend remained also after taking confounding factors into account. The only exceptions were Mn, Pt, Sb among the PW: increase levels between T0 and T2 were recorded, which cannot be specifically attributable to the plant activity. The median urinary and blood concentrations of the metals were lower than those reported in the literature and were below the occupational reference values at all three-time points. Our results are consistent with those reported for the cohort of local residents and with the ambient air measurements.

Boukhobza, I. & Crans, D.C. (2017) Application of HPLC to measure vanadium in environmental, biological and clinical matrices. *Arabian Journal of Chemistry,* 13(1): 1198-1228.
Available at:
https://www.sciencedirect.com/science/article/pii/S1878535217301892/pdfft?md5=53c8c95f8cfdf85080df3c307f8cb4b4&pid=1-s2.0-S1878535217301892-main.pdf
Keywords: Vanadium; HPLC separation; Speciation; Characterization; Quantitation; Environmental samples; Biological samples; Clinical samples

Abstract:
Vanadate and vanadium compounds exist in many environmental, biological and clinical matrices, and despite the need only limited progress has been made on the analysis of vanadium compounds. The vanadium coordination chemistry of different oxidation states is known, and the result of the characterization and speciation analysis depends on the subsequent chemistry and the methods of analysis. Many studies have used a range of methods for the characterization and determination of metal ions in a variety of materials. One successful technique is high performance liquid chromatography (HPLC) that has been used mainly for measuring total vanadium level and metal speciation. Some cases have been reported where complexes of different oxidation states of vanadium have been separated by HPLC. Specifically reversed phase (RP) HPLC has frequently been used for the measurement of vanadium. Other HPLC methods such as normal phase, anion-exchange, cation-exchange, size exclusion and other RP-HPLC modes such as, ion-pair and micellar have been used to separate selected vanadium compounds. We will present a review that summarizes and critically analyzes the reported methods for analysis of vanadium salts and vanadium compounds in different sample matrices. We will compare various HPLC methods and modes including sample preparation, chelating reagents, mobile phase and detection methods. The comparison will allow us to identify the best analytical HPLC method and mode for measuring vanadium levels and what information such methods provide with regard to speciation and quantitation of the vanadium compounds. ".

Bourliva, A., Papadopoulou, L., da Silva, E.F.*, et al.* (2020) In vitro assessment of oral and respiratory bioaccesibility of trace elements of environmental concern in Greek fly ashes: Assessing health risk via ingestion and inhalation. *Science of the Total Environment,* 704.
Keywords: Cancer risk; Fly ash; Health risk; Human bioaccessibility; Trace element; Barium compounds; Calcium compounds; Chromium; Chromium compounds; Health; Particle size; Risk assessment; Trace elements; Bioaccessibility; Carcinogenic risk; Environmental concerns; Human health problems; Oral bioaccessibility; Particle-size fractions; Health risks; barium; cadmium; cobalt; copper; manganese; nickel; vanadium; zinc; atmospheric

pollution; cancer; lignite; respiratory disease; Article; bioaccumulation; electric power plant; gastrointestinal tract; Greece; health hazard; ingestion; inhalation; priority journal; respiratory system; environmental exposure; pollutant; Coal Ash; Environmental Pollutants

Abstract:
Fly ash engender significant environmental and human health problems due to enhanced contents of potentially harmful trace elements (TrElems). This study aims to evaluate human exposure to TrElems via a combined ingestion (i.e., oral bioaccessibility) and inhalation (i.e., respiratory bioaccessibility) pathway. Five fly ash samples were collected from power plants operating in the main lignite basins of Greece, while the ingestible (<250 μm) and inhalable (<10 μm) particle size fractions were utilized. The Unified Bioaccessibility Method (UBM) was utilized to assess the oral bioaccessibility, while the respiratory bioaccessible fractions were extracted using the Artificial Lysosomal Fluid (ALF). All studied FAs exhibited significantly higher contents in Ba, Cr, Ni, V and Zn. Cadmium was presented relative enriched in the finer size fraction (<10 μm), while Ba, Co, Cr, Cu, Mn, Ni and V were depleted. The UBM-extractable concentrations fluctuated greatly among the studied FAs, while notably lower bioaccessible contents were recorded in the gastrointestinal phase. On the other hand, ALF-extractable concentrations were surprisingly higher than the corresponding UBM-extractable ones in the gastric phase. The oral bioaccessibility of the studied TrElems ranged from 12.5 to 100%, while respiratory bioaccessibility presented high values exceeding 45% on average. A significant effect of fly ash type on human bioaccessibility was revealed. Thus, high-Ca FAs exhibited significantly higher bioaccessibility of the studied TrElems via ingestion, while a relatively higher bioaccessibility via inhalation was observed for high-Si FAs. Regarding non-carcinogenic health risk via ingestion and inhalation, Cr and Co exhibited the highest HQing and HQinh values, however there were significantly lower than safe level (HQ < 1). On the contrary, Cr was the dominant contributor to carcinogenic risk with CR values being well above threshold or even tolerable risk levels. © 2019 Elsevier B.V.

Chung, C.-., You, C.-., Hsu, S.-*., et al.* (2019) Sulfur isotope analysis for representative regional background atmospheric aerosols collected at Mt. Lulin, Taiwan. *Scientific Reports,* 9(1).
Available at: https://www.nature.com/articles/s41598-019-56048-z.pdf

Abstract:
Air pollution resulted from fossil fuel burning has been an environmental issue in developing countries in Asia. Sulfur-bearing compounds, in particular, are species that are regulated and monitored routinely. To assess how the species affect at local and global scales, regional background level has to be defined. Here, we report analysis of sulfur isotopes in atmospheric sulfate, the oxidation end product of sulfur species, in particulate phase collected at the Lulin observatory located at 2862 m above mean sea level in 2010. The averaged sulfate concentration for 44 selected samples is 2.7 ± 2.3 (1-σ standard deviation) μg m−3, and the averaged δ34S is 2.2 ± 1.6‰, with respect to the international standard Vienna Canyon Diablo Troilite. Regardless of the origins of air masses, no noticeable difference between the low-altitude Pacific and high-altitude free troposphere sulfate aerosols is observed. Also, no identifiable seasonal cycle in seen. Correlation analysis with respect to coal burning tracers such as lead and oil industry tracers such as vanadium shows sulfate concentration is in better correlation with vanadium (R2 = 0.86, p-value < 0.001) than with lead (R2 = 0.45, p-value < 0.001) but no statistically significant correlation is found in δ34S with any of physical quantities measured. We suggest the sulfate collected at Lulin can best represent the regional background level in the Western Pacific, a quantity that is

needed in order to quantitatively assess the budget of sulfur in local to country scales. © 2019, The Author(s).

Domingo-Relloso, A., Grau-Perez, M., Briongos-Figuero, L.*, et al.* (2019) The association of urine metals and metal mixtures with cardiovascular incidence in an adult population from Spain: the Hortega Follow-Up Study. *International Journal of Epidemiology,* 48(6): 1839-1849.
Keywords: BKMR; cardiovascular incidence; cohort study; population-based; Urine metals

Abstract:
BACKGROUND: The association of low-level exposure to metals and metal mixtures with cardiovascular incidence in the general population has rarely been studied. We flexibly evaluated the association of urinary metals and metal mixtures concentrations with cardiovascular diseases in a representative sample of a general population from Spain. METHODS: Urine antimony (Sb), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), vanadium (V) and zinc (Zn) were measured in 1171 adults without clinical cardiovascular diseases, who participated in the Hortega Study. Cox proportional hazard models were used for evaluating the association between single metals and cardiovascular incidence. We used a Probit extension of Bayesian Kernel Machine Regression (BKMR-P) to handle metal mixtures in a survival setting. RESULTS: In single-metal models, the hazard ratios [confidence intervals (CIs)] of cardiovascular incidence, comparing the 80th to the 20th percentiles of metal distributions, were 1.35 (1.06, 1.72) for Cu, 1.43 (1.07, 1.90) for Zn, 1.51 (1.13, 2.03) for Sb, 1.46 (1.13, 1.88) for Cd, 1.64 (1.05, 2.58) for Cr and 1.31 (1.01, 1.71) for V. BKMR-P analysis was confirmatory of these findings, supporting that Cu, Zn, Sb, Cd, Cr and V are related to cardiovascular incidence in the presence of the other metals. Cd and Sb showed the highest posterior inclusion probabilities. CONCLUSIONS: Urine Cu, Zn, Sb, Cd, Cr and V were independently associated with increased cardiovascular risk at levels relevant for the general population of Spain. Urine metals in the mixture were also jointly associated with cardiovascular incidence, with Cd and Sb being the most important components of the mixture. © The Author(s) 2019; all rights reserved. Published by Oxford University Press on behalf of the International Epidemiological Association.

Garvin, M.C., Schijf, J., Kaufman, S.R.*, et al.* (2020) A survey of trace metal burdens in increment cores from eastern cottonwood (Populus deltoides) across a childhood cancer cluster, Sandusky County, OH, USA. *Chemosphere,* 238.
Available at:
https://www.sciencedirect.com/science/article/pii/S0045653519317527/pdfft?md5=1d44d75fbf11fd7368a875bdc5562489&pid=1-s2.0-S0045653519317527-main.pdf
Keywords: Cancer cluster; Dendrochemistry; Eastern cottonwood; Scan statistic; Trace metals; Cotton; Diseases; Forestry; Groundwater; Metals; Surveys; Trace analysis; Scan statistics; Trace metal; Trace elements; arsenic; cadmium; chromium; cobalt; lead; nickel; vanadium; trace element; aerosol; bioaccumulation; cancer; concentration (composition); core analysis; dendroecology; microwave radiation; spatial analysis; statistical data; wood; annual ring; Article; childhood cancer; concentration (parameter); inductively coupled plasma mass spectrometry; method detection limit; Ohio; Populus; Populus deltoides; chemistry; child; environmental monitoring; human; neoplasm; questionnaire; soil; tree; Sandusky County; United States; Humans; Neoplasms; Surveys and Questionnaires; Trees

Abstract:
A dendrochemical study of cottonwood trees (Populus deltoides) was conducted across a childhood cancer cluster in eastern Sandusky County (Ohio, USA). The justification for this

study was that no satisfactory explanation has yet been put forward, despite extensive local surveys of aerosols, groundwater, and soil. Concentrations of eight trace metals were measured by ICP-MS in microwave-digested 5-year sections of increment cores, collected during 2012 and 2013. To determine whether the onset of the first cancer cases could be connected to an emergence of any of these contaminants, cores spanning the period 1970–2009 were taken from 51 trees of similar age, inside the cluster and in a control area to the west. The abundance of metals in cottonwood tree annual rings served as a proxy for their long-term, low-level accumulation from the same sources whereby exposure of the children may have occurred. A spatial analysis of cumulative metal burdens (lifetime accumulation in the tree) was performed to search for significant 'hotspots', employing a scan statistic with a mask of variable radius and center. For Cd, Cr, and Ni, circular hotspots were found that nearly coincide with the cancer cluster and are similar in size. No hotspots were found for Co, Cu, and Pb, while As and V were largely below method detection limits. Whereas our results do not implicate exposure to metals as a causative factor, we conclude that, after 1970, cottonwood trees have accumulated more Cd, Cr, and Ni, inside the childhood cancer cluster than elsewhere in Sandusky County. © 2019 The Authors.

Guo, X., Zhang, N., Hu, X.*, et al.* (2020) Characteristics and potential inhalation exposure risks of PM2.5–bound environmental persistent free radicals in Nanjing, a mega–city in China. *Atmospheric Environment,* 224.**

Keywords: Half–life; Inhalation exposure; Oxidative stress; Reactive oxygen species; Temporal variation; Biological organs; Free radicals; Health risks; Organic pollutants; Oxygen; Transition metals; Air pollutants; Healthy persons; Limited information; Potential health risks; Toxic elements; Weak correlation; cadmium; carbon monoxide; chromium; copper; dissolved oxygen; free radical; iron; manganese; nickel; nitrous oxide; ozone; reactive oxygen metabolite; sulfur oxide; vanadium; zinc; megacity; organic pollutant; particle size; particulate matter; pollution exposure; public health; air pollutant; Article; China; city; concentration (parameter); controlled study; electron transport; environmental exposure; half life time; health hazard; human; priority journal; room temperature; simulation; Nanjing [Jiangsu]

Abstract:
PM2.5–bound toxic elements and organic pollutants have been extensively investigated, while limited information is available for environmental persistent free radicals (EPFRs) associated with PM2.5, which may lead to oxidative stress in the human lung when exposed to PM2.5. In this study, the levels and types of PM2.5–bound EPFRs present in Nanjing, a mega–city in China, were analyzed. PM2.5–bound EPFRs were found to mainly be a mixture of carbon– and oxygen–centered radicals. The concentration of PM2.5–bound EPFRs ranged from 2.78 × 1012 to 1.72 × 1013 spins m−3, with an average value of 7.61 × 1012 spins m−3. The half–life of the PM2.5–bound EPFRs was calculated to be an average of 83.5 days when stored at room temperature, with only weak correlations observed between EPFRs and conventional air pollutants (NO2, O3, CO and PM2.5)/PM2.5–bound transition metals (Cu, Zn, Cr, Mn, V, Cd, and Ni) and significant correlations between EPFRs and SO2/PM2.5–bound Fe. PM2.5–bound EPFRs can induce the formation of reactive oxygen species (ROS) in both water and a H2O2 solution, which are used to simulate lung solution of a healthy person and patient, respectively. Therefore, PM2.5–bound EPFRs can lead to potential oxidative stress in humans. Overall, PM2.5–bound EPFRs show an obvious temporal variation and can pose potential health risks to humans via the induction of ROS in the lung solution. © 2020 Elsevier Ltd.

Gutiérrez-González, E., García-Esquinas, E., de Larrea-Baz, N.F.*, et al.* (2019) Toenails as biomarker of exposure to essential trace metals: A review. *Environmental Research,* 179. Available at: https://www.sciencedirect.com/science/article/pii/S0013935119305845/pdfft?md5=8f83da1d38a405eae76693aa3e527ee8&pid=1-s2.0-S0013935119305845-main.pdf
Keywords: Biomarker; Biomonitoring; Essential trace essential metals; Exposure; Systematic review; Toenail; boron; cobalt; copper; iron; manganese; molybdenum; selenium; silicon; trace metal; vanadium; zinc; bioaccumulation; biochemical composition; blood; food industry; hair; pollution exposure; urine; alcoholic beverage; biological monitoring; blood level; dietary supplement; environmental factor; finger nail; human; lifestyle; long term exposure; nutrient; occupational exposure; priority journal; quality control; Review; toe nail; urine level

Abstract:
Health problems associated with essential trace metals can result from both inadequate (i.e., low intake) and excessive exposures (i.e., from environmental and/or occupational source). Thus, measuring the exposure level is a real challenge for epidemiologists. Among non-invasive biomarkers that intend to measure long-term exposure to essential trace metals, the toenail is probably the biological matrix with the greatest potential. This systematic review collects the current evidence regarding the validity of toenail clippings as exposure biomarker for trace metals such as boron, cobalt, copper, iron, manganese, molybdenum, selenium, silicon, vanadium and zinc. Special attention was paid to the time-window of exposure reflected by the toenail, the intraindividual variability in exposure levels over time in this matrix, and the relationship of toenail with other biomarkers, personal characteristics and environmental sources. Our search identified 139 papers, with selenium and zinc being the most studied elements. The variability among studies suggests that toenail levels may reflect different degrees of exposure and probably correspond to exposures occurred 3–12 months before sampling (i.e., for manganese/selenium). Few studies assessed the reproducibility of results over time and, for samples obtained 1–6 years apart, the correlation coefficient were between 0.26 and 0.66. Trace metal levels in toenails did not correlate well with those in the blood and urine and showed low-moderate correlation with those in the hair and fingernails. Available data suggests that for some elements (Se, Mn, Zn) toenail concentrations reflect long-term external exposures in fairly reproducible levels, while for other metals, this association has not yet been assessed. Among dietary factors, only toenail selenium showed clear associations with the intake of supplements or specific foods. The toenail levels could also represent occupational exposure, for instance, Mn exposure in welders. The scarcity of information on other essential trace elements, together with the great heterogeneity among studies makes the validation of the usage of toenails as biomarkers of exposure to these elements difficult. Standardization of sample collection, quality control, analytical techniques and reporting procedures might facilitate further research focused on the clear understanding of the significance of essential levels in this promising matrix and would enhance its utility in epidemiological research. © 2019.

Herrero, M., Rovira, J., Esplugas, R.*, et al.* (2020) Human exposure to trace elements, aromatic amines and formaldehyde in swimsuits: Assessment of the health risks. *Environmental Research,* 181.
Keywords: Aromatic amines; Formaldehyde; Human exposure; Risk assessment; Swimsuits; Trace elements; aluminum; aromatic amine; arsenic; barium; beryllium; bismuth; boron; cadmium; chromium; chromium derivative; cobalt; copper; iron; lead; magnesium; manganese; mercury; molybdenum; nickel; polyamide; polybutylene terephthalate;

polyester; silver; strontium; thallium; titanium; trace element; vanadium; zinc ion; amino acid; aromatic hydrocarbon; health care; pollution exposure; toxicity test; adolescent; adult; cancer risk; child; color; female; health hazard; human; hydrophobicity; limit of detection; male; polymerization; preschool child; priority journal; scanning electron microscopy; summer

Abstract:
Nowadays, most of the swimsuits are mainly made of artificial fibres, which have interesting properties such as water repellence and fast drying. Swimsuits contain a wide range of additives, which can mean a hazard for the environment and/or human health. In this study, the concentrations of formaldehyde (free and water soluble), 24 aromatic amines, and 28 trace elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sr, Sn, Tl, Ti, V and Zn) were analysed in 39 swimsuits covering a wide range of materials, colours and brands. Dermal exposure and health risks were assessed for adults (men and women) aged > 18 years old, babies between 2 and < 3 years old, children (boys and girls) between 3 and < 6 years old and 6 and < 11 years old, and teenagers (boys and girls) between 11 and < 16 years old, wearing swimsuits for 4 h or 8 h. Formaldehyde and aromatic amines were below their respective detection limits in all samples (<16 and < 1.5 mg/kg, respectively). Regarding trace elements, Ti showed the highest mean levels (1844 mg/kg), being significantly higher in polyamide (3759 mg/kg) than in polyester (24.1 mg/kg) swimsuits. These high Ti levels were confirmed by environmental scanning electron microscope in a single sample made of polyamide. Increased concentrations of Cr were also observed, but only in polyamide black fabrics, with values ranging from 624 to 932 mg/kg. Non-cancer risks (hazard quotients) derived from the exposure to trace elements were in a safe zone for all analysed trace elements. Furthermore, the carcinogenic risks were evaluated for As, Cr and Pb, exhibiting values below the 10−5 threshold, with the exception of Cr in babies and children-girls. For Ti, health risks could not be calculated due to the lack of information on toxicological data. However, because Ti was the element with the highest concentrations in swimsuits, and taking into account the potential toxicity of TiO2 nanoparticles, further research is needed to assess the migration of this element from fibres to skin. © 2019 Elsevier Inc.

Hussain Shah, S.Z., Rashid, A., Naveed, A.K.*, et al.* (2019) Genotoxic And Cytotoxic Effects Of Oral Vanadyl Sulphate. *Journal of Ayub Medical College, Abbottabad : JAMC,* 31(4): 522-526. Available at:
http://jamc.ayubmed.edu.pk/index.php/jamc/article/download/6206/2767
Keywords: Hepatotoxicity; Oxidative Stress; DNA Damage; Comet Assay; Vanadyl sulphate

Abstract:
BACKGROUND: Vanadyl sulphate is available as herbal medicine against diabetes mellitus and body building supplement, over the counter worldwide. The available data on its safety is controversial and inadequate. The objective of this study was to analyse its safety in usual therapeutic dose range. METHODS: It was an experimental study carried out at the Department of Biochemistry & Molecular Biology, Army Medical College, National University of Medical Sciences (NUMS), Rawalpindi, Pakistan, from Jun 2014 to Oct 2018. The study was carried out on 105 Sprague Dawley rats for duration of 24 weeks. The animals were randomly distributed in three groups of 35 each. The group I rats were marked as control while rats of group II & III were administered vanadyl sulphate 0.06mg/day and 0.3mg/day respectively. Alanine amino transferase (ALT) and Malondialdehyde (MDA) were measured in serum while comet assay was performed on WBCs. RESULTS: The plasma levels of ALT and MDA were significantly raised in group II and III subjects. Single cell gel electrophoresis

(SCGE) / comet assay showed minimal "tail moment" in control group and increased tail moment in group II and III in a dose dependent manner which indicates dsDNA breaks. CONCLUSIONS: It was observed that vanadyl sulphate causes hepatocellular toxicity, oxidative stress and damage to the DNA in usual therapeutic/ supplemental doses. Due to hazardous effects, its use in humans as alternate medicine may be reviewed.

Kolakkandi, V., Sharma, B., Rana, A.*, et al.* (2020) Spatially resolved distribution, sources and health risks of heavy metals in size-fractionated road dust from 57 sites across megacity Kolkata, India. *Science of the Total Environment,* 705.**
Keywords: Contamination indices; Health risk assessment; Receptor modeling; Size fraction; Trace metals; Construction industry; Contamination; Dust; Factorization; Health; Health risks; Heavy metals; Housing; Industrial emissions; Land use; Roads and streets; Trace elements; Construction activities; Contamination index; Index of Geo accumulations; Metallurgical process; Positive Matrix Factorization; Receptor model; Trace metal; Risk assessment; aluminum; calcium; chromium; copper; heavy metal; iron; lead; magnesium; manganese; nickel; vanadium; zinc; health risk; megacity; particle size; pollutant source; pollution exposure; spatial distribution; adult; air quality; Article; cancer risk; carcinogenesis; child; comparative study; controlled study; environmental impact; exhaust gas; exposure; hazard assessment; health hazard; human; India; industrial area; ingestion; inhalation; metallurgy; pollution; priority journal; quantitative analysis; road dust; spatial analysis; Kolkata; West Bengal

Abstract:
This work reports the first assessment of contamination levels, source contributions and health risks associated with heavy metals (HMs) in road dust from Kolkata, the second-most polluted metropolis in India. To this end, samples collected from 57 locations across 6 land-use categories: residential, roadside, traffic, railway, port and industrial areas in the city during 2018 were analyzed for 11 major and trace metals (Ca, Mg, Fe, Al, Mn, Ni, V, Cu, Zn, Cr, Pb) in three size fractions: 4) in west-central and northern parts (the older sections) of the city represented by industrial, port, and traffic-congested residential areas. Using positive matrix factorization (PMF), the following sources were apportioned for the three size fractions: crustal dust (48–66%), construction activities (18–20%), vehicular abrasion (7–21%), industrial emissions (5–8%), a Cr-dominated mixed source (6%) and an unassigned source (7%). Finally, health risk assessment in the form of cumulative hazard index (HI) and incremental lifetime cancer risk (ILCR) found that children (mean HIchildren: 1.29 and ILCRchildren: 2E-04) are comparatively more vulnerable than adults (mean HIadults: 0.22 and ILCRadults: 8E-05) to HM exposure, with the ingestion exposure pathway dominating over dermal contact and inhalation. © 2019 Elsevier B.V.

Kot, K., Kosik-Bogacka, D., Ziętek, P.*, et al.* (2020) Impact of varied factors on iron, nickel, molybdenum and vanadium concentrations in the knee joint. *International Journal of Environmental Research and Public Health,* 17(3). Available at: https://www.mdpi.com/1660-4601/17/3/813/pdf
Keywords: Anterior cruciate ligament; Cartilage; Infrapatellar fat pad; Meniscus; Spongy bone; Trace elements; iron; molybdenum; nickel; vanadium; bone; concentration (composition); diet; medicine; trace element; adult; aged; alcohol consumption; Article; atomic absorption spectrometry; clinical article; concentration (parameter); controlled study; dietary supplement; environmental factor; female; human; knee arthroscopy; knee meniscus; male; muscle toxicity; osteoporosis; Poland; rheumatoid arthritis; Poland [Central Europe]

Abstract:
The aim of this study was to determine the concentrations of iron, nickel, molybdenum, and vanadium in the knee joint. We also examined the relationships between the concentrations of these metals in the knee joint and the influence of varied factors on the concentration of Fe, Ni, Mo, and V. The study of these trace elements is important, because these elements are used alone and in combination in diet supplements, and they are components of biomaterials implanted in medicine. The study materials, consisting of the spongy bone, cartilage, meniscus, anterior cruciate ligament (ACL), and infrapatellar fat pad, were obtained from 34 women and 12 men from northwestern Poland. The concentrations of Ni, Fe, Mo, and V were determined using spectrophotometric atomic absorption in inductively coupled argon plasma (ICP-AES). We found significantly higher Mo concentrations in the ACL of women than men. There was a significant difference in the Mo concentration in the spongy bone between patients from cities with fewer than 100,000 inhabitants and patients from cities with more than 100,000 residents. Iron concentrations in the spongy bone were higher in non-smoking patients and those who did not consume alcohol. Vanadium concentrations were higher in the infrapatellar fat pads in abstainers. In patients who had not undergone arthroscopy surgery, V concentration was lower in cartilage. The concentrations of V in the cartilage and infrapatellar fat pad were higher in osteoporotic patients than in non-osteoporotic patients. There were significant differences in Fe concentrations in the meniscus, with the lowest in osteoporotic patients. We noted lower Mo concentrations in the spongy bone of patients with rheumatoid arthritis. Furthermore, we noted some new interactions among metals in the studied structures of the knee joint. The results reported in this study show the influence of gender, place of residence, smoking, consumption of alcohol, arthroscopy surgery, osteoporosis, and rheumatoid arthritis on the Fe, Ni, Mo, and V concentrations in the studied structures of the knee joint.

Kumar, S., Sharma, A. & Kshetrimayum, C. (2019) Environmental & occupational exposure & female reproductive dysfunction. *Indian Journal of Medical Research,* 150(6): 532-545.
Available at: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7038808/
Keywords: Environmental; female; fertility; lifestyle factors; metals; miscarriage; occupational; oxidative stress; pregnancy; reproductive impairment; arsenic; benzene; cadmium; carbon disulfide; chlorphenotane; chromium; cigarette smoke; drug metabolite; lead; mercury; mono (3 carboxylpropyl) phthalate; pesticide; toluene; toxic gas; unclassified drug; vanadium; zinc; selenium; trace element; abdominal pain; air pollutant; attention deficit disorder; blood level; child health; clinical outcome; disease association; dysmenorrhea; environmental exposure; female sterility; gestational age; gynecologic disease; hormonal impairment; human; infertility; ionizing radiation; job stress; lead blood level; maternal urine; menstrual cycle; molecular alteration; nerve cell differentiation; occupational exposure; paternal exposure; pregnancy outcome; prevalence; progeny; Review; risk factor; smoking; spontaneous abortion; steroidogenesis; stillbirth; air pollution; Article; awareness; birth weight; DNA damage; DNA methylation; drug manufacture; fetus development; incidence; inflammation; menarche; prematurity; reproductive health; tobacco

Abstract:
All individuals are exposed to certain chemical, physical, biological, environmental as well as occupational factors. The data pertaining to role of these factors on female reproduction are scanty as compared to male. The available data suggest the adverse effects of certain toxicants, viz., metals such as lead, cadmium and mercury, pesticides such as bis(4-chlorophenyl)-1,1,1-trichloroethane and organic solvent such as benzene, toluene and

ionizing radiation on the female reproductive system affecting directly the organ system or impacting in directly through hormonal impairments, molecular alterations, oxidative stress and DNA methylation impairing fertility as well as pregnancy and its outcomes. Thus, there is a need for awareness and prevention programme about the adverse effects of these factors and deterioration of female reproductive health, pregnancy outcome and offspring development as some of these chemicals might affect the developing foetus at very low doses by endocrine disruptive mechanism. © 2020 Indian Journal of Medical Research, published by Wolters Kluwer - Medknow.

Li, W., Xiao, L., Zhou, Y.*, et al.* (2020) Plasma CC16 mediates the associations between urinary metals and fractional exhaled nitric oxide: A cross-sectional study. *Environmental Pollution,* 258.**
Keywords: Club cell secretory protein; FeNO; Mediation analysis; Urinary metals; Antimony; Biomarkers; Mass spectrometry; Nickel; Nitric oxide; Pathology; Proteins; Vanadium; Airway inflammation; Cross-sectional study; Enzyme linked immunosorbent assay; Exhaled nitric oxides; Low concentrations; Iron compounds

Abstract:
Capsule: We found positive associations between urinary metals and FeNO, which were stronger among participants with low plasma CC16 concentration. The associations were mediated by plasma CC16. © 2019 Elsevier Ltd Exposure to environmental metals has been reported to be associated with airway inflammation. Fractional exhaled nitric oxide (FeNO) is an important inflammatory biomarker of the airway. However, the associations between metal exposures and FeNO change and the underlying mechanisms remain unclear. To investigate the associations between urinary metals and FeNO, and the potential role of Club cell secretory protein (CC16), a lung epithelial biomarker, in these associations. We conducted a cross-sectional study from the Wuhan-Zhuhai cohort and measured eight urinary metals, plasma CC16 and FeNO among 3067 subjects by using inductively coupled plasma-mass spectrometry, enzyme-linked immunosorbent assay kit and Nano Coulomb Nitric Oxide Analyzer, respectively. Mixed linear models were used to quantify dose-relationships between urinary metals and FeNO, as well as urinary metals and plasma CC16. The potential role of plasma CC16 in the associations between urinary metals and FeNO was estimated using mediationanalyses. After adjusting for covariates, one percent increase in urinary vanadium, nickel or antimony was associated with a respective 6.60% (95% CI: 3.52%, 9.68%), 2.18% (0.45%, 3.91%), 4.87% (1.47%, 8.27%) increase in FeNO level. The adverse associations were much stronger among participants with low concentration of plasma CC16 than those with high CC16 level. Moreover, plasma CC16 decreased monotonically with increasing quartiles of urinary vanadium, nickel or antimony. Mediation analyses found that CC16 mediated the associations between urinary metals and FeNO by 5.64%, 39.06% and 25.18% for vanadium, nickel and antimony respectively. CC16 plays an important role in airway inflammation. General population with lower plasma CC16 concentration is more likely to suffer from airway inflammation when exposed to high levels of vanadium, nickel or antimony. © 2019 Elsevier Ltd.

Li, W., Xiao, L., Zhou, Y.*, et al.* (2019) Plasma CC16 mediates the associations between urinary metals and fractional exhaled nitric oxide: A cross-sectional study. *Environmental Pollution (Barking, Essex : 1987),* **: 113713.
Keywords: Club cell secretory protein; FeNO; Mediation analysis; Urinary metals

Abstract:
Exposure to environmental metals has been reported to be associated with airway

inflammation. Fractional exhaled nitric oxide (FeNO) is an important inflammatory biomarker of the airway. However, the associations between metal exposures and FeNO change and the underlying mechanisms remain unclear. To investigate the associations between urinary metals and FeNO, and the potential role of Club cell secretory protein (CC16), a lung epithelial biomarker, in these associations. We conducted a cross-sectional study from the Wuhan-Zhuhai cohort and measured eight urinary metals, plasma CC16 and FeNO among 3067 subjects by using inductively coupled plasma-mass spectrometry, enzyme-linked immunosorbent assay kit and Nano Coulomb Nitric Oxide Analyzer, respectively. Mixed linear models were used to quantify dose-relationships between urinary metals and FeNO, as well as urinary metals and plasma CC16. The potential role of plasma CC16 in the associations between urinary metals and FeNO was estimated using mediationanalyses. After adjusting for covariates, one percent increase in urinary vanadium, nickel or antimony was associated with a respective 6.60% (95% CI: 3.52%, 9.68%), 2.18% (0.45%, 3.91%), 4.87% (1.47%, 8.27%) increase in FeNO level. The adverse associations were much stronger among participants with low concentration of plasma CC16 than those with high CC16 level. Moreover, plasma CC16 decreased monotonically with increasing quartiles of urinary vanadium, nickel or antimony. Mediation analyses found that CC16 mediated the associations between urinary metals and FeNO by 5.64%, 39.06% and 25.18% for vanadium, nickel and antimony respectively. CC16 plays an important role in airway inflammation. General population with lower plasma CC16 concentration is more likely to suffer from airway inflammation when exposed to high levels of vanadium, nickel or antimony.

Liu, Y., Yuan, Y., Xiao, Y.*, et al.* (2020) Associations of plasma metal concentrations with the decline in kidney function: A longitudinal study of Chinese adults. *Ecotoxicology and Environmental Safety,* 189: 110006.

Keywords: Kidney function; Metals; Principal component analysis; Prospective study

Abstract:
Metals are widespread pollutants in the environment which have been reported to be associated with kidney dysfunction in many existing epidemiological studies. However, most of the studies are cross-sectional design and mainly focus on several toxic metals including arsenic, lead and cadmium. Therefore, we conducted this prospective study within the Dongfeng-Tongji cohort to evaluate the associations of plasma multiple metals with the decline in kidney function among Chinese middle-aged and elderly. In total, 1434 participants free of chronic diseases at baseline were included in analysis. We measured baseline plasma concentrations of 23 metals and calculated estimated glomerular filtration rate (eGFR) using the Chronic Kidney Disease Epidemiology Collaboration (CKD-EPI) equation based on serum creatinine, age, sex and ethnicity. Bonferroni correction was used for multiple testing to reduce the probability of a type I error. Principal component analysis was conducted to evaluate the combined effect of multiple metal co-exposure. Most of the plasma metal concentrations were within the literature reported reference values, whereas the concentration of lead and nickel exceeded the guideline value. We found that plasma concentrations of aluminum, arsenic, barium, lead, molybdenum, rubidium, strontium, vanadium and zinc were significantly associated with the decline in kidney function measured by annual eGFR decline, rapid renal function decline (defined as an annual decline in eGFR >/= 5 mL/min/1.73 m(2)) or incident eGFR < 60 mL/min/1.73 m(2), with the adjusted beta coefficients (95% CI) for annual eGFR decline 0.50 (0.30, 0.69), 0.98 (0.74, 1.23), 0.56 (0.32, 0.79), 0.21 (0.03, 0.39), 0.35 (0.16, 0.54), 0.94 (0.71, 1.17), 0.37 (0.15, 0.60), 0.78 (0.54, 1.02), and 0.74 (0.57, 0.91), respectively. The metals exposures were linked with increased risks of impaired kidney function. Associations of principal components representing these metals with the decline in kidney function were significant and suggest a

possible additional health risk by co-exposure. Participants engaged in manufacturing had higher plasma levels of several metals compared with those who had been involved in management- or administration-related work. Our findings suggest that exposure to multiple metals contribute to the decline in kidney function among the middle-aged and elderly. Co-exposure to multiple metals may have synergetic effect on the kidney function. Further studies are warranted to confirm our findings and clarify the potential mechanisms.

Lopes Costa, S.S., Alves, J.C., Almeida, T.S.*, et al.* (2019) Seasonality of airborne trace element sources in Aracaju, Northeastern, Brazil. *Journal of Environmental Management,* 247: 19-28.
Keywords: Air quality of urban areas; Enrichment factor; Geoaccumulation index; PM10 and TSP; Trace elements

Abstract:
In this work the urban area of Aracaju city, located in the State of Sergipe, Northeastern Brazil was the site for simultaneous collection of suspended particles (TSP) and inhalable particulate matter (PM10) aiming an evaluation of the air quality parameters. Concentrations of Cd, Co, Cu, Fe, Mn, Ni, Pb and V in TSP and PM10 were determined by inductively coupled plasma mass spectrometry (ICP-MS). Iron was the most abundant element found in both particulate samples. Through chemometric tools, it was possible to point out that the contributions to the TSP and PM10 formation are similar, and strong correlations were observed between Fe-Mn (0.83) and Cd-Pb (0.93) in TSP, and Fe-Mn (0.90), Fe-Cu (0.81) and Cd-Pb (0.97) in PM10, an evidence that these species are from sources related mainly to soil resuspension and vehicular traffic. Enrichment factor (EF) and geoaccumulation index (Igeo) showed an influence of fossil fuel burning in the composition of TSP and PM10. Through principal component analysis (PCA) and hierarchical cluster analysis (HCA) it was observed particle size distribution groupings according to its aerodynamic size. Evaluation of the concentrations obtained for the collected samples according to the seasons (dry and rainy), indicated the influence of both, biogenic (resuspension of soil and marine aerosols) and anthropic (vehicle traffic and biomass burning) sources. © 2019 Elsevier Ltd.

Montoya-Mendoza, J., Alarcón-Reyes, E., Castañeda-Chávez, M.R.*, et al.* (2019) Heavy metals in muscle tissue of pterois volitans from the veracruz reef system national park, mexico. *International Journal of Environmental Research and Public Health,* 16(23).
Available at: https://www.mdpi.com/1660-4601/16/23/4611/pdf
Keywords: Lionfish; Reef; Trace metals; cadmium; lead; vanadium; zinc; concentration (composition); fish; health risk; heavy metal; muscle; trace metal; animal tissue; Article; atomic absorption spectrometry; concentration (parameter); controlled study; dry weight; health hazard; Mexico; muscle tissue; nonhuman; Pterois volitans; Scorpaeniformes; Mexico [North America]; Pterois

Abstract:
Concentrations of cadmium (Cd), lead (Pb), vanadium (V), and zinc (Zn) were measured in the muscle of 30 specimens of Pterois volitans, captured on April 2018, in the Veracruz Reef System National Park (VRSNP), Veracruz, Mexico. Concentrations, in the samples, were quantified with atomic absorption spectrophotometry (AAS), after microwave digestion. Results of the mean concentration, in descending order were V = 7.3 ± 0.7; Pb = 0.66 ± 0.07; Zn = 0.43 ± 0.14; and Cd = 0.03 ± 0.01 mg kg^{-1} dry weight. These values did not exceeded limits established in the Mexican National Standard (NOM-242-SSA1-2009), of Cd and Pb (0.5 mg kg^{-1}) wet weight. This means that consumption of lionfish from this site does not

pose a potential risk for human health. © 2019 by the authors. Licensee MDPI, Basel, Switzerland.

Mudge, S.M., Pfaffhuber, K.A., Fobil, J.N.*, et al.* (2019) Using elemental analyses and multivariate statistics to identify the off-site dispersion from informal e-waste processing. *Environmental Science.Processes & Impacts,* 21(12): 2042-2057.

Abstract:
Electronic waste (e-waste) is informally processed and recycled in Agbogbloshie in Accra (Ghana), which may be the largest such site in West Africa. This industry can lead to significant environmental contamination. In this study, surface dust samples were collected at a range of sites within Accra to establish the offsite consequences of such activities. Fifty-one samples were collected and analysed for 69 elements by ICP-mass spectrometry after nitric acid digestion. The data indicated a significant enrichment in metals associated with solder and copper wire at the site itself and a downwind dispersion of this source material to a distance of approximately 2.0 km. Chlorine and bromine were also elevated at this site as residues from polyvinyl chloride combustion and flame retardants respectively. The elemental composition indicated that only low technology electrical equipment was being treated this way. Multivariate statistical analyses by principal components analysis and polytopic vector analysis identified three sources contributing to the system; (i) burn site residue dispersing within 2 km from the source site, (ii) marine matter on the beaches alone and (iii) the baseline soil conditions of the city of Accra. Risk ratios and hazard quotients developed from the measured concentrations indicated that copper was providing the greatest risk to inhabitants in most cases although nickel, vanadium, chromium and zinc also contributed.

Nakatsubo, R., Oshita, Y., Aikawa, M.*, et al.* (2020) Influence of marine vessel emissions on the atmospheric PM2.5 in Japan's around the congested sea areas. *Science of the Total Environment,* 702.

Keywords: Japan; Marine vessel emissions; Nickel; PM2.5; PMF; Vanadium; Air quality; Atmospheric movements; Factorization; Vanadium compounds; Air pollutants; Marine vessels; PM2.5 concentration; Positive Matrix Factorization; Source analysis; Strong correlation; Marine pollution; fuel oil; atmospheric pollution; concentration (composition); factor analysis; particulate matter; traffic emission; vessel; air pollutant; air pollution control; Article; concentration (parameter); environmental impact; environmental impact assessment; exhaust gas; observational study; pollution transport; priority journal; seashore; Seto Inland Sea; ship; Akashi Strait; Honshu; Hyogo; Kinki

Abstract:
In recent years, PM2.5 concentrations in Japan have decreased as China's measures against the emission of air pollutants were strengthened and the subsequent transport of air pollutants to Japan decreased. On the other hand, along the coast of the Seto inland sea in Japan, the PM2.5 concentration remains high. In this study, in order to evaluate the impact of air pollutants from marine vessels on PM2.5 along the coast of the Seto inland sea, PM2.5 was seasonally collected in the vicinity of a congested sea lane (Akashi Strait) in 2016 and 2017, and a receptor-source analysis was performed to determine the main components of the collected PM2.5. In Japan's congested sea lane, the vanadium (V) concentration was very high and showed a strong correlation with the nickel (Ni) concentration. Also, the V/Ni ratio rose when the wind blew from the sea lane. Positive Matrix Factorization (PMF) analysis clarified that the contributions from marine vessel emissions to PM2.5 at the current observation sites were 2.5–2.7 μg m−3 (17.3–21.4%), and the marine vessel emissions were

the main source of PM2.5 along the coast of the Seto inland sea. Fuel oil regulations for marine vessels to be introduced in January 2020 are expected to improve the air quality of coastal areas. © 2019 Elsevier B.V.

O'Brien, K.M., White, A.J., Jackson, B.P.*, et al.* (2019) Toenail-Based Metal Concentrations and Young-Onset Breast Cancer. *American Journal of Epidemiology,* 188(4): 646-655.
Keywords: Adult; Age of Onset; Breast Neoplasms/chemically induced/epidemiology; Cadmium/analysis/toxicity; Environmental Exposure/adverse effects/analysis; Female; Humans; Logistic Models; Metals/analysis/toxicity; Middle Aged; Nails/chemistry; Odds Ratio; Siblings; Toes; breast cancer; cadmium; metals; toenails; young-onset breast cancer

Abstract:
Several metals have carcinogenic properties, but their associations with breast cancer are not established. We studied cadmium, a metalloestrogen, and 9 other metals-arsenic, cobalt, chromium, copper, mercury, molybdenum, lead, tin, and vanadium--in relation to young-onset breast cancer (diagnosis age <50 years), which tends to be more aggressive than and have a different risk profile from later-onset disease. Recent metal exposure was measured by assessing element concentrations, via inductively coupled plasma mass spectrometry, in toenail clippings of 1,217 disease-discordant sister pairs in the US-based Sister (2003-2009) and Two Sister (2008-2010) studies. Conditional logistic regression was used to calculate odds ratios and 95% confidence intervals. After correcting for differential calendar time of sample collection, no statistically significant associations were observed between any metals and breast cancer. Vanadium had the largest odds ratio (for fourth vs. first quartile, odds ratio = 1.36, 95% confidence interval: 0.84, 2.21; P for trend = 0.17). Cadmium was associated with a small increase in risk, with no evidence of a dose-response relationship (for fourth vs. first quartile, odds ratio = 1.15, 95% confidence interval: 0.82, 1.60; P for trend = 0.67). Positive associations between urinary cadmium concentrations and breast cancer have been reported in case-control studies, but we observed no such association between young-onset breast cancer and toenail concentrations of any assessed metals.

Olise, F.S., Ogundele, L.T., Olajire, M.A.*, et al.* (2019) Biomonitoring of environmental pollution in the vicinity of iron and steel smelters in southwestern Nigeria using transplanted lichens and mosses. *Environmental Monitoring and Assessment,* 191(11).
Keywords: Airborne particulates; Biomonitors; PMF; XRF

Abstract:
This study identified specific emission sources of atmospheric pollution in the vicinity of two secondary iron and steel smelting factories in Osun state, southwestern Nigeria, using transplanted biomonitors. A total of 120 biomonitors consisting of lichen and moss were grown under a controlled environment and later transplanted to the surroundings of each factory for monitoring of air pollutants for 3 months in both wet and dry seasons. The elemental contents (K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb and Sr) of the biomonitors were determined by X-ray florescence (XRF) spectroscopy. The source identification was performed by applying positive matrix factorization (PMF) receptor modelling approach using the elemental data set from the two smelters. Among the measured elements, Fe had the highest average concentration in the lichen and moss samples as well as in both seasons. The average concentrations of Co, Ni, Cu, Zn, As and Br were low. The varying average elemental concentrations of lichen and moss reflect the pattern of impact of smelting on atmospheric airborne pollution around the factories. The four factors resolved by PMF and their respective contributions were metal processing

(39.0%), Fe source (28.0%), crustal/soil (22.0%) and road dust (11.0%) for moss and Fe source (34.0%), crustal/soil (26.0%), coal combustion (25.0%) and road dust (15.0%) for lichen. The study showcases lichen and moss as cheaper and yet efficient uninterrupted monitoring tools of air pollution sources associated with iron and steel smelting industrial activities. © 2019, Springer Nature Switzerland AG.

Parker, G.J., Ong, C.H., Manges, R.B.*, et al.* (2019) A novel method of collecting and chemically characterizing milligram quantities of indoor airborne particulate matter. *Aerosol and Air Quality Research,* 19(11): 2387-2395.
Available at:
https://pdfs.semanticscholar.org/ec49/b0062b624fd291b9d5fa3bd714fd74be046d.pdf
Keywords: Electrostatic precipitation; Indoor air; Metals; Particulate matter

Abstract:
Because people spend the majority of the day indoors, it is important to evaluate indoor air, especially airborne particulate matter (PM), for its potential health effects. However, collecting milligram-sized samples of indoor PM, which are necessary for detailed chemical and biological assays, remains challenging because of the noise, power requirements, and size of traditional PM samplers. Therefore, we developed a novel method of collection using an electrostatic precipitator (ESP). Laboratory experiments were conducted to characterize the ESP collection efficiency (41–65%) and PM recovery (50–95%) for three aerosol types. After characterization, the ESPs were deployed in 21 homes in eastern Iowa for 30 days, during which they collected 6–87 mg of indoor PM. The samples were acid digested and subsequently analyzed by inductively coupled plasma mass spectrometry for their magnesium, aluminum, vanadium, manganese, iron, nickel, copper, zinc, arsenic, and lead content. Crustal metals (magnesium, iron, and aluminum), ranging from 3,000 to 25,000 ng mg–1 in concentration, contributed the largest mass fractions of the PM. The relative abundances of the metals were similar between homes, although the PM mass fractions were highly variable. This ESP sampling method can be applied in future studies to collect milligram-sized quantities of indoor PM, enabling a detailed analysis of its composition and potential health effects. © Taiwan Association for Aerosol Research.

Pedro, E.M., da Rosa Franchi Santos, L.F., Scavuzzi, B.M.*, et al.* (2019) Trace Elements Associated with Systemic Lupus Erythematosus and Insulin Resistance. *Biological Trace Element Research,* 191(1): 34-44.
Keywords: Adolescent; Adult; Aged; Cross-Sectional Studies; Female; Humans; Insulin Resistance; Lupus Erythematosus, Systemic/blood; Male; Middle Aged; Trace Elements/blood; Glucose homeostasis; Heavy metals; SLE disease activity index (SLEDAI); Trace elements

Abstract:
Systemic lupus erythematosus (SLE) is a chronic inflammatory autoimmune disease of multifactorial origin. Studies have shown that trace elements such as zinc and copper may help maintain optimum function of the immune system and metabolism, while toxic metals such as lead may increase systemic autoimmunity. The current study aimed to assess the relationship between serum concentration of lithium (Li), vanadium (V), copper (Cu), zinc (Zn), molybdenum (Mo), cadmium (Cd), and lead (Pb) and SLE diagnosis, disease activity measured by SLE disease activity index (SLEDAI) and insulin resistance (IR). This case-control, cross-sectional study included 225 patients, 120 healthy controls, and 105 SLE patients. Serum concentration of Li, V, Cu, Zn, Mo, Cd, and Pb was measured. Serum concentrations of V ($p < 0.001$), Zn ($p < 0.001$), and Pb ($p < 0.001$) were lower and Mo ($p < 0.001$) and Li ($p <$

0.001) were higher in patients with SLE compared to healthy controls. SLE diagnosis was associated with higher serum Li ($p < 0.001$) concentration and lower V ($p < 0.001$), Zn ($p = 0.003$), and Pb ($p = 0.020$). Toxic metals and trace elements were not associated with disease activity. Levels of Cd were higher in patients with IR ($p = 0.042$). There was no significant association between IR and the other metals. The results indicate that SLE patients have different profiles of trace elements and toxic metals compared to healthy controls. While some toxic metals and trace elements were found to be associated with SLE diagnosis, they had no effect on disease activity and IR.

Qiao, J., Zhu, Y., Jia, X.*, et al.* (2020) Distributions of arsenic and other heavy metals, and health risk assessments for groundwater in the Guanzhong Plain region of China. *Environmental Research,* 181.
Keywords: Groundwater; Health risk assessment; Heavy metal; aluminum; arsenic; cadmium; chromium; cobalt; copper; ground water; iron; lead; manganese; molybdenum; nickel; vanadium; zinc; concentration (composition); health risk; risk assessment; water quality; China; health hazard; human; monsoon climate; precipitation; priority journal; statistics; water pollution; water sampling; Guanzhong Plain; Shaanxi

Abstract:
We assessed the quality of groundwater in the Guanzhong Plain region of China, where we evaluated the levels of As and 12 other heavy metals. © 2019 Elsevier Inc. The aim of this study was to evaluate the quality of shallow groundwater and deep groundwater in the Guanzhong Plain region of China, as well as the related health risk to humans. In total, 130 groundwater samples were collected comprising 116 from shallow groundwater (dug wells) and 14 from deep groundwater (drilled wells). The water samples were analyzed to determine the levels of As and 12 other heavy metals (Al, Cd, Mn, Cr, V, Fe, Ni, Cu, Zn, Co, Pb, and Mo). The results showed that the concentrations of As and other heavy metals in the deep groundwater samples were lower than the safe limits, but the Cr concentrations in some shallow groundwater samples exceeded the safe limits. The heavy metal pollution index and heavy metal evaluation index both showed that As and other heavy metals were pollutants at low levels in all of the shallow and deep groundwater sample. Health risk assessments showed that the deep groundwater samples had no associated non-carcinogenic health risks, whereas the shallow groundwater samples had non-carcinogenic health risks due to contamination with Cr and As. Some shallow groundwater samples had associated carcinogenic health risks due to contamination with Cr and As, whereas the deep groundwater samples only had carcinogenic health risks because of contamination with Cr. These results suggest that local residents and government departments should be made aware of Cr and As pollution in shallow groundwater. © 2019 Elsevier Inc.

Rafiee, A., Delgado-Saborit, J.M., Sly, P.D.*, et al.* (2020) Environmental chronic exposure to metals and effects on attention and executive function in the general population. *Science of the Total Environment,* 705.
Keywords: Biomonitoring; Cognitive performance; Exposure assessment; Heavy metals; TMT test; Atomic emission spectroscopy; Dental alloys; Dental amalgams; Efficiency; Inductively coupled plasma; Water pipelines; Brain dysfunctions; Cognitive efficiency; Executive function; Inductively coupled plasma atomic emission spectroscopy; Mean concentrations; Testing; aluminum; antimony; arsenic; barium; beryllium; boron; cadmium; chromium; cobalt; copper; dental amalgam; iron; lead; lithium; manganese; mercury; metal; nickel; tin; vanadium; zinc; age; cognition; gender; health impact; heavy metal; pollution exposure; risk assessment; smoking; adolescent; adult; aged; Article; attention; cigarette smoking; concentration (parameter); controlled study; cross-sectional study; demography;

environmental exposure; female; hair; health status; human; inductively coupled plasma atomic emission spectrometry; Iran; lifestyle; long term exposure; male; neurotoxicity; priority journal; social status; traffic; trail making test; Tehran [Iran]; Tehran [Tehran (PRV)]

Abstract:
Heavy metals are neurotoxic, associated with brain dysfunction, and have been linked with cognitive decline in adults. This study was aimed to characterize chronic exposure to metals (Cd, Be, Co, Hg, Sn, V, Al, Ba, Cr, Cu, Fe, Li, Mn, Ni, Pb, and Zn) and metalloids (As, B, Sb) and assess its impact on cognitive performance of Tehran's residents, capital of Iran. Scalp hair samples gathered from 200 volunteered participants (110 men and 90 women), aged 14–70 years and quantified by inductively coupled plasma atomic emission spectroscopy (ICP-OES). Attention and executive function, two measures of cognitive performance, were characterized using the trail making test (TMT) part A and B, respectively. Mental flexibility was characterized as the Delta TMT B-A scores and cognitive efficiency or dissimulation as the ration between TMT B and A scores. A comprehensive questionnaire was used to gather information on demographic and socioeconomic as well as lifestyle and health status. The highest and lowest mean concentrations were observed for B (325 μg/g) and As (0.29 μg/g), respectively. Results indicated that chronic metal exposure measured in hair changed significantly based on gender and age ($p < 0.05$). The levels of Cr, Fe, Ni, Si, Hg, Pb and B were significantly higher in males' hair, whereas those of Ag and Ba were greater in females' hair ($p < 0.05$). The results of the cognitive TMT test were significantly different between gender and age groups ($p < 0.05$). Moreover, results revealed that As, Hg, Mn, and Pb levels in hair were significantly associated with poorer participants' performance scores in the TMT test ($p < 0.05$). Age, gender, cigarette smoking, water-pipe smoking, traffic density in the area of residence, and dental amalgam filling were significant factors affecting the TMT test scores. The results suggest that chronic exposure to metals has detrimental effects on attention, executive function, mental flexibility and cognitive efficiency. © 2019 Elsevier B.V.

Ramírez, O., Sánchez de la Campa, A.M., Sánchez-Rodas, D.*, et al.* (2020) Hazardous trace elements in thoracic fraction of airborne particulate matter: Assessment of temporal variations, sources, and health risks in a megacity. *Science of the Total Environment,* 710.**
Keywords: Antimony speciation; Cancer risk; Heavy metals; PM10; PMF model; Source apportionment; Antimony compounds; Charcoal; Chromium compounds; Combustion; Copper smelting; Deforestation; Diseases; Factorization; Fire hazards; Fires; Fossil fuels; Health risks; Industrial emissions; Particles (particulate matter); Risk assessment; Steelmaking; Trace elements; Urban growth; Pmf models; Iron and steel industry; antimony; arsenic; barium; cadmium; chromium; cobalt; copper; lead; nickel; tin; trace element; vanadium; zinc; assessment method; cancer; concentration (composition); health risk; heavy metal; megacity; particulate matter; seasonal variation; spatiotemporal analysis; speciation (chemistry); airborne particle; Article; Colombia; dust; exhaust gas; forest fire; health hazard; inhalation; priority journal; urban area; Bogota

Abstract:
The deleterious health effects of thoracic fractions seem to be more related to the chemical composition of the particles than to their mass concentration. The presence of hazardous materials in PM10 (e.g., heavy metals and metalloids) causes risks to human health. In this study, twelve trace elements (Cd, Cr, Pb, Zn, Cu, Ni, Sn, Ba, Co, As, V, and Sb) in 315 samples of ambient PM10 were analyzed. The samples were collected at an urban background site in a Latin American megacity (Bogota, Colombia) for one year. The concentrations and temporal variabilities of these elements were examined. According to the results, Cu (52 ng/m3), Zn (44 ng/m3), Pb (25 ng/m3), and Ba (20 ng/m3) were the traces with the highest

concentrations, particularly during the dry season (January to March), which was characterized by barbecue (BBQ) charcoal combustion and forest fires. In addition, the differences between the results of weekdays and weekends were identified. The determined enrichment factor (EF) indicated that Zn, Pb, Sn, Cu, Cd, and Sb mainly originated from anthropogenic sources. Moreover, a speciation analysis of inorganic Sb (EF > 300) was conducted, which revealed that Sb(V) was the main Sb species in the PM10 samples (>80%). Six causes for the hazardous elements were identified based on the positive matrix factorization (PMF) model: fossil fuel combustion and forest fires (60%), road dust (19%), traffic-related emissions (9%), copper smelting (8%), the iron and steel industry (2%), and an unidentified industrial sector (2%). Furthermore, a health risk assessment of the carcinogenic elements was performed. Accordingly, the cancer risk of inhalation exposure to Co, Ni, As, Cd, Sb(III), and Pb was negligible for children and adults at the sampling site. For adults, the adjusted Cr(VI) level was slightly higher than the minimal acceptable risk level during the study period (1.4 × 10−6). © 2019 Elsevier B.V.

Rutigliano, F.A., Marzaioli, R., De Crescenzo, S.*, et al.* (2019) Human health risk from consumption of two common crops grown in polluted soils. *Science of the Total Environment,* 691: 195-204.
Keywords: Bio-accumulation factor; Health risk index; Lettuce; Soil contamination; Trace elements; Zucchini

Abstract:
Contamination of agricultural soils by trace elements is a recurrent hazard for human health because of the possibility of pollutants entering the food chain. Aim of this study was to assess the human health risk from consumption of the common leafy (Lactuca sativa L.) and fruit (Cucurbita pepo L.) crops, in an agricultural area of Southern Italy. Along with agricultural practices, a major pollutant source is recurrent flooding from the highly polluted Solofrana river. Soil samples and edible parts of crops from 14 sites (10 flooded and 4 not flooded) were analyzed for total amounts of As, Cd, Co, Cr, Cu, Ni, Pb, V, Zn. The bio-accumulation factor (BAF) and Health Risk Index (HRI) were calculated for each element, crop and site and as average values of all sites (BAFmean and HRImean). Moreover, the Hazard Index (HI) was determined for each site, as the sum of HRI for all elements. Cr and Cu, mostly derived from river flooding and agricultural practices, respectively, were the only elements whose levels exceeded law thresholds and/or the natural background of the study area. Of the two considered crops, L. sativa accumulated more Cd, Cr and Ni, whereas C. pepo was a more effective bioaccumulator of Zn. Both HRImean (for As, Cd, Cr and Ni) and HI were higher for L. sativa than for C. pepo. A low health risk was associated to major soil pollutants (Cr and Cu) found in the study area; in contrast, combined data on soil pollution and plant bio-accumulation points to accumulation of Cd and As, mainly in lettuce, as a potential risk for human health. The results suggest that soil pollution data alone is not sufficient to assess health risk. © 2019 Elsevier B.V.

Samuel-Nakamura, C., Hodge, F.S., Sokolow, S.*, et al.* (2019) Metal(loid)s in Cucurbita pepo in a Uranium Mining Impacted Area in Northwestern New Mexico, USA. *International Journal of Environmental Research and Public Health,* 16(14): 10.3390/ijerph16142569.
Available at: https://www.mdpi.com/1660-4601/16/14/2569/pdf
Keywords: Adult; Aged; Aged, 80 and over; Arsenic/analysis; Cucurbita/chemistry; Drinking Water/standards; Female; Humans; Male; Metals, Heavy/analysis; Middle Aged; Mining; New Mexico; Selenium/analysis; Soil; Soil Pollutants/analysis; United States; United States Environmental Protection Agency; Uranium/analysis; Water Pollutants, Chemical/analysis; American Indian; Dine; Navajo; cadmium; food chain; irrigation water; lead; squash

Abstract:
More than 500 unreclaimed mines and associated waste sites exist on the Navajo Nation reservation as a result of uranium (U) mining from the 1940s through the 1980s. For this study, the impact of U-mine waste on a common, locally grown crop food was examined. The goal of this site-specific study was to determine metal(loid) concentration levels of arsenic (As), cadmium (Cd), cesium (Cs), molybdenum (Mo), lead (Pb), thorium (Th), U, vanadium (V) and selenium (Se) in Cucurbita pepo Linnaeus (squash), irrigation water, and soil using inductively coupled plasma-mass spectrometry. The concentrations of metal(loid)s were greatest in roots > leaves > edible fruit (p 30 years) for V ($p = 0.001$), As ($p < 0.001$), U ($p = 0.002$), Cs ($p = 0.012$), Th ($p = 0.040$), Mo ($p = 0.047$), and Cd ($p = 0.042$). Lead and Cd crop irrigation water concentrations exceeded the United States Environmental Protection Agency (USEPA) Maximum Contaminant Levels for drinking water for those metals. Edible squash concentration levels were 0.116 mg/kg of As, 0.248 mg/kg of Pb, 0.020 mg/kg of Cd, and 0.006 mg/kg of U. Calculated human ingestion of edible squash did not exceed Provisional Tolerable Weekly Intake or Tolerable Upper Limit levels from intake based solely on squash consumption. There does not appear to be a food-ingestion risk from metal(loid)s solely from consumption of squash. Safer access and emphasis on consuming regulated water was highlighted. Food intake recommendations were provided. Continued monitoring, surveillance, and further research are recommended.

Semenova, Y., Zhunussov, Y., Pivina, L.*, et al.* (2019) Trace element biomonitoring in hair and blood of occupationally unexposed population residing in polluted areas of East Kazakhstan and Pavlodar regions. *Journal of Trace Elements in Medicine and Biology,* 56: 31-37.
Keywords: Blood; Environmental exposure; Hair; Metals; Trace elements; barium; beryllium; bismuth; cerium; cesium; chromium; cobalt; copper; europium; gadolinium; hafnium; indium; lanthanum; lead; lithium; manganese; molybdenum; neodymium; niobium; scandium; silver; thallium; thorium; tin; trace element; tungsten; uranium; vanadium; yttrium; Article; biological monitoring; controlled study; human; inductively coupled plasma mass spectrometry; industrial area; Kazakhstan; occupational exposure; pollution; priority journal; rural area; adult; aged; chemistry; demography; female; geography; male; middle aged; Environmental Pollution; Humans; Residence Characteristics

Abstract:
Introduction: Eastern and North-Eastern regions of Kazakhstan are considered to be environmentally disadvantaged due to industrial pollution and activity of the former Semipalatinsk Nuclear Test Site. Ferrous metallurgy is represented by the world's largest ferroalloy plant located in Aksu. In addition to a ferroalloy plant, Aksu is the home for the largest thermal power plant in Kazakhstan. Objective: Biomonitoring of 31 hair and blood trace elements (Ag, Ba, Be, Bi, Cs, Co, Ce, Cr, Cu, Eu, Gd, Hf, In, La, Li, Mn, Mo, Nb, Nd, Pb, Sc, Sn, Tl, Th, U, V, W, Y, Yb, Zn, and Zr) in non-occupationally exposed population residing in polluted areas of East Kazakhstan and Pavlodar regions. Methods: Five case groups, residing in the vicinity to the former Semipalatinsk Nuclear Test Site (Akzhar, Borodulikha, and Karaul) or in proximity to industrial plants (Aksu and Ust-Kamenogorsk) have been assessed vs. controls from a rural settlement in Kurchum. In total, 204 hair and blood samples were analyzed by inductively coupled plasma mass spectrometry. Results: The observed blood concentrations of trace elements were in agreement with earlier studies on residents of industrially polluted areas. Elevated levels of blood Ba, Mn, Pb, V, and Zn were detected in residents of Aksu and Ust-Kamenogorsk. The elemental composition of head hair was characterized by greater stability between the study sites. Conclusion: Residency near the

former Semipalatinsk Test Site could be considered as safe, while the environmental status of industrial settlements appears to be rather adverse. © 2019 Elsevier GmbH.

Skalny, A.V., Tinkov, A.A., Bohan, T.G.*, et al.* (2020) The Impact of Maternal Overweight on Hair Essential Trace Element and Mineral Content in Pregnant Women and Their Children. *Biological Trace Element Research,* 193: 64-72.
Keywords: Chromium; Maternal obesity; Pregnancy; Vanadium; Zinc

Abstract:
The aim of the present study was to investigate hair essential trace elements and mineral levels in 105 pregnant normal-weight (control) and 55 overweight and obese women in the third trimester of pregnancy, as well as in their children at the age of 9 months. The hair essential trace elements and mineral levels were assessed using inductively coupled plasma mass-spectrometry. Overweight pregnant women had significantly reduced Cr (- 24%; p = 0.047) and Zn (- 13%; p = 0.008) content, as well as elevated hair Na and K levels as compared to the controls. Children from overweight and obese mothers had lower hair Mo (- 18%; p = 0.017), Se (- 8%; p = 0.043), and V (- 24%; p = 0.028) levels, as well as elevated Sr content (19%; p = 0.025). Correlation analysis revealed a significant relationship between maternal and child hair levels of Co (r = 0.170; p = 0.038), Cu (r = 0.513; p < 0.001), Mn (r = 0.240; p = 0.003), and Na (r = 0.181; p = 0.027) in the whole sample. Pre-pregnancy maternal body mass index (BMI) positively correlated with maternal hair K (r = 0.336; p < 0.001) and Na (r = 0.212; p = 0.008) and negatively correlated with V (r = - 0.204; p = 0.011) and Zn (r = - 0.162; p = 0.045) levels. The results indicate that impaired trace element and mineral metabolism may play a role in the link between maternal obesity, complications of pregnancy and child's postnatal development. Hypothetically, dietary improvement may be used as a tool to reduce these risks. However, further experimental and clinical studies are required to investigate the relationship between obesity and trace element metabolism in pregnancy.

Street, R.A., Mathee, A., Tanda, S.*, et al.* (2020) Recycling of scrap metal into artisanal cookware in the informal sector: A public health threat from multi metal exposure in South Africa. *Science of the Total Environment,* 699.
Keywords: Aluminum cookware; Exposure; ICPMS; Metals; Toxicity; Health risks; High resolution transmission electron microscopy; Inductively coupled plasma mass spectrometry; Leaching; Recycling; Scrap metal reprocessing; Surface structure; Acid solutions; Informal sector; Metal exposures; Multi-metals; Silicon concentration; Total content; Scrap metal; acetic acid; aluminum; antimony; arsenic; barium; cadmium; chromium; cobalt; copper; iron; lead; manganese; mercury; metal; molybdenum; nickel; selenium; silicon; silver; tin; vanadium; zinc; concentration (composition); cooking appliance; inductively coupled plasma method; public health; Article; concentration (parameter); e-waste; energy dispersive X ray spectroscopy; environmental exposure; health hazard; life threat; limit of detection; manufacturing industry; priority journal; South Africa; transmission electron microscopy; X ray fluorescence spectrometry

Abstract:
Recycling of scrap metal into artisanal cookware is widespread in poorly resourced countries. The aim of the study was to determine the risk of metal exposure from the use of artisanal cookware available in South Africa. Twenty cookware samples were purchased from local manufacturers and informal traders across South Africa. Aluminum and silicon concentrations were determined using XRF and the total content of 18 elements (Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V and Zn) were evaluated using ICPMS.

Leaching of metals from cut pieces of cookware over a 2-h period of boiling in a 3% acetic acid solution was repeated 3 times and revealed multi-metal migration that was compared to EU maximum permissible levels. The mean Al migration of 509 mg L−1 was over 100 times the EU maximum permissible level allowed for cookware. Lead was detected in all samples with 11 (55%), 12 (60%) and 9 (45%) of samples being over the maximum EU permissible level (10 μg Pb L−1) for 1st, 2nd and 3rd migrations respectively. The mean As migration concentrations in the first leaching event ranged from 0.23 to 24.1 μg L−1 with four pots (20%) over the maximum EU permissible limit for As (2 μg L−1). Notably, all four pots were well below the maximum EU permissible As limit by the 3rd migration. Cadmium and mercury were detected in each pot across all three migrations however the levels were relatively low. Transmission electron microscopy revealed dramatic changes in surface structure after leaching of cookware. © 2019.

Tsai, M.-., Chen, M.-., Lin, C.-*., et al.* (2019) Children's environmental health based on birth cohort studies of Asia (2) – air pollution, pesticides, and heavy metals. *Environmental Research,* 179.
Keywords: Air pollution; Asia; Birth cohort; Heavy metals; Pesticides; arsenic; cadmium; heavy metal; lead; manganese; organochlorine pesticide; pesticide; pyrethroid; thallium; vanadium; atmospheric pollution; child health; cohort analysis; environmental quality; PCB; pesticide residue; phthalate; pollution exposure; pregnancy; smoke; tobacco; air pollutant; allergic disease; Article; child; child growth; childhood; childhood obesity; environmental exposure; environmental health; fetus growth; human; infancy; pregnancy outcome; prenatal exposure; priority journal; problem behavior; systematic review; Nicotiana tabacum

Abstract:
The life style and child raising environment in Asia are quite different compared with Western countries. Besides, the children's environmental threats and difficulties in conducting studies could be different. To address children's environmental health in Asia area, the Birth Cohort Consortium of Asia (BiCCA) was co-established in 2011. We reviewed the mercury, polychlorinated biphenyls, perfluoroalkyl substances, phthalates, and environmental tobacco smoke in pervious based on birth cohort studies in Asia. The aim of this study was to summarize the traditional environmental pollution and the target subjects were also based on the birth cohort in Asia area. Environmental pollutants included air pollutants, pesticides focusing on organochlorine pesticides, diakylphosphates, and pyrethroid, and heavy metals including lead, arsenic, cadmium, manganese, vanadium, and thallium. Fetal growth and pregnancy outcomes, childhood growth and obesity, neurodevelopment and behavioral problems, and allergic disease and immune function were classified to elucidate the children's health effects. In total, 106 studies were selected in this study. The evidences showed air pollution or pesticides may affect growth during infancy or childhood, and associated with neurodevelopmental or behavioral problems. Prenatal exposure to lead or manganese was associated with neurodevelopmental or behavioral problems, while exposure to arsenic or cadmium may influence fetal growth. In addition to the harmonization and international collaboration of birth cohorts in Asia; however, understand the whole picture of exposure scenario and consider more discipline in the research are necessary. © 2019 Elsevier Inc.

Tzafriri-Milo, R., Benaltabet, T., Torfstein, A*., et al.* (2019) The Potential Use of Invasive Ascidians for Biomonitoring Heavy Metal Pollution. *Frontiers in Marine Science,* 6: 611.
Keywords: benthic ecology; metal accumulation; biomonitoring Programs; tunicates; Red Sea; Mediterranean Sea; REPRODUCTIVE MECHANISMS; STYELA-PLICATA; TRACE-METALS; BIOACCUMULATION; VANADIUM; ACCUMULATION; CD; CU; CONTAMINATION;

BIOINDICATOR; Environmental Sciences & Ecology; Marine & Freshwater Biology

Abstract:
Heavy metal (HM) inputs into marine environments and their effect on marine organisms are of major concern. Here, we examined the potential use of two invasive ascidian species, Phallusia nigra and Microcosmus exasperatus, as bio-indicators of 11 HMs in the Mediterranean and Red Sea coasts of Israel. Individuals were collected on a seasonal basis from three sites over 1 year, and analysis was carried out separately for the tunic and the body. Both species accumulated high levels of HMs, which varied seasonally and spatially. In M. exasperatus the majority of HMs were found in the tunic, and in P. nigra in the body, suggesting the need to analyze total individuals in future studies. Hepato-Somatic Index values for M. exasperatus were significantly lower at the polluted site. Investigation of a popular public beach revealed high levels of certain dissolved HMs in both the water and in the ascidians. The wide geographic distribution and high filtration capacity of invasive ascidians offer great potential for their use in monitoring metal pollution in marine environments.

Wang, X., Gao, D., Zhang, G.*, et al.* (2019) Exposure to multiple metals in early pregnancy and gestational diabetes mellitus: A prospective cohort study. *Environment International,* 135: 105370.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412019323979/pdfft?md5=7f459a82f1f8aa3097e059d76a9c473a&pid=1-s2.0-S0160412019323979-main.pdf
Keywords: GDM; Urinary metals; Single-metal models; Multiple-metal models; BKMR models

Abstract:
BACKGROUND:
A growing number of epidemiologic studies have estimated associations between type 2 diabetes mellitus and exposure to metals. However, studies on the associations of internal assessments of metal exposure and gestational diabetes mellitus (GDM) are limited in scope and have inconsistent outcomes.
OBJECTIVES:
This investigation aimed to explore the associations between urinary nickel (Ni), arsenic (As), cadmium (Cd), antimony (Sb), cobalt (Co), or vanadium (V) in early pregnancy and the subsequent risk of GDM in Chinese pregnant women.
METHODS:
The study population included 2090 women with singleton pregnancy from the Tongji Maternal and Child Health Cohort (TMCHC). Urine samples were collected before 20 gestational weeks, and an oral glucose tolerance test (OGTT) was conducted at 24-28 gestational weeks to diagnose GDM. The concentrations of urinary metals were measured using inductively coupled plasma mass spectrometry (ICP-MS) and were corrected for urinary creatinine. The associations between the risk of GDM and urinary metals were assessed using Poisson regression with a robust error variance with generalized estimating equations (GEE) models and Bayesian kernel machine regression (BKMR).
RESULTS:
A total of 241 participants (11.53%) were diagnosed with GDM. Five metals (Ni, As, Sb, Co, and V) were found significantly and positively associated with GDM based on single-metal models. In multiple-metal models, for each unit increase of ln-transformed urinary Ni or Sb, the risk of GDM increased 18% [relative risk (RR):1.18, 95%confidence interval (CI): 1.00, 1.38 or RR: 1.18, 95%CI: 1.00, 1.39, respectively]. The BKMR analysis revealed a statistically significant and positive joint effect of the six metals on the risk of GDM, when the urinary

levels of the six metals were all above the 55th percentile, compared to the median levels. The effect of metal Ni was significant when the concentrations of the other metals were all fixed at their 25th percentile, and metal Sb displayed a significant and positive effect when all the other metals were fixed at 25th, 50th, and 75th percentiles.
CONCLUSIONS:
To the best of our knowledge, this study is the first to demonstrate that increased concentrations of urinary Ni in early pregnancy are associated with an elevated risk of GDM, either evaluated individually or as a metal mixture. All six metals mixed exposure was positively associated with the risk of GDM, while Sb and Ni were demonstrated more important effects than the other four metals in the mixture.

Wei, T., Dong, Z., Kang, S.*, et al.* (2019) Atmospheric deposition and contamination of trace elements in snowpacks of mountain glaciers in the northeastern Tibetan Plateau. *Science of the Total Environment,* 689: 754-764.
Keywords: Anthropogenic sources; Contamination; Glacier snowpack; Northeastern Tibetan plateau; Trace elements

Abstract:
To investigate the large-scale trace element deposition and anthropogenic pollution in mountain glaciers of the northeastern Tibetan Plateau (TP) and its surrounding regions, we analyzed Al and 13 trace elements (As, Cd, Co, Cr, Cs, Cu, Mn, Mo, Ni, Pb, Sb, V, and Zn) in glacier snowpacks collected at the Yuzhufeng, Laohugou No.12, and Qiyi glaciers (YG, LG12, and QG, respectively) in the northeastern TP as well as in the Miaoergou Glacier (MG) in the eastern Tianshan Mountains in June 2017. The concentrations and enrichment factors (EFs) of most trace elements (e.g., As, Cd, Co, Cr, Cu, Ni, and Sb) showed that the largest value appeared in the MG, followed by LG12, and the lowest value appeared in the QG, thereby implying a decreasing influence of anthropogenic emissions on these elements from the west (MG) to the east (QG). The YG inversely exhibited high concentrations but low EFs for As, Cd, Co, Cr, Cs, Cu, Pb, and Sb. Compared to the surrounding regions of the southern and western TP (e.g., Nam–Co, Mt. Everest, and Pamirs), Japan, and Kathmandu, the trace element concentrations were relatively higher at the YG and MG but relatively lower at the LG12 and QG. The spatial distribution characteristics of trace elements (e.g., Pb and Sb) exhibited a gradually decreasing concentration from west to east in the Tianshan Mountains, and from south to north in the TP, implying two potential transport routes of atmospheric pollutants from Central and South Asia to the northeastern TP. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) backward trajectory model and Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations/Cloud-Aerosol Lidar with Orthogonal Polarization (CALIPSO/CALIOP) data reflected that these trace elements in the MG, LG12, and QG predominately originated from the western and surrounding areas, whereas in the YG they were mainly derived from a local source and South Asia through long-distance transport. © 2019 Elsevier B.V.

Zhou, L., Liu, G., Shen, M.*, et al.* (2020) Source identification of heavy metals and stable carbon isotope in indoor dust from different functional areas in Hefei, China. *Science of the Total Environment,* 710.
Keywords: Heavy metals; Indoor dust; Source identification; Stable carbon isotope; Air conditioning; Carbon; Health risks; Indoor air pollution; Isotopes; Metal analysis; Concentration analysis; Heavy metal concentration; Negative correlation; Potential health risks; Stable carbon isotopes; Suspended particulate matters; Dust; antimony; cadmium; carbon 13; chromium; heavy metal; lead; manganese; nickel; vanadium; zinc; carbon isotope; concentration (composition); indoor air; stable isotope; air pollutant; Article; China;

concentration (parameter); controlled study; cooking; family size; isotope analysis; priority journal; smoking; Anhui; Hefei

Abstract:
Dust on air conditioning filters can represent the re-suspended particulate matter in indoor air, which may pose potential health risks to humans. However, source identification and influence factors of indoor dust are controversial. The present study investigated the distribution of Cd, Cr, Mn, Ni, Pb, Sb, V, and Zn, as well as stable carbon isotope, in indoor dust from three different functional zones in Hefei to discuss the sources and influence factors of indoor dust. PCA analysis of heavy metals showed that indoor sources (such as cooking and smoking) were the main sources. Negative correlation appeared between family size and heavy metal concentrations. This was because people acted as a sink of pollutants. Concentration analysis of heavy metals revealed that smoking and cooking had weak relevance with heavy metal concentrations. While through the δ13C analysis, cooking had a significant correlation with δ13C of indoor dust, instructing that cooking was a significant source of indoor dust. Besides, smoking also had a certain correlation with δ13C of indoor dust, instructing that smoking was one of the sources of indoor dust. © 2019.

2. HEALTH EFFECTS

Alghamdi, M.A., Hassan, S.K., Alzahrani, N.A.*, et al.* (2019) Risk assessment and implications of schoolchildren exposure to classroom heavy metals particles in Jeddah, Saudi Arabia. *International Journal of Environmental Research and Public Health,* 16(24).
Available at: https://www.mdpi.com/1660-4601/16/24/5017/pdf
Keywords: Classrooms air conditioner filter particles; Contamination level; Health risk; Heavy metals; Indoor air quality; Schools; arsenic; cadmium; carcinogen; chromium; cobalt; copper; heavy metal; iron; lead; manganese; nickel; vanadium; zinc; air quality; cancer; indoor air; particulate matter; pollution exposure; public space; risk assessment; air conditioning; airborne particle; Article; cancer risk; child; controlled study; environmental enrichment; environmental exposure; health hazard; human; indoor air pollution; ingestion; inhalation; residential area; Saudi Arabia; school; school child; skin; suburban area; urban area; Jeddah; Makkah [Saudi Arabia]

Abstract:
Classrooms Air Conditioner Filter (CACF) particles represent all of the exposed particles that have migrated to the interior environment. This study was conducted to assess the heavy metals contamination in CACF particles from Jeddah primary schools located in urban, suburban and residential areas; and to evaluate their health risks of children exposure (non-carcinogenic and carcinogenic). Heavy metals levels in CACF particles of schools were in the following order: urban schools > suburban schools > residential schools. Fe, Mn and Zn were the dominant species. Geo-accumulation index (Igeo), contamination factor (CF) and pollution load index (PLI) values indicated that the contamination levels was in the following order Cd > Pb > Zn > As > Cu > Ni > Mn > Cr > Co >V > Fe. School CACF particles was moderately contaminated with As and Zn and moderately to heavily contaminated with Pb and Cd. Enrichment factors (EFs) indicated that Zn, Cd, Pb, As and Cu in CACF particles were severe enriched. The hazard quotient (HQs) and hazards index (HI) values for heavy metals were lower than the acceptable level of one. As, Pb, Cr and Mn were exhibited high non-cancer effects for children. The lifetime cancer risk (LCR) and total lifetime cancer risk (TLCR), HQs and HI values for the different exposure pathways of heavy metals decreased in the following order: ingestion > dermal contact > inhalation. Carcinogenic and non-carcinogenic risk rank order of schools were urban schools > suburban schools > residential schools. The LCR and TLCR of heavy metals was in the following order: Co > Ni >Cr > Cd > As

> Pb. The ingestion lifetime cancer risk (LCRing) and TLCR values from exposure to Ni and Cr in urban and suburban schools, Cd in urban schools, and Co in all Jeddah schools only exceed the acceptable range (1 × 10−6–1 × 10−4) Only LCRing and TLCR values from exposure to∑ carcinogens exceed the acceptable level. © 2019 by the authors. Licensee MDPI, Basel, Switzerland. T.

Areecheewakul, S., Adamcakova-Dodd, A., Givens, B.E.*, et al.* (2020) Toxicity assessment of metal oxide nanomaterials using in vitro screening and murine acute inhalation studies. *Nanoimpact,* : 100214.
Keywords: Nanomaterials; Nanoparticles; toxicity; Inhalation toxicity; Metal oxides

Abstract:
Characterizations and in vitro toxicity screening were performed on metal oxide engineered nanomaterials (ENMs) independently comprising ZnO, CuO, CeO2, Fe2O3, WO3, V2O5, TiO2, Al2O3 and MgO. Nanomaterials that exhibited the highest toxicity responses in the in vitro screening assays (ZnO, CuO, and V2O5) and the lesser explored material WO3 were tested for acute pulmonary toxicity in vivo. Female and male mice (C57Bl/6J) were exposed to aerosolized metal oxide ENMs in a nose-only exposure system and toxicity outcomes (biomarkers of cytotoxicity, immunotoxicity, inflammation, and lung histopathology) at 4 and 24 h after the start of exposure were assessed. The studies were performed as part of the NIEHS Nanomaterials Health Implications Research consortium with the purpose of investigating the effects of ENMs on various biological systems. ENMs were supplied by the Engineered Nanomaterials Resource and Coordination Core. Among the ENMs studied, the highest toxicity was observed for CuO and ZnO NPs in both in vitro and in vivo acute models. Compared to sham-exposed controls, there was a significant increase in bronchoalveolar lavage neutrophils and proinflammatory cytokines and a loss of macrophage viability at both 4 h and 24 h for ZnO and CuO but not seen for V2O5 or WO3. These effects were observed in both female and male mice. The cell viability performed after in vitro exposure to ENMs and assessment of lung inflammation after acute inhalation exposure in vivo were shown to be sensitive endpoints to predict ENM acute toxicity. ".

Ashrap, P., Watkins, D.J., Mukherjee, B.*, et al.* (2020) Predictors of urinary and blood Metal(loid) concentrations among pregnant women in Northern Puerto Rico. *Environmental Research,* 183: 109178.
Keywords: Biomarkers; Blood; Exposure assessment; Metals; Pregnancy; Urine

Abstract:
Given the potential adverse health effects related to toxic trace metal exposure and insufficient or excessive levels of essential trace metals in pregnant women and their fetuses, the present study characterizes biomarkers of metal and metalloid exposure at repeated time points during pregnancy among women in Puerto Rico. We recruited 1040 pregnant women from prenatal clinics and collected urine, blood, and questionnaire data on demographics, product use, food consumption, and water usage at up to three visits. All samples were analyzed for 16 metal(loid)s: arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), titanium (Ti), uranium (U), vanadium (V), and zinc (Zn). Urine samples were additionally analyzed for molybdenum (Mo), platinum (Pt), antimony (Sb), tin (Sn), and tungsten (W). Mean concentrations of most metal(loid)s were higher among participants compared to the general US female population. We found weak to moderate correlations for inter-matrix comparisons, and moderate to strong correlations between several metal(loid)s measured within each biological matrix. Blood concentrations

of Cu, Zn, Mn, Hg, and Pb were shown to reflect reliable biomarkers of exposure. For other metals, repeated samples are recommended for exposure assessment in epidemiology studies. Predictors of metal(loid) biomarkers included fish and rice consumption (urinary As), fish and canned food (blood Hg), drinking public water (blood Pb), smoking (blood Cd), and iron/folic acid supplement use (urinary Cs, Mo, and Sb). Characterization of metal(loid) biomarker variation over time and between matrices, and identification of important exposure sources, may inform future epidemiology studies and exposure reduction strategies.

Aullón Alcaine, A., Schulz, C., Bundschuh, J.*, et al.* (2020) Hydrogeochemical controls on the mobility of arsenic, fluoride and other geogenic co-contaminants in the shallow aquifers of northeastern La Pampa Province in Argentina. *Science of the Total Environment,* 715: 136671.
Keywords: Arsenic; Fluoride; Shallow groundwater; La Pampa; Loess sediments; Volcanic ash

Abstract:
Elevated Arsenic (As) and Fluoride (F) concentrations in groundwater have been studied in the shallow aquifers of northeastern of La Pampa province, in the Chaco-Pampean plain, Argentina. The source of As and co-contaminants is mainly geogenic, from the weathering of volcanic ash and loess (rhyolitic glass) that erupted from the Andean volcanic range. In this study we have assessed the groundwater quality in two semi-arid areas of La Pampa. We have also identified the spatial distribution of As and co-contaminants in groundwater and determined the major factors controlling the mobilization of As in the shallow aquifers. The groundwater samples were circum-neutral to alkaline (7.4 to 9.2), oxidizing (Eh ~0.24 V) and characterized by high salinity (EC = 456–11,400 μS/cm) and Na+–HCO3– water types in recharge areas. Carbonate concretions ("tosca") were abundant in the upper layers of the shallow aquifer. The concentration of total As (5.6 to 535 μg/L) and F (0.5 to 14.2 mg/L) were heterogeneous and exceeded the recommended WHO Guidelines and the Argentine Standards for drinking water. The predominant As species were arsenate As(V) oxyanions, determined by thermodynamic calculations. Arsenic was positively correlated with bicarbonate (HCO3−), fluoride (F), boron (B) and vanadium (V), but negatively correlated with iron (Fe), aluminium (Al), and manganese (Mn), which were present in low concentrations. The highest amount of As in sediments was from the surface of the dry lake. The mechanisms for As mobilization are associated with multiple factors: geochemical reactions, hydrogeological characteristics of the local aquifer and climatic factors. Desorption of As(V) at high pH, and ion competition for adsorption sites are considered the principal mechanisms for As mobilization in the shallow aquifers. In addition, the long-term consumption of the groundwater could pose a threat for the health of the local community and low cost remediation techniques are required to improve the drinking water quality. ".

Benvenga, S., Elia, G., Ragusa, F.*, et al.* (2020) Endocrine disruptors and thyroid autoimmunity. *Best Practice & Research.Clinical Endocrinology & Metabolism* : 101377.
Keywords: Graves' disease; autoimmune thyroid diseases; autoimmune thyroiditis; endocrine disruptors; myo-inositol; selenium/selenomethionine

Abstract:
Many papers evaluated the effect of the environmental, or occupational endocrine disruptors (ED), on the thyroid gland, that can lead to thyroid autoimmunity. A higher prevalence of autoimmune thyroid diseases (AITD) was observed in people living in polluted areas near to petrochemical plants, and in petrochemical workers, but also in area contaminated with organochlorine pesticides, or with polychlorinated biphenyls, or near

aluminum foundries. The exposure to Hg in chloralkali workers, or in swordfish consumers has been also found to increase AITD prevalence. Vanadium has been shown to increase the inflammatory response of thyrocytes. A beneficial effect of omega-3 fatty acids, and of myo-inositol and selenomethionine have been shown to counteract the appearance of AITD in subjects exposed to environmental or occupational ED. More large studies are needed to investigate the potential roles of ED in the induction of AITD, and of agents or habits that are able to prevent them.

Bourliva, A., Papadopoulou, L., da Silva, E.F.*, et al.* (2020) In vitro assessment of oral and respiratory bioaccesibility of trace elements of environmental concern in Greek fly ashes: Assessing health risk via ingestion and inhalation. *Science of the Total Environment,* 704
Keywords: Cancer risk; Fly ash; Health risk; Human bioaccessibility; Trace element; Barium compounds; Calcium compounds; Chromium; Chromium compounds; Health; Particle size; Risk assessment; Trace elements; Bioaccessibility; Carcinogenic risk; Environmental concerns; Human health problems; Oral bioaccessibility; Particle-size fractions; Health risks; barium; cadmium; cobalt; copper; manganese; nickel; vanadium; zinc; atmospheric pollution; cancer; lignite; respiratory disease; Article; bioaccumulation; electric power plant; gastrointestinal tract; Greece; health hazard; ingestion; inhalation; priority journal; respiratory system; environmental exposure; pollutant; Coal Ash; Environmental Pollutants

Abstract:
Fly ash engender significant environmental and human health problems due to enhanced contents of potentially harmful trace elements (TrElems). This study aims to evaluate human exposure to TrElems via a combined ingestion (i.e., oral bioaccessibility) and inhalation (i.e., respiratory bioaccessibility) pathway. Five fly ash samples were collected from power plants operating in the main lignite basins of Greece, while the ingestible (<250 μm) and inhalable (<10 μm) particle size fractions were utilized. The Unified Bioaccessibility Method (UBM) was utilized to assess the oral bioaccessibility, while the respiratory bioaccessible fractions were extracted using the Artificial Lysosomal Fluid (ALF). All studied FAs exhibited significantly higher contents in Ba, Cr, Ni, V and Zn. Cadmium was presented relative enriched in the finer size fraction (<10 μm), while Ba, Co, Cr, Cu, Mn, Ni and V were depleted. The UBM-extractable concentrations fluctuated greatly among the studied FAs, while notably lower bioaccessible contents were recorded in the gastrointestinal phase. On the other hand, ALF-extractable concentrations were surprisingly higher than the corresponding UBM-extractable ones in the gastric phase. The oral bioaccessibility of the studied TrElems ranged from 12.5 to 100%, while respiratory bioaccessibility presented high values exceeding 45% on average. A significant effect of fly ash type on human bioaccessibility was revealed. Thus, high-Ca FAs exhibited significantly higher bioaccessibility of the studied TrElems via ingestion, while a relatively higher bioaccessibility via inhalation was observed for high-Si FAs. Regarding non-carcinogenic health risk via ingestion and inhalation, Cr and Co exhibited the highest HQing and HQinh values, however there were significantly lower than safe level (HQ < 1). On the contrary, Cr was the dominant contributor to carcinogenic risk with CR values being well above threshold or even tolerable risk levels. © 2019 Elsevier B.V.

Domingo-Relloso, A., Grau-Perez, M., Briongos-Figuero, L.*, et al.* (2019) The association of urine metals and metal mixtures with cardiovascular incidence in an adult population from Spain: the Hortega Follow-Up Study. *International Journal of Epidemiology,* 48(6): 1839-1849.
Keywords: BKMR; cardiovascular incidence; cohort study; population-based; Urine metals

Abstract:
BACKGROUND: The association of low-level exposure to metals and metal mixtures with cardiovascular incidence in the general population has rarely been studied. We flexibly evaluated the association of urinary metals and metal mixtures concentrations with cardiovascular diseases in a representative sample of a general population from Spain. METHODS: Urine antimony (Sb), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), vanadium (V) and zinc (Zn) were measured in 1171 adults without clinical cardiovascular diseases, who participated in the Hortega Study. Cox proportional hazard models were used for evaluating the association between single metals and cardiovascular incidence. We used a Probit extension of Bayesian Kernel Machine Regression (BKMR-P) to handle metal mixtures in a survival setting. RESULTS: In single-metal models, the hazard ratios [confidence intervals (CIs)] of cardiovascular incidence, comparing the 80th to the 20th percentiles of metal distributions, were 1.35 (1.06, 1.72) for Cu, 1.43 (1.07, 1.90) for Zn, 1.51 (1.13, 2.03) for Sb, 1.46 (1.13, 1.88) for Cd, 1.64 (1.05, 2.58) for Cr and 1.31 (1.01, 1.71) for V. BKMR-P analysis was confirmatory of these findings, supporting that Cu, Zn, Sb, Cd, Cr and V are related to cardiovascular incidence in the presence of the other metals. Cd and Sb showed the highest posterior inclusion probabilities. CONCLUSIONS: Urine Cu, Zn, Sb, Cd, Cr and V were independently associated with increased cardiovascular risk at levels relevant for the general population of Spain. Urine metals in the mixture were also jointly associated with cardiovascular incidence, with Cd and Sb being the most important components of the mixture. © The Author(s) 2019; all rights reserved. Published by Oxford University Press on behalf of the International Epidemiological Association.

Garvin, M.C., Schijf, J., Kaufman, S.R.*, et al.* (2020) A survey of trace metal burdens in increment cores from eastern cottonwood (Populus deltoides) across a childhood cancer cluster, Sandusky County, OH, USA. *Chemosphere,* 238.
Available at:
https://www.sciencedirect.com/science/article/pii/S0045653519317527/pdfft?md5=1d44d75fbf11fd7368a875bdc5562489&pid=1-s2.0-S0045653519317527-main.pdf
Keywords: Cancer cluster; Dendrochemistry; Eastern cottonwood; Scan statistic; Trace metals; Cotton; Diseases; Forestry; Groundwater; Metals; Surveys; Trace analysis; Scan statistics; Trace metal; Trace elements; arsenic; cadmium; chromium; cobalt; lead; nickel; vanadium; trace element; aerosol; bioaccumulation; cancer; concentration (composition); core analysis; dendroecology; microwave radiation; spatial analysis; statistical data; wood; annual ring; Article; childhood cancer; concentration (parameter); inductively coupled plasma mass spectrometry; method detection limit; Ohio; Populus; Populus deltoides; chemistry; child; environmental monitoring; human; neoplasm; questionnaire; soil; tree; Sandusky County; United States; Humans; Neoplasms; Surveys and Questionnaires; Trees

Abstract:
A dendrochemical study of cottonwood trees (Populus deltoides) was conducted across a childhood cancer cluster in eastern Sandusky County (Ohio, USA). The justification for this study was that no satisfactory explanation has yet been put forward, despite extensive local surveys of aerosols, groundwater, and soil. Concentrations of eight trace metals were measured by ICP-MS in microwave-digested 5-year sections of increment cores, collected during 2012 and 2013. To determine whether the onset of the first cancer cases could be connected to an emergence of any of these contaminants, cores spanning the period 1970–2009 were taken from 51 trees of similar age, inside the cluster and in a control area to the west. The abundance of metals in cottonwood tree annual rings served as a proxy for their long-term, low-level accumulation from the same sources whereby exposure of the children may have occurred. A spatial analysis of cumulative metal burdens (lifetime accumulation in

the tree) was performed to search for significant 'hotspots', employing a scan statistic with a mask of variable radius and center. For Cd, Cr, and Ni, circular hotspots were found that nearly coincide with the cancer cluster and are similar in size. No hotspots were found for Co, Cu, and Pb, while As and V were largely below method detection limits. Whereas our results do not implicate exposure to metals as a causative factor, we conclude that, after 1970, cottonwood trees have accumulated more Cd, Cr, and Ni, inside the childhood cancer cluster than elsewhere in Sandusky County. © 2019 The Authors.

Guo, X., Zhang, N., Hu, X.*, et al.* (2020) Characteristics and potential inhalation exposure risks of PM2.5–bound environmental persistent free radicals in Nanjing, a mega–city in China. *Atmospheric Environment,* 224.**
Keywords: Half–life; Inhalation exposure; Oxidative stress; Reactive oxygen species; Temporal variation; Biological organs; Free radicals; Health risks; Organic pollutants; Oxygen; Transition metals; Air pollutants; Healthy persons; Limited information; Potential health risks; Toxic elements; Weak correlation; cadmium; carbon monoxide; chromium; copper; dissolved oxygen; free radical; iron; manganese; nickel; nitrous oxide; ozone; reactive oxygen metabolite; sulfur oxide; vanadium; zinc; megacity; organic pollutant; particle size; particulate matter; pollution exposure; public health; air pollutant; Article; China; city; concentration (parameter); controlled study; electron transport; environmental exposure; half life time; health hazard; human; priority journal; room temperature; simulation; Nanjing [Jiangsu]

Abstract:
PM2.5–bound toxic elements and organic pollutants have been extensively investigated, while limited information is available for environmental persistent free radicals (EPFRs) associated with PM2.5, which may lead to oxidative stress in the human lung when exposed to PM2.5. In this study, the levels and types of PM2.5–bound EPFRs present in Nanjing, a mega–city in China, were analyzed. PM2.5–bound EPFRs were found to mainly be a mixture of carbon– and oxygen–centered radicals. The concentration of PM2.5–bound EPFRs ranged from 2.78 × 1012 to 1.72 × 1013 spins m−3, with an average value of 7.61 × 1012 spins m−3. The half–life of the PM2.5–bound EPFRs was calculated to be an average of 83.5 days when stored at room temperature, with only weak correlations observed between EPFRs and conventional air pollutants (NO2, O3, CO and PM2.5)/PM2.5–bound transition metals (Cu, Zn, Cr, Mn, V, Cd, and Ni) and significant correlations between EPFRs and SO2/PM2.5–bound Fe. PM2.5–bound EPFRs can induce the formation of reactive oxygen species (ROS) in both water and a H2O2 solution, which are used to simulate lung solution of a healthy person and patient, respectively. Therefore, PM2.5–bound EPFRs can lead to potential oxidative stress in humans. Overall, PM2.5–bound EPFRs show an obvious temporal variation and can pose potential health risks to humans via the induction of ROS in the lung solution. © 2020 Elsevier Ltd.

Herrero, M., Rovira, J., Esplugas, R.*, et al.* (2020) Human exposure to trace elements, aromatic amines and formaldehyde in swimsuits: Assessment of the health risks. *Environmental Research,* 181.**
Keywords: Aromatic amines; Formaldehyde; Human exposure; Risk assessment; Swimsuits; Trace elements; aluminum; aromatic amine; arsenic; barium; beryllium; bismuth; boron; cadmium; chromium; chromium derivative; cobalt; copper; iron; lead; magnesium; manganese; mercury; molybdenum; nickel; polyamide; polybutylene terephthalate; polyester; silver; strontium; thallium; titanium; trace element; vanadium; zinc ion; amino acid; aromatic hydrocarbon; health care; pollution exposure; toxicity test; adolescent; adult; cancer risk; child; color; female; health hazard; human; hydrophobicity; limit of detection;

male; polymerization; preschool child; priority journal; scanning electron microscopy; summer

Abstract:
Nowadays, most of the swimsuits are mainly made of artificial fibres, which have interesting properties such as water repellence and fast drying. Swimsuits contain a wide range of additives, which can mean a hazard for the environment and/or human health. In this study, the concentrations of formaldehyde (free and water soluble), 24 aromatic amines, and 28 trace elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sr, Sn, Tl, Ti, V and Zn) were analysed in 39 swimsuits covering a wide range of materials, colours and brands. Dermal exposure and health risks were assessed for adults (men and women) aged > 18 years old, babies between 2 and < 3 years old, children (boys and girls) between 3 and < 6 years old and 6 and < 11 years old, and teenagers (boys and girls) between 11 and < 16 years old, wearing swimsuits for 4 h or 8 h. Formaldehyde and aromatic amines were below their respective detection limits in all samples (<16 and < 1.5 mg/kg, respectively). Regarding trace elements, Ti showed the highest mean levels (1844 mg/kg), being significantly higher in polyamide (3759 mg/kg) than in polyester (24.1 mg/kg) swimsuits. These high Ti levels were confirmed by environmental scanning electron microscope in a single sample made of polyamide. Increased concentrations of Cr were also observed, but only in polyamide black fabrics, with values ranging from 624 to 932 mg/kg. Non-cancer risks (hazard quotients) derived from the exposure to trace elements were in a safe zone for all analysed trace elements. Furthermore, the carcinogenic risks were evaluated for As, Cr and Pb, exhibiting values below the 10−5 threshold, with the exception of Cr in babies and children-girls. For Ti, health risks could not be calculated due to the lack of information on toxicological data. However, because Ti was the element with the highest concentrations in swimsuits, and taking into account the potential toxicity of TiO2 nanoparticles, further research is needed to assess the migration of this element from fibres to skin. © 2019 Elsevier Inc.

Hussain Shah, S.Z., Rashid, A., Naveed, A.K.*, et al.* (2019) Genotoxic And Cytotoxic Effects Of Oral Vanadyl Sulphate. *Journal of Ayub Medical College, Abbottabad : JAMC,* 31(4): 522-526. Keywords: Hepatotoxicity; Oxidative Stress; DNA Damage; Comet Assay; Vanadyl sulphate

Abstract:
BACKGROUND: Vanadyl sulphate is available as herbal medicine against diabetes mellitus and body building supplement, over the counter worldwide. The available data on its safety is controversial and inadequate. The objective of this study was to analyse its safety in usual therapeutic dose range. METHODS: It was an experimental study carried out at the Department of Biochemistry & Molecular Biology, Army Medical College, National University of Medical Sciences (NUMS), Rawalpindi, Pakistan, from Jun 2014 to Oct 2018. The study was carried out on 105 Sprague Dawley rats for duration of 24 weeks. The animals were randomly distributed in three groups of 35 each. The group I rats were marked as control while rats of group II & III were administered vanadyl sulphate 0.06mg/day and 0.3mg/day respectively. Alanine amino transferase (ALT) and Malondialdehyde (MDA) were measured in serum while comet assay was performed on WBCs. RESULTS: The plasma levels of ALT and MDA were significantly raised in group II and III subjects. Single cell gel electrophoresis (SCGE) / comet assay showed minimal "tail moment" in control group and increased tail moment in group II and III in a dose dependent manner which indicates dsDNA breaks. CONCLUSIONS: It was observed that vanadyl sulphate causes hepatocellular toxicity,

oxidative stress and damage to the DNA in usual therapeutic/ supplemental doses. Due to hazardous effects, its use in humans as alternate medicine may be reviewed.

Kim, S., Gates, B.L., Leonard, B.C.*, et al.* (2020) Engineered metal oxide nanomaterials inhibit corneal epithelial wound healing in vitro and in vivo. *Nanoimpact,* 17: 100198.
Available at:
https://www.sciencedirect.com/science/article/pii/S2452074819301077/pdfft?md5=67eb1a0002df9eff3eb8aa9145b77f6d&pid=1-s2.0-S2452074819301077-main.pdf
Keywords: Metal oxide engineered nanomaterials; Nanometals; Corneal epithelium; Corneal wound healing; Nanotoxicity

Abstract:
Ocular exposure to metal oxide engineered nanomaterials (ENMs) is common as exemplified by zinc(II) oxide (ZnO), a major constituent of sunscreens and cosmetics. The ocular surface that includes the transparent cornea and its protective tear film are common sites of exposure for metal ENMs. Despite the frequency of exposure of the ocular surface, there is a knowledge gap regarding the effects of metal oxide ENMs on the cornea in health and disease. Therefore, we studied the effects of metal oxide ENMs on the cornea in the presence or absence of injury. Cell viability of immortalized human corneal epithelial (hTCEpi) cells was assessed following treatment with 11 metal oxide ENMs with a concentration ranging from 0.5 to 250 μg/ml for 24 h. An epithelial wound healing assay with a monolayer of hTCEpi cells was then performed using 11 metal oxide ENMs at select concentrations based on data from the viability assays. Subsequently, based on the in vitro results, in vivo testing of precorneal tear film (PTF) quantity and stability as well as a corneal epithelial wound healing were tested in the presence or absence ZnO or vanadium(V) oxide (V2O5) at a concentration of 50 μg/ml. We found that WO3, ZnO, V2O5 and CuO ENMs significantly reduced hTCEpi cell viability in comparison to vehicle control or the other metal oxide ENMs tested. Furthermore, ZnO and V2O5 ENMs also significantly decreased hTCEpi cell migration. Although ZnO and V2O5 did not alter PTF parameters of rabbits in vivo, corneal epithelial wound healing was significantly delayed by topical ZnO while V2O5 did not alter wound healing. Finally, hyperspectral images confirmed penetration of ZnO and V2O5 through all corneal layers and into the iris stroma. Considering the marked epithelial toxicity and corneal penetration of ZnO, further investigations on the impact of this ENM on the eye are warranted. ".

Kolakkandi, V., Sharma, B., Rana, A.*, et al.* (2020) Spatially resolved distribution, sources and health risks of heavy metals in size-fractionated road dust from 57 sites across megacity Kolkata, India. *Science of the Total Environment,* 705.
Keywords: Contamination indices; Health risk assessment; Receptor modeling; Size fraction; Trace metals; Construction industry; Contamination; Dust; Factorization; Health; Health risks; Heavy metals; Housing; Industrial emissions; Land use; Roads and streets; Trace elements; Construction activities; Contamination index; Index of Geo accumulations; Metallurgical process; Positive Matrix Factorization; Receptor model; Trace metal; Risk assessment; aluminum; calcium; chromium; copper; heavy metal; iron; lead; magnesium; manganese; nickel; vanadium; zinc; health risk; megacity; particle size; pollutant source; pollution exposure; spatial distribution; adult; air quality; Article; cancer risk; carcinogenesis; child; comparative study; controlled study; environmental impact; exhaust gas; exposure; hazard assessment; health hazard; human; India; industrial area; ingestion; inhalation; metallurgy; pollution; priority journal; quantitative analysis; road dust; spatial analysis; Kolkata; West Bengal

Abstract:
This work reports the first assessment of contamination levels, source contributions and health risks associated with heavy metals (HMs) in road dust from Kolkata, the second-most polluted metropolis in India. To this end, samples collected from 57 locations across 6 land-use categories: residential, roadside, traffic, railway, port and industrial areas in the city during 2018 were analyzed for 11 major and trace metals (Ca, Mg, Fe, Al, Mn, Ni, V, Cu, Zn, Cr, Pb) in three size fractions: 4) in west-central and northern parts (the older sections) of the city represented by industrial, port, and traffic-congested residential areas. Using positive matrix factorization (PMF), the following sources were apportioned for the three size fractions: crustal dust (48–66%), construction activities (18–20%), vehicular abrasion (7–21%), industrial emissions (5–8%), a Cr-dominated mixed source (6%) and an unassigned source (7%). Finally, health risk assessment in the form of cumulative hazard index (HI) and incremental lifetime cancer risk (ILCR) found that children (mean HIchildren: 1.29 and ILCRchildren: 2E-04) are comparatively more vulnerable than adults (mean HIadults: 0.22 and ILCRadults: 8E-05) to HM exposure, with the ingestion exposure pathway dominating over dermal contact and inhalation. © 2019 Elsevier B.V.

Kot, K., Kosik-Bogacka, D., Ziętek, P.*, et al.* (2020) Impact of varied factors on iron, nickel, molybdenum and vanadium concentrations in the knee joint. *International Journal of Environmental Research and Public Health,* 17(3).
Keywords: Anterior cruciate ligament; Cartilage; Infrapatellar fat pad; Meniscus; Spongy bone; Trace elements; iron; molybdenum; nickel; vanadium; bone; concentration (composition); diet; medicine; trace element; adult; aged; alcohol consumption; Article; atomic absorption spectrometry; clinical article; concentration (parameter); controlled study; dietary supplement; environmental factor; female; human; knee arthroscopy; knee meniscus; male; muscle toxicity; osteoporosis; Poland; rheumatoid arthritis; Poland [Central Europe]

Abstract:
The aim of this study was to determine the concentrations of iron, nickel, molybdenum, and vanadium in the knee joint. We also examined the relationships between the concentrations of these metals in the knee joint and the influence of varied factors on the concentration of Fe, Ni, Mo, and V. The study of these trace elements is important, because these elements are used alone and in combination in diet supplements, and they are components of biomaterials implanted in medicine. The study materials, consisting of the spongy bone, cartilage, meniscus, anterior cruciate ligament (ACL), and infrapatellar fat pad, were obtained from 34 women and 12 men from northwestern Poland. The concentrations of Ni, Fe, Mo, and V were determined using spectrophotometric atomic absorption in inductively coupled argon plasma (ICP-AES). We found significantly higher Mo concentrations in the ACL of women than men. There was a significant difference in the Mo concentration in the spongy bone between patients from cities with fewer than 100,000 inhabitants and patients from cities with more than 100,000 residents. Iron concentrations in the spongy bone were higher in non-smoking patients and those who did not consume alcohol. Vanadium concentrations were higher in the infrapatellar fat pads in abstainers. In patients who had not undergone arthroscopy surgery, V concentration was lower in cartilage. The concentrations of V in the cartilage and infrapatellar fat pad were higher in osteoporotic patients than in non-osteoporotic patients. There were significant differences in Fe concentrations in the meniscus, with the lowest in osteoporotic patients. We noted lower Mo concentrations in the spongy bone of patients with rheumatoid arthritis. Furthermore, we noted some new interactions among metals in the studied structures of the knee joint. The results reported in this study show the influence of gender, place of residence, smoking,

consumption of alcohol, arthroscopy surgery, osteoporosis, and rheumatoid arthritis on the Fe, Ni, Mo, and V concentrations in the studied structures of the knee joint. © 2020 by the authors. Licensee MDPI, Basel, Switzerland.

Kumar, S., Sharma, A. & Kshetrimayum, C. (2019) Environmental & occupational exposure & female reproductive dysfunction. *Indian Journal of Medical Research,* 150(6): 532-545.
Available at: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7038808/
Keywords: Environmental; female; fertility; lifestyle factors; metals; miscarriage; occupational; oxidative stress; pregnancy; reproductive impairment; arsenic; benzene; cadmium; carbon disulfide; chlorphenotane; chromium; cigarette smoke; drug metabolite; lead; mercury; mono (3 carboxylpropyl) phthalate; pesticide; toluene; toxic gas; unclassified drug; vanadium; zinc; selenium; trace element; abdominal pain; air pollutant; attention deficit disorder; blood level; child health; clinical outcome; disease association; dysmenorrhea; environmental exposure; female sterility; gestational age; gynecologic disease; hormonal impairment; human; infertility; ionizing radiation; job stress; lead blood level; maternal urine; menstrual cycle; molecular alteration; nerve cell differentiation; occupational exposure; paternal exposure; pregnancy outcome; prevalence; progeny; Review; risk factor; smoking; spontaneous abortion; steroidogenesis; stillbirth; air pollution; Article; awareness; birth weight; DNA damage; DNA methylation; drug manufacture; fetus development; incidence; inflammation; menarche; prematurity; reproductive health; tobacco

Abstract:
All individuals are exposed to certain chemical, physical, biological, environmental as well as occupational factors. The data pertaining to role of these factors on female reproduction are scanty as compared to male. The available data suggest the adverse effects of certain toxicants, viz., metals such as lead, cadmium and mercury, pesticides such as bis(4-chlorophenyl)-1,1,1-trichloroethane and organic solvent such as benzene, toluene and ionizing radiation on the female reproductive system affecting directly the organ system or impacting in directly through hormonal impairments, molecular alterations, oxidative stress and DNA methylation impairing fertility as well as pregnancy and its outcomes. Thus, there is a need for awareness and prevention programme about the adverse effects of these factors and deterioration of female reproductive health, pregnancy outcome and offspring development as some of these chemicals might affect the developing foetus at very low doses by endocrine disruptive mechanism. © 2020 Indian Journal of Medical Research, published by Wolters Kluwer - Medknow.

Li, W., Xiao, L., Zhou, Y.*, et al.* (2020) Plasma CC16 mediates the associations between urinary metals and fractional exhaled nitric oxide: A cross-sectional study. *Environmental Pollution,* 258.
Keywords: Club cell secretory protein; FeNO; Mediation analysis; Urinary metals; Antimony; Biomarkers; Mass spectrometry; Nickel; Nitric oxide; Pathology; Proteins; Vanadium; Airway inflammation; Cross-sectional study; Enzyme linked immunosorbent assay; Exhaled nitric oxides; Low concentrations; Iron compounds

Abstract:
Capsule: We found positive associations between urinary metals and FeNO, which were stronger among participants with low plasma CC16 concentration. The associations were mediated by plasma CC16. © 2019 Elsevier Ltd Exposure to environmental metals has been reported to be associated with airway inflammation. Fractional exhaled nitric oxide (FeNO) is an important inflammatory biomarker of the airway. However, the associations between

metal exposures and FeNO change and the underlying mechanisms remain unclear. To investigate the associations between urinary metals and FeNO, and the potential role of Club cell secretory protein (CC16), a lung epithelial biomarker, in these associations. We conducted a cross-sectional study from the Wuhan-Zhuhai cohort and measured eight urinary metals, plasma CC16 and FeNO among 3067 subjects by using inductively coupled plasma-mass spectrometry, enzyme-linked immunosorbent assay kit and Nano Coulomb Nitric Oxide Analyzer, respectively. Mixed linear models were used to quantify dose-relationships between urinary metals and FeNO, as well as urinary metals and plasma CC16. The potential role of plasma CC16 in the associations between urinary metals and FeNO was estimated using mediationanalyses. After adjusting for covariates, one percent increase in urinary vanadium, nickel or antimony was associated with a respective 6.60% (95% CI: 3.52%, 9.68%), 2.18% (0.45%, 3.91%), 4.87% (1.47%, 8.27%) increase in FeNO level. The adverse associations were much stronger among participants with low concentration of plasma CC16 than those with high CC16 level. Moreover, plasma CC16 decreased monotonically with increasing quartiles of urinary vanadium, nickel or antimony. Mediation analyses found that CC16 mediated the associations between urinary metals and FeNO by 5.64%, 39.06% and 25.18% for vanadium, nickel and antimony respectively. CC16 plays an important role in airway inflammation. General population with lower plasma CC16 concentration is more likely to suffer from airway inflammation when exposed to high levels of vanadium, nickel or antimony.

Li, W., Xiao, L., Zhou, Y.*, et al.* (2019) Plasma CC16 mediates the associations between urinary metals and fractional exhaled nitric oxide: A cross-sectional study. *Environmental Pollution (Barking, Essex : 1987),* : 113713.
Keywords: Club cell secretory protein; FeNO; Mediation analysis; Urinary metals

Abstract:
Exposure to environmental metals has been reported to be associated with airway inflammation. Fractional exhaled nitric oxide (FeNO) is an important inflammatory biomarker of the airway. However, the associations between metal exposures and FeNO change and the underlying mechanisms remain unclear. To investigate the associations between urinary metals and FeNO, and the potential role of Club cell secretory protein (CC16), a lung epithelial biomarker, in these associations. We conducted a cross-sectional study from the Wuhan-Zhuhai cohort and measured eight urinary metals, plasma CC16 and FeNO among 3067 subjects by using inductively coupled plasma-mass spectrometry, enzyme-linked immunosorbent assay kit and Nano Coulomb Nitric Oxide Analyzer, respectively. Mixed linear models were used to quantify dose-relationships between urinary metals and FeNO, as well as urinary metals and plasma CC16. The potential role of plasma CC16 in the associations between urinary metals and FeNO was estimated using mediationanalyses. After adjusting for covariates, one percent increase in urinary vanadium, nickel or antimony was associated with a respective 6.60% (95% CI: 3.52%, 9.68%), 2.18% (0.45%, 3.91%), 4.87% (1.47%, 8.27%) increase in FeNO level. The adverse associations were much stronger among participants with low concentration of plasma CC16 than those with high CC16 level. Moreover, plasma CC16 decreased monotonically with increasing quartiles of urinary vanadium, nickel or antimony. Mediation analyses found that CC16 mediated the associations between urinary metals and FeNO by 5.64%, 39.06% and 25.18% for vanadium, nickel and antimony respectively. CC16 plays an important role in airway inflammation. General population with lower plasma CC16 concentration is more likely to suffer from airway inflammation when exposed to high levels of vanadium, nickel or antimony.

Liu, Y., Yuan, Y., Xiao, Y.*, et al.* (2020) Associations of plasma metal concentrations with the decline in kidney function: A longitudinal study of Chinese adults. *Ecotoxicology and Environmental Safety,* 189: 110006.
Keywords: Kidney function; Metals; Principal component analysis; Prospective study

Abstract:
Metals are widespread pollutants in the environment which have been reported to be associated with kidney dysfunction in many existing epidemiological studies. However, most of the studies are cross-sectional design and mainly focus on several toxic metals including arsenic, lead and cadmium. Therefore, we conducted this prospective study within the Dongfeng-Tongji cohort to evaluate the associations of plasma multiple metals with the decline in kidney function among Chinese middle-aged and elderly. In total, 1434 participants free of chronic diseases at baseline were included in analysis. We measured baseline plasma concentrations of 23 metals and calculated estimated glomerular filtration rate (eGFR) using the Chronic Kidney Disease Epidemiology Collaboration (CKD-EPI) equation based on serum creatinine, age, sex and ethnicity. Bonferroni correction was used for multiple testing to reduce the probability of a type I error. Principal component analysis was conducted to evaluate the combined effect of multiple metal co-exposure. Most of the plasma metal concentrations were within the literature reported reference values, whereas the concentration of lead and nickel exceeded the guideline value. We found that plasma concentrations of aluminum, arsenic, barium, lead, molybdenum, rubidium, strontium, vanadium and zinc were significantly associated with the decline in kidney function measured by annual eGFR decline, rapid renal function decline (defined as an annual decline in eGFR >/= 5 mL/min/1.73 m(2)) or incident eGFR < 60 mL/min/1.73 m(2), with the adjusted beta coefficients (95% CI) for annual eGFR decline 0.50 (0.30, 0.69), 0.98 (0.74, 1.23), 0.56 (0.32, 0.79), 0.21 (0.03, 0.39), 0.35 (0.16, 0.54), 0.94 (0.71, 1.17), 0.37 (0.15, 0.60), 0.78 (0.54, 1.02), and 0.74 (0.57, 0.91), respectively. The metals exposures were linked with increased risks of impaired kidney function. Associations of principal components representing these metals with the decline in kidney function were significant and suggest a possible additional health risk by co-exposure. Participants engaged in manufacturing had higher plasma levels of several metals compared with those who had been involved in management- or administration-related work. Our findings suggest that exposure to multiple metals contribute to the decline in kidney function among the middle-aged and elderly. Co-exposure to multiple metals may have synergetic effect on the kidney function. Further studies are warranted to confirm our findings and clarify the potential mechanisms.

Melendez-Garcia, N., Garcia-Ibarra, F., Bizarro-Nevares, P.*, et al.* (2020) Changes in Ovarian and Uterine Morphology and Estrous Cycle in CD-1 Mice After Vanadium Inhalation. *International Journal of Toxicology,* 39(1): 20-29.
Keywords: 17beta-estradiol; ERalpha; PM; ovary; particulate matter; progesterone; uterus; vanadium

Abstract:
Vanadium is a metal present in particulate matter and its reprotoxic effects have been demonstrated in males and pregnant females in animal models. However, the effects of this metal on the reproductive organs of nonpregnant females have not been sufficiently studied. In a vanadium inhalation model in nonpregnant female mice, we found anestrous and estrous cycle irregularity, as well as low serum concentrations of 17beta-estradiol and progesterone. A decrease in the diameter of secondary and preovulatory follicles, as well as a thickening of the myometrium and endometrial stroma, was observed in the vanadium-treated mice. There was no difference against the control group with respect to the

presence of the estrogen receptor alpha in the uterus of the animals during the estrous stage. Our results indicate that when vanadium is administered by inhalation, effects are observed on the female reproductive organs and the production of female sex hormones.

O'Brien, K.M., White, A.J., Jackson, B.P.*, et al.* (2019) Toenail-Based Metal Concentrations and Young-Onset Breast Cancer. *American Journal of Epidemiology,* 188(4): 646-655.
Keywords: Adult; Age of Onset; Breast Neoplasms/chemically induced/epidemiology; Cadmium/analysis/toxicity; Environmental Exposure/adverse effects/analysis; Female; Humans; Logistic Models; Metals/analysis/toxicity; Middle Aged; Nails/chemistry; Odds Ratio; Siblings; Toes; breast cancer; cadmium; metals; toenails; young-onset breast cancer

Abstract:
Several metals have carcinogenic properties, but their associations with breast cancer are not established. We studied cadmium, a metalloestrogen, and 9 other metals-arsenic, cobalt, chromium, copper, mercury, molybdenum, lead, tin, and vanadium--in relation to young-onset breast cancer (diagnosis age <50 years), which tends to be more aggressive than and have a different risk profile from later-onset disease. Recent metal exposure was measured by assessing element concentrations, via inductively coupled plasma mass spectrometry, in toenail clippings of 1,217 disease-discordant sister pairs in the US-based Sister (2003-2009) and Two Sister (2008-2010) studies. Conditional logistic regression was used to calculate odds ratios and 95% confidence intervals. After correcting for differential calendar time of sample collection, no statistically significant associations were observed between any metals and breast cancer. Vanadium had the largest odds ratio (for fourth vs. first quartile, odds ratio = 1.36, 95% confidence interval: 0.84, 2.21; P for trend = 0.17). Cadmium was associated with a small increase in risk, with no evidence of a dose-response relationship (for fourth vs. first quartile, odds ratio = 1.15, 95% confidence interval: 0.82, 1.60; P for trend = 0.67). Positive associations between urinary cadmium concentrations and breast cancer have been reported in case-control studies, but we observed no such association between young-onset breast cancer and toenail concentrations of any assessed metals.

Parker, G.J., Ong, C.H., Manges, R.B.*, et al.* (2019) A novel method of collecting and chemically characterizing milligram quantities of indoor airborne particulate matter. *Aerosol and Air Quality Research,* 19(11): 2387-2395.
Available at:
https://pdfs.semanticscholar.org/ec49/b0062b624fd291b9d5fa3bd714fd74be046d.pdf
Keywords: Electrostatic precipitation; Indoor air; Metals; Particulate matter

Abstract:
Because people spend the majority of the day indoors, it is important to evaluate indoor air, especially airborne particulate matter (PM), for its potential health effects. However, collecting milligram-sized samples of indoor PM, which are necessary for detailed chemical and biological assays, remains challenging because of the noise, power requirements, and size of traditional PM samplers. Therefore, we developed a novel method of collection using an electrostatic precipitator (ESP). Laboratory experiments were conducted to characterize the ESP collection efficiency (41–65%) and PM recovery (50–95%) for three aerosol types. After characterization, the ESPs were deployed in 21 homes in eastern Iowa for 30 days, during which they collected 6–87 mg of indoor PM. The samples were acid digested and subsequently analyzed by inductively coupled plasma mass spectrometry for their magnesium, aluminum, vanadium, manganese, iron, nickel, copper, zinc, arsenic, and lead content. Crustal metals (magnesium, iron, and aluminum), ranging from 3,000 to 25,000 ng

mg–1 in concentration, contributed the largest mass fractions of the PM. The relative abundances of the metals were similar between homes, although the PM mass fractions were highly variable. This ESP sampling method can be applied in future studies to collect milligram-sized quantities of indoor PM, enabling a detailed analysis of its composition and potential health effects. © Taiwan Association for Aerosol Research.

Pedro, E.M., da Rosa Franchi Santos, L.F., Scavuzzi, B.M.*, et al.* (2019) Trace Elements Associated with Systemic Lupus Erythematosus and Insulin Resistance. *Biological Trace Element Research,* 191(1): 34-44.
Keywords: Adolescent; Adult; Aged; Cross-Sectional Studies; Female; Humans; Insulin Resistance; Lupus Erythematosus, Systemic/blood; Male; Middle Aged; Trace Elements/blood; Glucose homeostasis; Heavy metals; SLE disease activity index (SLEDAI); Trace elements

Abstract:
Systemic lupus erythematosus (SLE) is a chronic inflammatory autoimmune disease of multifactorial origin. Studies have shown that trace elements such as zinc and copper may help maintain optimum function of the immune system and metabolism, while toxic metals such as lead may increase systemic autoimmunity. The current study aimed to assess the relationship between serum concentration of lithium (Li), vanadium (V), copper (Cu), zinc (Zn), molybdenum (Mo), cadmium (Cd), and lead (Pb) and SLE diagnosis, disease activity measured by SLE disease activity index (SLEDAI) and insulin resistance (IR). This case-control, cross-sectional study included 225 patients, 120 healthy controls, and 105 SLE patients. Serum concentration of Li, V, Cu, Zn, Mo, Cd, and Pb was measured. Serum concentrations of V ($p < 0.001$), Zn ($p < 0.001$), and Pb ($p < 0.001$) were lower and Mo ($p < 0.001$) and Li ($p < 0.001$) were higher in patients with SLE compared to healthy controls. SLE diagnosis was associated with higher serum Li ($p < 0.001$) concentration and lower V ($p < 0.001$), Zn ($p = 0.003$), and Pb ($p = 0.020$). Toxic metals and trace elements were not associated with disease activity. Levels of Cd were higher in patients with IR ($p = 0.042$). There was no significant association between IR and the other metals. The results indicate that SLE patients have different profiles of trace elements and toxic metals compared to healthy controls. While some toxic metals and trace elements were found to be associated with SLE diagnosis, they had no effect on disease activity and IR.

Qiao, J., Zhu, Y., Jia, X.*, et al.* (2020) Distributions of arsenic and other heavy metals, and health risk assessments for groundwater in the Guanzhong Plain region of China. *Environmental Research,* 181.
Keywords: Groundwater; Health risk assessment; Heavy metal; aluminum; arsenic; cadmium; chromium; cobalt; copper; ground water; iron; lead; manganese; molybdenum; nickel; vanadium; zinc; concentration (composition); health risk; risk assessment; water quality; China; health hazard; human; monsoon climate; precipitation; priority journal; statistics; water pollution; water sampling; Guanzhong Plain; Shaanxi

Abstract:
We assessed the quality of groundwater in the Guanzhong Plain region of China, where we evaluated the levels of As and 12 other heavy metals. © 2019 Elsevier Inc. The aim of this study was to evaluate the quality of shallow groundwater and deep groundwater in the Guanzhong Plain region of China, as well as the related health risk to humans. In total, 130 groundwater samples were collected comprising 116 from shallow groundwater (dug wells) and 14 from deep groundwater (drilled wells). The water samples were analyzed to determine the levels of As and 12 other heavy metals (Al, Cd, Mn, Cr, V, Fe, Ni, Cu, Zn, Co,

Pb, and Mo). The results showed that the concentrations of As and other heavy metals in the deep groundwater samples were lower than the safe limits, but the Cr concentrations in some shallow groundwater samples exceeded the safe limits. The heavy metal pollution index and heavy metal evaluation index both showed that As and other heavy metals were pollutants at low levels in all of the shallow and deep groundwater sample. Health risk assessments showed that the deep groundwater samples had no associated non-carcinogenic health risks, whereas the shallow groundwater samples had non-carcinogenic health risks due to contamination with Cr and As. Some shallow groundwater samples had associated carcinogenic health risks due to contamination with Cr and As, whereas the deep groundwater samples only had carcinogenic health risks because of contamination with Cr. These results suggest that local residents and government departments should be made aware of Cr and As pollution in shallow groundwater.

Rafiee, A., Delgado-Saborit, J.M., Sly, P.D.*, et al.* (2020) Environmental chronic exposure to metals and effects on attention and executive function in the general population. *Science of the Total Environment,* 705.

Keywords: Biomonitoring; Cognitive performance; Exposure assessment; Heavy metals; TMT test; Atomic emission spectroscopy; Dental alloys; Dental amalgams; Efficiency; Inductively coupled plasma; Water pipelines; Brain dysfunctions; Cognitive efficiency; Executive function; Inductively coupled plasma atomic emission spectroscopy; Mean concentrations; Testing; aluminum; antimony; arsenic; barium; beryllium; boron; cadmium; chromium; cobalt; copper; dental amalgam; iron; lead; lithium; manganese; mercury; metal; nickel; tin; vanadium; zinc; age; cognition; gender; health impact; heavy metal; pollution exposure; risk assessment; smoking; adolescent; adult; aged; Article; attention; cigarette smoking; concentration (parameter); controlled study; cross-sectional study; demography; environmental exposure; female; hair; health status; human; inductively coupled plasma atomic emission spectrometry; Iran; lifestyle; long term exposure; male; neurotoxicity; priority journal; social status; traffic; trail making test; Tehran [Iran]; Tehran [Tehran (PRV)]

Abstract:
Heavy metals are neurotoxic, associated with brain dysfunction, and have been linked with cognitive decline in adults. This study was aimed to characterize chronic exposure to metals (Cd, Be, Co, Hg, Sn, V, Al, Ba, Cr, Cu, Fe, Li, Mn, Ni, Pb, and Zn) and metalloids (As, B, Sb) and assess its impact on cognitive performance of Tehran's residents, capital of Iran. Scalp hair samples gathered from 200 volunteered participants (110 men and 90 women), aged 14–70 years and quantified by inductively coupled plasma atomic emission spectroscopy (ICP-OES). Attention and executive function, two measures of cognitive performance, were characterized using the trail making test (TMT) part A and B, respectively. Mental flexibility was characterized as the Delta TMT B-A scores and cognitive efficiency or dissimulation as the ration between TMT B and A scores. A comprehensive questionnaire was used to gather information on demographic and socioeconomic as well as lifestyle and health status. The highest and lowest mean concentrations were observed for B (325 μg/g) and As (0.29 μg/g), respectively. Results indicated that chronic metal exposure measured in hair changed significantly based on gender and age ($p < 0.05$). The levels of Cr, Fe, Ni, Si, Hg, Pb and B were significantly higher in males' hair, whereas those of Ag and Ba were greater in females' hair ($p < 0.05$). The results of the cognitive TMT test were significantly different between gender and age groups ($p < 0.05$). Moreover, results revealed that As, Hg, Mn, and Pb levels in hair were significantly associated with poorer participants' performance scores in the TMT test ($p < 0.05$). Age, gender, cigarette smoking, water-pipe smoking, traffic density in the area of residence, and dental amalgam filling were significant factors affecting the TMT test

scores. The results suggest that chronic exposure to metals has detrimental effects on attention, executive function, mental flexibility and cognitive efficiency. © 2019 Elsevier B.V.

Ramírez, O., Sánchez de la Campa, A.M., Sánchez-Rodas, D.*, et al.* (2020) Hazardous trace elements in thoracic fraction of airborne particulate matter: Assessment of temporal variations, sources, and health risks in a megacity. *Science of the Total Environment,* 710.**
Keywords: Antimony speciation; Cancer risk; Heavy metals; PM10; PMF model; Source apportionment; Antimony compounds; Charcoal; Chromium compounds; Combustion; Copper smelting; Deforestation; Diseases; Factorization; Fire hazards; Fires; Fossil fuels; Health risks; Industrial emissions; Particles (particulate matter); Risk assessment; Steelmaking; Trace elements; Urban growth; Pmf models; Iron and steel industry; antimony; arsenic; barium; cadmium; chromium; cobalt; copper; lead; nickel; tin; trace element; vanadium; zinc; assessment method; cancer; concentration (composition); health risk; heavy metal; megacity; particulate matter; seasonal variation; spatiotemporal analysis; speciation (chemistry); airborne particle; Article; Colombia; dust; exhaust gas; forest fire; health hazard; inhalation; priority journal; urban area; Bogota

Abstract:
The deleterious health effects of thoracic fractions seem to be more related to the chemical composition of the particles than to their mass concentration. The presence of hazardous materials in PM10 (e.g., heavy metals and metalloids) causes risks to human health. In this study, twelve trace elements (Cd, Cr, Pb, Zn, Cu, Ni, Sn, Ba, Co, As, V, and Sb) in 315 samples of ambient PM10 were analyzed. The samples were collected at an urban background site in a Latin American megacity (Bogota, Colombia) for one year. The concentrations and temporal variabilities of these elements were examined. According to the results, Cu (52 ng/m3), Zn (44 ng/m3), Pb (25 ng/m3), and Ba (20 ng/m3) were the traces with the highest concentrations, particularly during the dry season (January to March), which was characterized by barbecue (BBQ) charcoal combustion and forest fires. In addition, the differences between the results of weekdays and weekends were identified. The determined enrichment factor (EF) indicated that Zn, Pb, Sn, Cu, Cd, and Sb mainly originated from anthropogenic sources. Moreover, a speciation analysis of inorganic Sb (EF > 300) was conducted, which revealed that Sb(V) was the main Sb species in the PM10 samples (>80%). Six causes for the hazardous elements were identified based on the positive matrix factorization (PMF) model: fossil fuel combustion and forest fires (60%), road dust (19%), traffic-related emissions (9%), copper smelting (8%), the iron and steel industry (2%), and an unidentified industrial sector (2%). Furthermore, a health risk assessment of the carcinogenic elements was performed. Accordingly, the cancer risk of inhalation exposure to Co, Ni, As, Cd, Sb(III), and Pb was negligible for children and adults at the sampling site. For adults, the adjusted Cr(VI) level was slightly higher than the minimal acceptable risk level during the study period (1.4 × 10−6). © 2019 Elsevier B.V.

Rutigliano, F.A., Marzaioli, R., De Crescenzo, S.*, et al.* (2019) Human health risk from consumption of two common crops grown in polluted soils. *Science of the Total Environment,* 691: 195-204.
Keywords: Bio-accumulation factor; Health risk index; Lettuce; Soil contamination; Trace elements; Zucchini

Abstract:
Contamination of agricultural soils by trace elements is a recurrent hazard for human health because of the possibility of pollutants entering the food chain. Aim of this study was to assess the human health risk from consumption of the common leafy (Lactuca sativa L.) and

fruit (Cucurbita pepo L.) crops, in an agricultural area of Southern Italy. Along with agricultural practices, a major pollutant source is recurrent flooding from the highly polluted Solofrana river. Soil samples and edible parts of crops from 14 sites (10 flooded and 4 not flooded) were analyzed for total amounts of As, Cd, Co, Cr, Cu, Ni, Pb, V, Zn. The bio-accumulation factor (BAF) and Health Risk Index (HRI) were calculated for each element, crop and site and as average values of all sites (BAFmean and HRImean). Moreover, the Hazard Index (HI) was determined for each site, as the sum of HRI for all elements. Cr and Cu, mostly derived from river flooding and agricultural practices, respectively, were the only elements whose levels exceeded law thresholds and/or the natural background of the study area. Of the two considered crops, L. sativa accumulated more Cd, Cr and Ni, whereas C. pepo was a more effective bioaccumulator of Zn. Both HRImean (for As, Cd, Cr and Ni) and HI were higher for L. sativa than for C. pepo. A low health risk was associated to major soil pollutants (Cr and Cu) found in the study area; in contrast, combined data on soil pollution and plant bio-accumulation points to accumulation of Cd and As, mainly in lettuce, as a potential risk for human health. The results suggest that soil pollution data alone is not sufficient to assess health risk. © 2019 Elsevier B.V.

Skalny, A.V., Tinkov, A.A., Bohan, T.G.*, et al.* (2020) The Impact of Maternal Overweight on Hair Essential Trace Element and Mineral Content in Pregnant Women and Their Children. ***Biological Trace Element Research,*** **193: 64-72.**
Keywords: Chromium; Maternal obesity; Pregnancy; Vanadium; Zinc

Abstract:
The aim of the present study was to investigate hair essential trace elements and mineral levels in 105 pregnant normal-weight (control) and 55 overweight and obese women in the third trimester of pregnancy, as well as in their children at the age of 9 months. The hair essential trace elements and mineral levels were assessed using inductively coupled plasma mass-spectrometry. Overweight pregnant women had significantly reduced Cr (- 24%; p = 0.047) and Zn (- 13%; p = 0.008) content, as well as elevated hair Na and K levels as compared to the controls. Children from overweight and obese mothers had lower hair Mo (- 18%; p = 0.017), Se (- 8%; p = 0.043), and V (- 24%; p = 0.028) levels, as well as elevated Sr content (19%; p = 0.025). Correlation analysis revealed a significant relationship between maternal and child hair levels of Co (r = 0.170; p = 0.038), Cu (r = 0.513; p < 0.001), Mn (r = 0.240; p = 0.003), and Na (r = 0.181; p = 0.027) in the whole sample. Pre-pregnancy maternal body mass index (BMI) positively correlated with maternal hair K (r = 0.336; p < 0.001) and Na (r = 0.212; p = 0.008) and negatively correlated with V (r = - 0.204; p = 0.011) and Zn (r = - 0.162; p = 0.045) levels. The results indicate that impaired trace element and mineral metabolism may play a role in the link between maternal obesity, complications of pregnancy and child's postnatal development. Hypothetically, dietary improvement may be used as a tool to reduce these risks. However, further experimental and clinical studies are required to investigate the relationship between obesity and trace element metabolism in pregnancy.

Squadrone, S., Brizio, P., Abete, M.C.*, et al.* (2020) Trace elements profile in the blood of Huntington' disease patients. ***Journal of Trace Elements in Medicine and Biology,*** **57: 18-20.** Available at:
https://www.sciencedirect.com/science/article/pii/S0946672X19305553/pdfft?md5=4f8b8904b83d2d5ad9a21e94722899d2&pid=1-s2.0-S0946672X19305553-main.pdf
Keywords: Blood; HD; Metals; Neurodegeneration; antimony; arsenic; cadmium; chromium; cobalt; copper; iron; manganese; molybdenum; nickel; selenium; tin; trace element; vanadium; zinc; antimony blood level; arsenic blood level; Article; cadmium blood level;

chromium blood level; clinical article; cobalt blood level; controlled study; copper blood level; degenerative disease; female; homeostasis; human; Huntington chorea; iron blood level; male; manganese blood level; molybdenum blood level; nickel blood level; pathogenesis; priority journal; selenium blood level; tin blood level; trace metal blood level; vanadium blood level; zinc blood level

Abstract:
Huntington' disease (HD) is an autosomal dominant neurodegenerative disease characterized by progressive motor, psychiatric, and cognitive deterioration. HD is, together with spinocerebellar ataxias, spinobulbar muscular atrophy and dentatorubral-pallido-luysian atrophy, one of the nine disorders caused by an expansion of glutamine residues in the causative protein where the polyglutamine expansion cause aberrant protein folding. Since an excessive metal's accumulation in organs may induce protein misfolding and oxidative stress, we have studied the blood concentration of essential (Cr, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn) and nonessential (As, Cd, Sb, Sn, V) trace elements in HD patients. We found increased levels of the essential elements iron, chromium, selenium and zinc and of the nonessential element arsenic in the blood of HD patients. Since alteration in metals homeostasis may contribute to the pathogenesis of neurodegenerative disease and could eventually constitute a target for therapy, we may suggest the utilize of the blood metal profile as a further in vivo tool to study and characterize Huntington disease. © 2019 Elsevier GmbH.

Tsai, M.-, Chen, M.-, Lin, C.-*, et al.* (2019) Children's environmental health based on birth cohort studies of Asia (2) – air pollution, pesticides, and heavy metals. *Environmental Research,* 179.
Keywords: Air pollution; Asia; Birth cohort; Heavy metals; Pesticides; arsenic; cadmium; heavy metal; lead; manganese; organochlorine pesticide; pesticide; pyrethroid; thallium; vanadium; atmospheric pollution; child health; cohort analysis; environmental quality; PCB; pesticide residue; phthalate; pollution exposure; pregnancy; smoke; tobacco; air pollutant; allergic disease; Article; child; child growth; childhood; childhood obesity; environmental exposure; environmental health; fetus growth; human; infancy; pregnancy outcome; prenatal exposure; priority journal; problem behavior; systematic review; Nicotiana tabacum

Abstract:
The life style and child raising environment in Asia are quite different compared with Western countries. Besides, the children's environmental threats and difficulties in conducting studies could be different. To address children's environmental health in Asia area, the Birth Cohort Consortium of Asia (BiCCA) was co-established in 2011. We reviewed the mercury, polychlorinated biphenyls, perfluoroalkyl substances, phthalates, and environmental tobacco smoke in pervious based on birth cohort studies in Asia. The aim of this study was to summarize the traditional environmental pollution and the target subjects were also based on the birth cohort in Asia area. Environmental pollutants included air pollutants, pesticides focusing on organochlorine pesticides, diakylphosphates, and pyrethroid, and heavy metals including lead, arsenic, cadmium, manganese, vanadium, and thallium. Fetal growth and pregnancy outcomes, childhood growth and obesity, neurodevelopment and behavioral problems, and allergic disease and immune function were classified to elucidate the children's health effects. In total, 106 studies were selected in this study. The evidences showed air pollution or pesticides may affect growth during infancy or childhood, and associated with neurodevelopmental or behavioral problems. Prenatal exposure to lead or manganese was associated with neurodevelopmental or behavioral problems, while exposure to arsenic or cadmium may influence fetal growth. In

addition to the harmonization and international collaboration of birth cohorts in Asia; however, understand the whole picture of exposure scenario and consider more discipline in the research are necessary. © 2019 Elsevier Inc.

Wang, X., Gao, D., Zhang, G.*, et al.* (2019) Exposure to multiple metals in early pregnancy and gestational diabetes mellitus: A prospective cohort study. *Environment International,* 135: 105370.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412019323979/pdfft?md5=7f459a82f1f8aa3097e059d76a9c473a&pid=1-s2.0-S0160412019323979-main.pdf
Keywords: GDM; Urinary metals; Single-metal models; Multiple-metal models; BKMR models
Abstract:
BACKGROUND:
A growing number of epidemiologic studies have estimated associations between type 2 diabetes mellitus and exposure to metals. However, studies on the associations of internal assessments of metal exposure and gestational diabetes mellitus (GDM) are limited in scope and have inconsistent outcomes.
OBJECTIVES:
This investigation aimed to explore the associations between urinary nickel (Ni), arsenic (As), cadmium (Cd), antimony (Sb), cobalt (Co), or vanadium (V) in early pregnancy and the subsequent risk of GDM in Chinese pregnant women.
METHODS:
The study population included 2090 women with singleton pregnancy from the Tongji Maternal and Child Health Cohort (TMCHC). Urine samples were collected before 20 gestational weeks, and an oral glucose tolerance test (OGTT) was conducted at 24-28 gestational weeks to diagnose GDM. The concentrations of urinary metals were measured using inductively coupled plasma mass spectrometry (ICP-MS) and were corrected for urinary creatinine. The associations between the risk of GDM and urinary metals were assessed using Poisson regression with a robust error variance with generalized estimating equations (GEE) models and Bayesian kernel machine regression (BKMR).
RESULTS:
A total of 241 participants (11.53%) were diagnosed with GDM. Five metals (Ni, As, Sb, Co, and V) were found significantly and positively associated with GDM based on single-metal models. In multiple-metal models, for each unit increase of ln-transformed urinary Ni or Sb, the risk of GDM increased 18% [relative risk (RR):1.18, 95%confidence interval (CI): 1.00, 1.38 or RR: 1.18, 95%CI: 1.00, 1.39, respectively]. The BKMR analysis revealed a statistically significant and positive joint effect of the six metals on the risk of GDM, when the urinary levels of the six metals were all above the 55th percentile, compared to the median levels. The effect of metal Ni was significant when the concentrations of the other metals were all fixed at their 25th percentile, and metal Sb displayed a significant and positive effect when all the other metals were fixed at 25th, 50th, and 75th percentiles.
CONCLUSIONS:
To the best of our knowledge, this study is the first to demonstrate that increased concentrations of urinary Ni in early pregnancy are associated with an elevated risk of GDM, either evaluated individually or as a metal mixture. All six metals mixed exposure was positively associated with the risk of GDM, while Sb and Ni were demonstrated more important effects than the other four metals in the mixture.

Zhou, Y., Hong, F., Wang, X.*, et al.* (2019) Abnormal levels of aqueous humor trace elements in patients with cytomegalovirus retinitis. *Eye (Basingstoke),* 33(10): 1606-1612.

Abstract:
Purpose: To investigate the alterations of trace elements levels in aqueous humor of patients with cytomegalovirus retinitis (CMVR). Methods: A total of 15 eyes of 11 patients with CMVR and 24 eyes of 24 patients with senile cataract as control group were enrolled. Aqueous humor samples were assessed for calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), phosphorus (P), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), selenium (Se), strontium (Sr), and lead (Pb) by using inductively coupled-plasma-mass-spectrometry. Meanwhile, we examined the concentration of the CMV DNA load by using PCR and the concentration of interleukin (IL)-8 by using a cytometric bead array. Results: In patients with CMVR, the aqueous humor levels of P and Cu were significantly higher than those of controls ($p < 0.001$, $p < 0.001$, respectively). However, levels of K and Mg were significantly lower in patients with CMVR ($p < 0.001$, $p < 0.001$, respectively). The Spearman correlation test showed that the concentration of IL-8 in the aqueous humor was significantly associated with the aqueous level of Cu ($p = 0.009$, $r = 0.646$) and Se ($p = 0.031$, $r = 0.558$). In addition, the concentration of CMV DNA load in the aqueous humor was significantly associated with the aqueous level of Ca ($p = 0.027$, $r = -0.568$), Mn ($p = 0.020$, $r = 0.593$), and Cu ($p = 0.043$, $r = 0.527$). Conclusions: Our preliminary results demonstrated that the abnormal aqueous levels of trace elements (P and Cu) in CMVR patients. Thus, the roles of trace element changes in the development of CMVR and the influence of intraocular trace element for the prognosis of CMVR warrant further investigations. © 2019, The Royal College of Ophthalmologists.

Zwolak, I. (2020) Protective Effects of Dietary Antioxidants against Vanadium-Induced Toxicity: A Review. *Oxidative Medicine and Cellular Longevity,* 2020.
Available at: http://downloads.hindawi.com/journals/omcl/2020/1490316.pdf

Abstract:
Vanadium (V) in its inorganic forms is a toxic metal and a potent environmental and occupational pollutant and has been reported to induce toxic effects in animals and people. *In vivo* and *in vitro* data show that high levels of reactive oxygen species are often implicated in vanadium deleterious effects. Since many dietary (exogenous) antioxidants are known to upregulate the intrinsic antioxidant system and ameliorate oxidative stress-related disorders, this review evaluates their effectiveness in the treatment of vanadium-induced toxicity. Collected data, mostly from animal studies, suggest that dietary antioxidants including ascorbic acid, vitamin E, polyphenols, phytosterols, and extracts from medicinal plants can bring a beneficial effect in vanadium toxicity. These findings show potential preventive effects of dietary antioxidants on vanadium-induced oxidative stress, DNA damage, neurotoxicity, testicular toxicity, and kidney damage. The relevant mechanistic insights of these events are discussed. In summary, the results of studies on the role of dietary antioxidants in vanadium toxicology appear encouraging enough to merit further investigations.

3. BIOLOGICAL MECHANISMS

Alghrably, M., Czaban, I., Jaremko, L.*, et al.* (2019) Interaction of amylin species with transition metals and membranes. *Journal of Inorganic Biochemistry,* 191: 69-76.
Available at:
https://www.sciencedirect.com/science/article/pii/S0162013418304409/pdfft?md5=074dd49be274a383f058d68b8001f39a&pid=1-s2.0-S0162013418304409-main.pdf
Keywords: Animals; Cell Membrane/metabolism; Humans; Islet Amyloid Polypeptide/metabolism; Transition Elements/metabolism; Aggregation; Aggregation inhibition; Amylin; Complex formation; Diabetes type II; Transition metals

Abstract:
Islet Amyloid Polypeptide (IAPP), also known as amylin, is a 37-amino-acid peptide hormone that is secreted by pancreatic islet beta-cells. Amylin is complementary to insulin in regulating and maintaining blood glucose levels in the human body. The misfolding and aggregation of amylin is primarily associated with type 2 diabetes mellitus, which is classified as an amyloid disease. Recently, the interactions between amylin and specific metal ions, e.g., copper(II), zinc(II), and iron(II), were found to impact its performance and aggregation processes. Therefore, the focus in this review will be on how the chemistry and structural properties of amylin are affected by these interactions. In addition, the impact of amylin and other amyloidogenic peptides interacting with metal ions on the cell membranes is discussed. In particular, recent studies on the interactions of amylin with copper, zinc, iron, nickel, gold, ruthenium, and vanadium are discussed.

Almeida, M.C., Branco, R. & Morais, P.V. (2020) Response to vanadate exposure in Ochrobactrum tritici strains. *PloS One,* 15(2): e0229359.
Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7039435/pdf/pone.0229359.pdf

Abstract:
Vanadium is a transition metal that has been added recently to the EU list of Raw Critical Metals. The growing needs of vanadium primarily in the steel industry justify its increasing economic value. However, because mining of vanadium sources (i. e. ores, concentrates and vanadiferous slags) is expanding, so is vanadium environmental contamination. Bioleaching comes forth as smart strategy to deal with supply demand and environmental contamination. It requires organisms that are able to mobilize the metal and at the same time are resistant to the leachate generated. Here, we investigated the molecular mechanisms underlying vanadium resistance in Ochrobactrum tritici strains. The highly resistant strain 5bvl1 was able to grow at concentrations > 30 mM vanadate, while the O. tritici type strain only tolerated < 3 mM vanadate concentrations. Screening of O. tritici single mutants (chrA, chrC, chrF and recA) growth during vanadate exposure revealed that vanadate resistance was associated with chromate resistance mechanisms (in particular ChrA, an efflux pump and ChrC, a superoxide dismutase). We also showed that sensitivity to vanadate was correlated with increased accumulation of vanadate intracellularly, while in resistant cells this was not found. Other up-regulated proteins found during vanadate exposure were ABC transporters for methionine and iron, suggesting that cellular responses to vanadate toxicity may also induce changes in unspecific transport and chelation of vanadate.

Althumairy, D., Murakami, H.A., Zhang, D.*, et al.* (2020) Effects of vanadium(IV) compounds on plasma membrane lipids lead to G protein-coupled receptor signal transduction. *Journal of Inorganic Biochemistry,* 203.
Keywords: BMOV; G-protein-coupled receptor; Luteinizing hormone receptor; Plasma membrane rafts; Signal transduction; Vanadium; Vanadyl; chorionic gonadotropin; cyclic AMP; G protein coupled receptor; membrane lipid; vanadium derivative; animal cell; Article; bioaccumulation; CHO-K1 cell line; controlled study; female; fluorescence resonance energy transfer; lipid bilayer; nonhuman; second messenger

Abstract:
Luteinizing hormone receptors (LHR), expressed at physiological numbers 85,000 receptors per cell) are found in larger clusters in polarized homo-transfer fluorescence resonance energy transfer (homo-FRET) studies that were not affected by either hCG or vanadium

compounds. Intracellular cyclic adenylate monophosphate (cAMP) levels indicate that only clustered LHR are active and produce the intracellular second messenger, cAMP. When LHR are over-expressed, cell signaling is unaffected by binding of hCG or vanadium compounds. To confirm the existence of intact complex, the EPR spectra of vanadium compounds in cell media were obtained using 1 mM BMOV, BEOV or VOSO4. These data were used to determine intact complex in a 10 μM solution and verified by speciation calculations. Effects of BMOV and BEOV samples were about two-fold greater than those of aqueous vanadium(IV) making it likely that intact vanadium complex are responsible for effects of LHR function. This represents a new mechanism for activation of a G protein-coupled receptor; perturbations in the lipid bilayer by vanadium compounds lead to aggregation and accumulation of physiological numbers of LHR in membrane raft domains where they initiate signal transduction and production of cAMP, a second messenger involved in signaling.

Areecheewakul, S., Adamcakova-Dodd, A., Givens, B.E.*, et al.* (2020) Toxicity assessment of metal oxide nanomaterials using in vitro screening and murine acute inhalation studies. *Nanoimpact,* : 100214.
Keywords: Nanomaterials; Nanoparticles; toxicity; Inhalation toxicity; Metal oxides

Abstract:
Characterizations and in vitro toxicity screening were performed on metal oxide engineered nanomaterials (ENMs) independently comprising ZnO, CuO, CeO2, Fe2O3, WO3, V2O5, TiO2, Al2O3 and MgO. Nanomaterials that exhibited the highest toxicity responses in the in vitro screening assays (ZnO, CuO, and V2O5) and the lesser explored material WO3 were tested for acute pulmonary toxicity in vivo. Female and male mice (C57Bl/6J) were exposed to aerosolized metal oxide ENMs in a nose-only exposure system and toxicity outcomes (biomarkers of cytotoxicity, immunotoxicity, inflammation, and lung histopathology) at 4 and 24 h after the start of exposure were assessed. The studies were performed as part of the NIEHS Nanomaterials Health Implications Research consortium with the purpose of investigating the effects of ENMs on various biological systems. ENMs were supplied by the Engineered Nanomaterials Resource and Coordination Core. Among the ENMs studied, the highest toxicity was observed for CuO and ZnO NPs in both in vitro and in vivo acute models. Compared to sham-exposed controls, there was a significant increase in bronchoalveolar lavage neutrophils and proinflammatory cytokines and a loss of macrophage viability at both 4 h and 24 h for ZnO and CuO but not seen for V2O5 or WO3. These effects were observed in both female and male mice. The cell viability performed after in vitro exposure to ENMs and assessment of lung inflammation after acute inhalation exposure in vivo were shown to be sensitive endpoints to predict ENM acute toxicity. ".

Benvenga, S., Elia, G., Ragusa, F.*, et al.* (2020) Endocrine disruptors and thyroid autoimmunity. *Best Practice & Research.Clinical Endocrinology & Metabolism* : 101377.
Keywords: Graves' disease; autoimmune thyroid diseases; autoimmune thyroiditis; endocrine disruptors; myo-inositol; selenium/selenomethionine

Abstract:
Many papers evaluated the effect of the environmental, or occupational endocrine disruptors (ED), on the thyroid gland, that can lead to thyroid autoimmunity. A higher prevalence of autoimmune thyroid diseases (AITD) was observed in people living in polluted areas near to petrochemical plants, and in petrochemical workers, but also in area contaminated with organochlorine pesticides, or with polychlorinated biphenyls, or near aluminum foundries. The exposure to Hg in chloralkali workers, or in swordfish consumers

has been also found to increase AITD prevalence. Vanadium has been shown to increase the inflammatory response of thyrocytes. A beneficial effect of omega-3 fatty acids, and of myo-inositol and selenomethionine have been shown to counteract the appearance of AITD in subjects exposed to environmental or occupational ED. More large studies are needed to investigate the potential roles of ED in the induction of AITD, and of agents or habits that are able to prevent them.

El-Shafey, E.S. & Elsherbiny, E.S. (2019) Possible Selective Cytotoxicity of Vanadium Complex on Breast Cancer Cells Involving Pathophysiological Pathways. *Anti-Cancer Agents in Medicinal Chemistry,* 19(17): 2130-2139.
Keywords: AVO; Apoptosis; Notch1; autophagy; triple negative breast cancer; vanadium complex

Abstract:
BACKGROUND: Triple-Negative Breast Cancers (TNBC) are among the most aggressive and therapy resistant breast tumors. Development of new treatment strategies that target pathways involved in cancer cells resistance is an attractive candidate to overcome therapeutic resistance. OBJECTIVE: To clarify the antitumor activity of [VO (bpy)2 Cl] Cl complex as new therapeutic agent through studying the interplay between apoptosis, autophagy and notch signaling pathways. METHODS: Proliferation of MDA-MB-231 cells and IC50 value of vanadium complex were assessed by MTT assay. Flow cytometry was utilized to detect cell cycle distribution, apoptosis assay, LC3 levels and Acid Vascular Organelles (AVOs). Caspase 3 levels was detected by ELISA. Changes in Notch1 gene expression was assessed by real time PCR. AVOs qualitative detection was assessed by fluorescence microscope. RESULTS: The growth of MDA-MB-231 cells was suppressed after treatment with [VO (bpy)2 Cl] Cl complex, in a dose-dependent manner. The affinity for apoptotic cell death induction was shown through the increase in the sub G0 peak, the percentage of early and late apoptotic phases, and the elevation in caspase 3 levels. The affinity for autophagic cell death induction was observed through the increase in the G0/G1 phase, G2/M arrest, the increase of AVOs red fluorescence and elevated LC3 levels. The affinity for notch pathway inhibition was shown through the suppression of Notch 1 gene expression. CONCLUSION: [VO (bpy)2 Cl] Cl complex, could be a promising candidate as therapeutic agent targeting different therapeutic targets including apoptosis, autophagy and notch signaling pathways.

Gupta, P.K., Vaswani, S., Kumar, V.*, et al.* (2020) Investigations on Modulating Effect of Vanadium Supplementation on Growth and Metabolism Through Improved Immune Response, Antioxidative Profile and Endocrine Variables in Hariana heifers. *Biological Trace Element Research,* 194(2): 379-389.
Keywords: Antioxidant; Endocrine; Growth; Hariana; Immunity; Vanadium; DIABETIC-RATS; BROWN-ALGAE; VANADATE; LIVER; PERFORMANCE; OXIDATION; TOXICITY; ELEMENTS; HORMONE; METALS; Biochemistry & Molecular Biology; Endocrinology & Metabolism

Abstract:
This study was conducted to investigate the effect of vanadium (V) supplementation on growth, metabolism, antioxidant, and immunological and endocrine variables in Hariana heifers. Eighteen indigenous Hariana heifers (body weight 130.0 +/- 3.0 kg; age 10.0 +/- 2.0 months) were randomly blocked into three groups, each comprising of six animals. All the animals were on same dietary plan except that the respective groups were additionally supplemented with 0.0, 2.5, and 5.0 mg of V/kg dry matter (DM), during the experimental period of 90 days. There was a linear increase (p 0.05) of V supplementation were observed

on hemato-biochemical attributes, the mean plasma V concentration showed dose-dependent increase ($p < 0.001$) on V supplementation. The activity of SOD was significantly higher ($p < 0.001$), whereas mean values of LPO decreased linearly ($p < 0.05$) in V-supplemented groups. Plasma total antioxidant status (TAS) also increased linearly ($p < 0.05$) in V-supplemented groups. Plasma IgG levels increased linearly ($p < 0.05$). Plasma IGF-1 concentrations showed significant effect ($p < 0.05$) of V supplementation. Plasma T4 concentration increased linearly ($p < 0.05$). The results suggest that V supplementation may play a role in modulating the immunity and antioxidant status of growing Hariana heifers.

Kim, S., Gates, B.L., Leonard, B.C.*, et al.* (2020) Engineered metal oxide nanomaterials inhibit corneal epithelial wound healing in vitro and in vivo. *Nanoimpact,* 17: 100198.
Available at:
https://www.sciencedirect.com/science/article/pii/S2452074819301077/pdfft?md5=67eb1a0002df9eff3eb8aa9145b77f6d&pid=1-s2.0-S2452074819301077-main.pdf
Keywords: Metal oxide engineered nanomaterials; Nanometals; Corneal epithelium; Corneal wound healing; Nanotoxicity

Abstract:
Ocular exposure to metal oxide engineered nanomaterials (ENMs) is common as exemplified by zinc(II) oxide (ZnO), a major constituent of sunscreens and cosmetics. The ocular surface that includes the transparent cornea and its protective tear film are common sites of exposure for metal ENMs. Despite the frequency of exposure of the ocular surface, there is a knowledge gap regarding the effects of metal oxide ENMs on the cornea in health and disease. Therefore, we studied the effects of metal oxide ENMs on the cornea in the presence or absence of injury. Cell viability of immortalized human corneal epithelial (hTCEpi) cells was assessed following treatment with 11 metal oxide ENMs with a concentration ranging from 0.5 to 250 μg/ml for 24 h. An epithelial wound healing assay with a monolayer of hTCEpi cells was then performed using 11 metal oxide ENMs at select concentrations based on data from the viability assays. Subsequently, based on the in vitro results, in vivo testing of precorneal tear film (PTF) quantity and stability as well as a corneal epithelial wound healing were tested in the presence or absence ZnO or vanadium(V) oxide (V_2O_5) at a concentration of 50 μg/ml. We found that WO_3, ZnO, V_2O_5 and CuO ENMs significantly reduced hTCEpi cell viability in comparison to vehicle control or the other metal oxide ENMs tested. Furthermore, ZnO and V_2O_5 ENMs also significantly decreased hTCEpi cell migration. Although ZnO and V_2O_5 did not alter PTF parameters of rabbits in vivo, corneal epithelial wound healing was significantly delayed by topical ZnO while V_2O_5 did not alter wound healing. Finally, hyperspectral images confirmed penetration of ZnO and V_2O_5 through all corneal layers and into the iris stroma. Considering the marked epithelial toxicity and corneal penetration of ZnO, further investigations on the impact of this ENM on the eye are warranted. ".

Korbecki, J., Gutowska, I., Wiercioch, M.*, et al.* (2020) Sodium Orthovanadate Changes Fatty Acid Composition and Increased Expression of Stearoyl-Coenzyme A Desaturase in THP-1 Macrophages. *Biological Trace Element Research,* 193(1): 152-161.
Available at: https://link.springer.com/content/pdf/10.1007/s12011-019-01699-2.pdf
Keywords: Desaturase; Fatty acids; Macrophage; Sodium orthovanadate; THP-1; acyl coenzyme A desaturase; acyl coenzyme A desaturase 1; arachidonic acid; docosahexaenoic acid; docosapentaenoic acid; icosapentaenoic acid; linoleic acid; oleic acid; palmitic acid; palmitoleic acid; phorbol 13 acetate 12 myristate; stearic acid; vanadate sodium; Article; controlled study; FADS1 gene; FADS2 gene; gas chromatography; gene; gene expression; human; human cell; in vitro study; lipid composition; real time polymerase chain reaction;

SCD gene; THP-1 cell line; upregulation

Abstract:
Vanadium compounds are promising antidiabetic agents. In addition to regulating glucose metabolism, they also alter lipid metabolism. Due to the clear association between diabetes and atherosclerosis, the purpose of the present study was to assess the effect of sodium orthovanadate on the amount of individual fatty acids and the expression of stearoyl-coenzyme A desaturase (SCD or Δ9-desaturase), Δ5-desaturase, and Δ6-desaturase in macrophages. THP-1 macrophages differentiated with phorbol 12-myristate 13-acetate (PMA) were incubated in vitro for 48 h with 1 µM or 10 µM sodium orthovanadate (Na3VO4). The estimation of fatty acid composition was performed by gas chromatography. Expressions of the genes SCD, fatty acid desaturase 1 (FADS1), and fatty acid desaturase 2 (FADS2) were tested by qRT-PCR. Sodium orthovanadate in THP-1 macrophages increased the amount of saturated fatty acids (SFA) such as palmitic acid and stearic acid, as well as monounsaturated fatty acids (MUFA)—oleic acid and palmitoleic acid. Sodium orthovanadate caused an upregulation of SCD expression. Sodium orthovanadate at the given concentrations did not affect the amount of polyunsaturated fatty acids (PUFA) such as linoleic acid, arachidonic acid, eicosapentaenoic acid (EPA), docosapentaenoic acid (DPA), and docosahexaenoic acid (DHA). In conclusion, sodium orthovanadate changed SFA and MUFA composition in THP-1 macrophages and increased expression of SCD. Sodium orthovanadate did not affect the amount of any PUFA. This was associated with a lack of influence on the expression of FADS1 and FADS2. © 2019, The Author(s).

Kumar, A., Dixit, A., Sahoo, S.*, et al.* (2020) Crystal structure, DNA crosslinking and photo-induced cytotoxicity of oxovanadium(IV) conjugates of boron-dipyrromethene. *Journal of Inorganic Biochemistry,* 202.
Available at:
https://www.sciencedirect.com/science/article/pii/S0162013419305057/pdfft?md5=1dad4ffbccda9ddc1e8f0897324345cd&pid=1-s2.0-S0162013419305057-main.pdf
Keywords: Bioinorganic chemistry; Crystal structure; DNA crosslink; Photodynamic therapy; Vanadium; antineoplastic metal complex; boron derivative; cisplatin; dipyrromethene derivative; fluorescent dye; isothiocyanic acid; lipocortin 5; photosensitizing agent; propidium iodide; singlet oxygen; unclassified drug; valinomycin; vanadium derivative; antineoplastic activity; Article; breast cancer; cancer chemotherapy; comparative study; controlled study; density functional theory; DNA cross linking; DNA denaturation; drug conjugation; drug mechanism; drug synthesis; excision repair; female; fluorescence; human; human cell; mitochondrial membrane potential; photocytotoxicity; quantum yield; steady state; thymus; uterine cervix cancer; X ray crystallography

Abstract:
Cis-dichloro-oxovanadium(IV) complexes [VO(L1/L2)Cl2], where L1 is N-(4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4ʎ4,5ʎ4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-10-yl)benzyl)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine in 1 and L2 is N-(4-(5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-5H-4ʎ4,5ʎ4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-10-yl)benzyl)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine in 2) having 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene as boron-dipyrromethene (BODIPY) appended dipicolylamine bases were prepared, characterized and their photocytotoxicity studied. X-ray crystal structure of 1 showed distorted octahedral geometry with a VIVON3Cl2 core having Cl-V-Cl angle of 91.93(4)°. The complexes showed variable solution conductivity properties. They were non-electrolytes in dry DMF at 25 °C but showed 1:1 electrolytic behavior in an aqueous medium due to dissociation of one chloride ligand as evidenced from the mass

spectral study. Complexes 1 and 2 showed absorption bands at 500 and 535 nm, respectively. The calf thymus DNA melting study revealed their interaction through DNA crosslinking on exposure to light which was further confirmed from the alkaline agarose gel electrophoresis using plasmid supercoiled pUC19 DNA. Complex 2 showed disruption of the mitochondrial membrane potential in the JC-1 (1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachloroimidacarbocyanine iodide) assay. The complexes were photocytotoxic in visible light (400–700 nm, power: 10 J cm−2) in cervical cancer HeLa and breast cancer MCF-7 cells. Complex 2 having a photoactive diiodo-boron-dipyrromethene moiety gave a singlet oxygen quantum yield (ΦΔ) value of ~0.6. It showed singlet oxygen mediated apoptotic photodynamic therapy activity with remarkably low IC50 (half maximal inhibitory concentration) value of ~0.15 μM. The cis-disposition of chlorides gave a cis-divacant 4-coordinate intermediate structure from the density functional theory (DFT) study thus mimicking the DNA crosslinking property of cisplatin. © 2019.

Mortensen, N.P., Caffaro, M.M., Patel, P.R.*, et al.* (2020) Investigation of twenty metal, metal oxide, and metal sulfide nanoparticles' impact on differentiated Caco-2 monolayer integrity. *Nanoimpact,* 17: 100212.
Available at:
https://www.sciencedirect.com/science/article/pii/S2452074820300069/pdfft?md5=6fbcb6acc06344ac8dac45d77eadb90e&pid=1-s2.0-S2452074820300069-main.pdf
Keywords: Engineered nanomaterialsENM DosimetryCytotoxicityIntestinal integrityCaco-2 monolayer

Abstract:
The use of engineered nanomaterials (ENMs) in foods and consumer products is rising, increasing the potential for unintentional ingestion. While the cytotoxicity of many ENMs has been investigated, less attention has been given to adverse impact on the intestinal barrier integrity. Chronical disruption of gastrointestinal integrity can have far reaching health implications.
Using fully differentiated Caco-2 cells, the perturbation of intestinal barrier function and cytotoxicity were investigated for 20 metal, metal oxide, and metal sulfide ENMs. Caco-2 cells were exposed to 50 μg/mL ENMs for 24 h. ENM formulations were characterized at 0 and 24 h, and *In Vitro* Sedimentation, Diffusion and Dosimetry Modeling was applied to calculate the effective dose of exposure during 24 h. The apparent permeability coefficient (P_{app}) was determined for fluorescent labeled dextran (3000 Da) and tight junction integrity was evaluated by immunofluorescence microscopy. Cytotoxicity was investigated by determining lactate dehydrogenase release (LDH) and cell metabolic activity (tetrazolium based MTS) assays.
Four ENMs led to significantly increased P_{app}, (15.8% w/w% Ag-SiO_2 nanoparticle (NP), 60 nm CdS NP, 100 nm V_2O_5 flakes, and 50 nm ZnO NP), while one ENM (20 nm MgO NP) decreased P_{app}. With the exception of CdS NP, significantly increased P_{app} was not connected with cell cytotoxicity. The calculated effective dose concentration was not correlated with increased P_{app}.
Our results illustrate that while many metal, metal oxide, and metal sulfide ENMs do not adversely affect monolayer integrity or induce cytotoxicity in differentiated Caco-2 cells, a subset of ENMs may compromise the intestinal integrity. This study demonstrated the use of differentiated Caco-2 monolayer and P_{app} as an endpoint to identify and prioritize ENMs that should be investigated further. The interaction between ENMs and the intestinal epithelium needs to be evaluated to understand potential intestinal barrier dysfunction and resulting health implications.

Rivas-García, L., Quiles, J.L., Varela-López, A.*, et al.* (2020) In vitro study of the protective effect of manganese against vanadium-mediated nuclear and mitochondrial DNA damage. *Food and Chemical Toxicology,* 135.
Available at:
https://www.sciencedirect.com/science/article/pii/S0278691519306908/pdfft?md5=e8068321f9f44aa74d8e90e270b0cb99&pid=1-s2.0-S0278691519306908-main.pdf
Keywords: DNA; HepG2 cells; Manganese; Mitochondria; Nucleus; Vanadium; cell nucleus DNA; mitochondrial DNA; bis(maltolato)oxovanadium(IV); chloride; manganese chloride; manganese derivative; protective agent; pyrone derivative; vanadic acid; Article; cell viability; comet assay; concentration (parameter); controlled study; DNA damage; electrospray mass spectrometry; high performance liquid chromatography; in vitro study; incubation time; inductively coupled plasma mass spectrometry; proton nuclear magnetic resonance; quadrupole mass spectrometry; time of flight mass spectrometry; cell nucleus; cell survival; drug effect; Hep-G2 cell line; human; metabolism; mitochondrion; Chlorides; DNA, Mitochondrial; Hep G2 Cells; Humans; Manganese Compounds; Protective Agents; Pyrones; Vanadates

Abstract:
We aimed to study the effect of vanadium(V) exposure on cell viability, nuclear DNA (nDNA) and mitochondrial DNA (mtDNA) and to elucidate if these effects can be reverted by co-exposure to V and manganese (Mn). HepG2 cells were incubated with various concentrations of bis(maltolato)oxovanadium(IV) or MnCl2 for 32 h for viability study. The higher concentrations (59 μM V, 54 nM Mn and 59 μM V+54 nM Mn) were used to study DNA damage and uptake of V and Mn. Comet assay was used for the study of nDNA damage; mtDNA damage was studied by determining deletions and number of copies of the ND1/ND4 mtDNA region. Cellular content of V and Mn was determined using ICPMS. Cellular exposure to 59 μM V decreased viability (14%) and damaged nDNA and mtDNA. This effect was partially prevented by the co-exposure to V + Mn. Exposure to V increased the cellular content of V and Mn (812.3% and 153.5%, respectively). Exposure to Mn decreased the content of V and Mn (62% and 56%, respectively). Exposure to V + Mn increased V (261%) and decreased Mn (56%) content. The positive effects on cell viability and DNA damage when incubated with V + Mn could be due to the Mn-mediated inhibition of V uptake. © 2019 Elsevier Ltd.

Sizochenko, N., Syzochenko, M., Fjodorova, N.*, et al.* (2019) Evaluating genotoxicity of metal oxide nanoparticles: Application of advanced supervised and unsupervised machine learning techniques. *Ecotoxicology and Environmental Safety,* 185.
Keywords: Classification; Descriptors; Genotoxicity; Metal oxide nanoparticles; Nano-QSAR; Self-organizing map

Abstract:
Presence of missing data points in datasets is among main challenges in handling the toxicological data for nanomaterials. As the processing of missing data is an important part of data analysis, we have introduced a read-across approach that uses a combination of supervised and unsupervised machine learning techniques to fill the missing values. A series of classification models (supervised learning) was developed to predict class label, and self-organizing map approach (unsupervised learning) was used to estimate relative distances between nanoparticles and refine results obtained during supervised learning. In this study, genotoxicity of 49 silicon and metal oxide nanoparticles in Ames and Comet tests. Collected literature data did not demonstrate significant variations related to the change of size including selected bulk materials. Genotoxicity-related features of nanomaterials were

represented by ionic characteristics. General tendencies found in the current study were convincingly linked to known theories of genotoxic action at nano-level. Mechanisms of primary and secondary genotoxic effects were discussed in the context of developed models. © 2019 Elsevier Inc.

Tsave, O., Halevas, E., Yavropoulou, M.*, et al.* (2019) V (v)-Schiff base species induce adipogenesis through structure-specific influence of genetic targets. *New Journal of Chemistry,* 43(45): 17872-17890.

Abstract:
Vanadium has been known to exhibit numerous functions in biological systems, projecting exogenous activity linked to regulatory roles in cell metabolism and insulin mimesis. Poised to probe into the vanadium adipogenic potential, reflecting on efficient anti-diabetic drugs, research was launched in our labs to pursue the (a) synthesis of diversely structured Schiff base ligands, as vanadium chelating binders, containing a variably configured *o*-vanillin core with a specified common organic *o*-aminophenol tether, (b) synthesis of a family of well-defined soluble vanadium-Schiff base compounds, bearing the above mentioned Schiff ligands (and in one case 4,4′-bipyridine), (c) study of their toxicity profile and adipogenic activity in 3T3-L1 fibroblasts toward mature adipocytes, and (d) determination of molecular biological targets linked to the vanadium-induced cell differentiation process, thereby unravelling factors impacting signaling pathways influencing insulin mimesis. The results suggest that (a) all emerging vanadospecies contain V(V) mononuclear centers bound to Schiff bases (and 4,4′-bipyridine), (b) a well-defined (solid-state and solution) physicochemical profile of all species justifies their selection in biological studies, (c) the vanadium toxicity profile is strongly related to the form of V(V) (complexed forms, substrate-ligand nature), (d) there is a structure-specific behavior of vanadium influencing adipogenesis, and (e) molecular target loci are also influenced by vanadoforms in a structure-specific fashion, thereby collectively projecting an interwoven role of factors emanating from vanadium and impacting cell differentiation and insulin mimetic activity. The so far accrued knowledge constitutes the basis for further development of biomarker-driven structure-specific vanadodrugs, contributing through insulin biomimicry to therapeutic technologies in Diabetes mellitus.

Zhong, L., Dong, A., Feng, Y.*, et al.* (2020) Alteration of Metal Elements in Radiation Injury: Radiation-Induced Copper Accumulation Aggravates Intestinal Damage. *Dose-Response,* 18(1): 1559325820904547.
Available at: https://journals.sagepub.com/doi/pdf/10.1177/1559325820904547
Keywords: radiation; trace metal element; copper; radiation-induced intestinal injury; OXIDATIVE STRESS; ZINC; TOXICITY; ANTIOXIDANT; RADICALS; CELLS; Pharmacology & Pharmacy; Radiology, Nuclear Medicine & Medical Imaging; Toxicology

Abstract:
Ionizing radiation causes damage to a variety of tissues, especially radiation-sensitive tissues, such as the small intestine. Radiation-induced damage is caused primarily by increased oxidative stress in the body. Studies have shown that trace metal elements play an irreplaceable role in oxidative stress in humans, which may be associated with radiation-induced tissue damage. However, the alteration and functional significance of trace metal elements in radiation-induced injury is not clear. In this study, we explored the association between radiation-induced damage and 7 trace metal elements in mouse models. We found that the concentration of zinc and copper in mice serum was decreased significantly after irradiation, whereas that of nickel, manganese, vanadium, cobalt, and stannum was not

changed by inductively coupled plasma mass spectrometry. The role of copper in radiation-induced intestines was characterized in detail. The concentration of copper was increased in irradiated intestine but reduced in irradiated heart. Immunohistochemistry staining showed that copper transporter protein copper transport 1 expression was upregulated in irradiated mouse intestine, suggesting its potential involvement in radiation-induced copper accumulation. At the cellular level, the addition of CuCl2 potentiated radiation-induced reactive oxygen species in intestine-derived human intestinal epithelial cell and IEC-6 cells. Moreover, the level of copper in damaged cells may be related to the severity of radiation-induced damage as evidenced by a cell viability assay. These results indicate that copper may be involved in the progression of radiation-induced tissue damage and may be a potential therapeutic target.

Zwolak, I. (2020) Protective Effects of Dietary Antioxidants against Vanadium-Induced Toxicity: A Review. *Oxidative Medicine and Cellular Longevity,* 2020.
Available at: http://downloads.hindawi.com/journals/omcl/2020/1490316.pdf

Abstract:
Vanadium (V) in its inorganic forms is a toxic metal and a potent environmental and occupational pollutant and has been reported to induce toxic effects in animals and people. *In vivo* and *in vitro* data show that high levels of reactive oxygen species are often implicated in vanadium deleterious effects. Since many dietary (exogenous) antioxidants are known to upregulate the intrinsic antioxidant system and ameliorate oxidative stress-related disorders, this review evaluates their effectiveness in the treatment of vanadium-induced toxicity. Collected data, mostly from animal studies, suggest that dietary antioxidants including ascorbic acid, vitamin E, polyphenols, phytosterols, and extracts from medicinal plants can bring a beneficial effect in vanadium toxicity. These findings show potential preventive effects of dietary antioxidants on vanadium-induced oxidative stress, DNA damage, neurotoxicity, testicular toxicity, and kidney damage. The relevant mechanistic insights of these events are discussed. In summary, the results of studies on the role of dietary antioxidants in vanadium toxicology appear encouraging enough to merit further investigations.

4. USES OF VANADIUM

Cohen, D.J., Scott, K.M., Kulkarni, A.N.*, et al.* (2020) Acellular mineralized allogenic block bone graft does not remodel during the 10 weeks following concurrent implant placement in a rabbit femoral model. *Clinical Oral Implants Research,* 31(1): 37-48.
Keywords: Animals; Bone Transplantation; Dental Implantation, Endosseous; Dental Implants; Femur; Male; Osseointegration; Rabbits; Titanium; CT Imaging; animal experiments; bone implant interactions; bone substitutes; guided tissue regeneration/bone regeneration; histopathology/host mechanisms; morphometric analysis; periodontology

Abstract:
OBJECTIVES: Due to bone loss, endosseous implants often require addition of a bone graft to support adequate primary fixation, bone regeneration, and osseointegration. The aim of this study was to compare effectiveness of autogenic and allogenic bone grafts when used during simultaneous insertion of the implant. MATERIALS AND METHODS: 4-mm-diameter rabbit diaphyseal bone autografts or allografts (n = 16/group) with a 3.2-mm pre-drilled hole in the center were placed into a 4 mm defect in the proximal femur of 3.5 kg male New Zealand White rabbits. Machined 3.2 x 10 mm grit-blasted, acid-etched titanium-aluminum-vanadium (Ti6Al4V) implants were placed. Control implants were placed into progressively drilled 3.2-mm holes in the contralateral limbs. Post-insertion day 70, samples were

analyzed by micro-CT and calcified histology, or by mechanical torque and push-out testing followed by decalcified histology. RESULTS: Both grafts were integrated with the native bone. Micro-CT showed less bone volume (BV) and bone volume/total volume (BV/TV) in the allograft group, but histology showed no differences in BV or BV/TV between groups. Allograft lacked living cells, whereas autograft was cellularized. No difference was found in maximum removal torque between groups. Compressive loading at the graft-to-bone interface was significantly lower in allograft compared with autograft groups. CONCLUSIONS: There was less bone in contact with the implant and significantly less maximum compressive load in the allograft group compared with autograft. The allograft remained acellular as demonstrated by empty lacunae. Taken together, block allograft implanted simultaneously with an implant produces a poorer quality bone compared with autograft.

Ding, Y., Ren, G., Wang, G.*, et al.* (2020) V2O5 Nanobelts Mimick Tandem Enzymes To Achieve Nonenzymatic Online Monitoring of Glucose in Living Rat Brain. *Analytical Chemistry,* 92(6): 4583-4591.

Abstract:
The continuous detection of glucose is significant for revealing its role in neuron protection and for diagnosis of various diseases. In this study, for the first time, a nonenzymatic online optical detection platform (OODP) for glucose measurement in rat brain utilizing the tandem enzyme activity of V2O5 nanobelts is developed. V2O5 nanobelts were synthesized via a facile solvothermal strategy, and for the first time it is found that the V2O5 nanobelts possess dual enzyme-like activity, i.e., glucose oxidase (GOx)-like and peroxidase-like activity, and can act as a "tandem nanozyme". To investigate the mechanisms of the GOx-like property, we built an adsorption model, and the RPBE density functional calculations indicate that the glucose molecule can be adsorbed on the V2O5 plane. Based on the ability of V2O5 nanobelts to mimick tandem enzymes, a nonenzymatic online optical detection platform (OODP) for the continuous monitoring of glucose in rat brain was designed, which exhibits excellent stability, high selectivity, and a wide linear detection range from 0.2 to 5 mM and records cerebral glucose alterations in the calm/ischemia model. This facile but reliable nonenzymatic online optical glucose measurement compares favorably with natural enzyme-based online electrochemical glucose analytical systems, and its ready adoption by physiologists and pathologists will facilitate the understanding of brain function and the pathogenesis of diabetes.

El-Shafey, E.S. & Elsherbiny, E.S. (2019) Possible Selective Cytotoxicity of Vanadium Complex on Breast Cancer Cells Involving Pathophysiological Pathways. *Anti-Cancer Agents in Medicinal Chemistry,* 19(17): 2130-2139.
Keywords: AVO; Apoptosis; Notch1; autophagy; triple negative breast cancer; vanadium complex

Abstract:
BACKGROUND: Triple-Negative Breast Cancers (TNBC) are among the most aggressive and therapy resistant breast tumors. Development of new treatment strategies that target pathways involved in cancer cells resistance is an attractive candidate to overcome therapeutic resistance. OBJECTIVE: To clarify the antitumor activity of [VO (bpy)2 Cl] Cl complex as new therapeutic agent through studying the interplay between apoptosis, autophagy and notch signaling pathways. METHODS: Proliferation of MDA-MB-231 cells and IC50 value of vanadium complex were assessed by MTT assay. Flow cytometry was utilized to detect cell cycle distribution, apoptosis assay, LC3 levels and Acid Vascular Organelles

(AVOs). Caspase 3 levels was detected by ELISA. Changes in Notch1 gene expression was assessed by real time PCR. AVOs qualitative detection was assessed by fluorescence microscope. RESULTS: The growth of MDA-MB-231 cells was suppressed after treatment with [VO (bpy)2 Cl] Cl complex, in a dose-dependent manner. The affinity for apoptotic cell death induction was shown through the increase in the sub G0 peak, the percentage of early and late apoptotic phases, and the elevation in caspase 3 levels. The affinity for autophagic cell death induction was observed through the increase in the G0/G1 phase, G2/M arrest, the increase of AVOs red fluorescence and elevated LC3 levels. The affinity for notch pathway inhibition was shown through the suppression of Notch 1 gene expression. CONCLUSION: [VO (bpy)2 Cl] Cl complex, could be a promising candidate as therapeutic agent targeting different therapeutic targets including apoptosis, autophagy and notch signaling pathways.

Halevas, E., Papadopoulos, T.A., Swanson, C.H.*, et al.* (2019) In-depth synthetic, physicochemical and in vitro biological investigation of a new ternary V(IV) antioxidant material based on curcumin. *Journal of Inorganic Biochemistry,* 191: 94-111.
Keywords: Antioxidants/chemical synthesis/chemistry/pharmacology; Crystallography, X-Ray; Curcumin/chemical synthesis/chemistry/pharmacology; In Vitro Techniques; Reactive Oxygen Species/metabolism; Spectrum Analysis/methods; Bioreactivity profile and antioxidant agent; Cell metabolism inhibition and DNA degradation; Crystal structure and DFT calculations; Hybrid metallopharmaceutical; ROS-suppression; Vanadium-curcumin complex

Abstract:
Curcumin is a natural product with a broad spectrum of beneficial properties relating to pharmaceutical applications, extending from traditional remedies to modern cosmetics. The biological activity of such pigments, however, is limited by their solubility and bioavailability, thereby necessitating new ways of achieving optimal tissue cellular response and efficacy as drugs. Metal ion complexation provides a significant route toward improvement of curcumin stability and biological activity, with vanadium being a representative such metal ion, amply encountered in biological systems and exhibiting exogenous bioactivity through potential pharmaceuticals. Driven by the need to optimally increase curcumin bioavailability and bioactivity through complexation, synthetic efforts were launched to seek out stable species, ultimately leading to the synthesis and isolation of a new ternary V(IV)-curcumin-(2,2'-bipyridine) complex. Physicochemical characterization (elemental analysis, FT-IR, Thermogravimetry (TGA), UV-Visible, NMR, ESI-MS, Fluorescence, X-rays) portrayed the solid-state and solution properties of the ternary complex. Pulsed-EPR spectroscopy, in frozen solutions, suggested the presence of two species, cis- and trans-conformers. Density Functional Theory (DFT) calculations revealed the salient features and energetics of the two conformers, thereby complementing EPR spectroscopy. The well-described profile of the vanadium species led to its in vitro biological investigation involving toxicity, cell metabolism inhibition in S. cerevisiae cultures, Reactive Oxygen Species (ROS)-suppressing capacity, lipid peroxidation, and plasmid DNA degradation. A multitude of bio-assays and methodologies, in comparison to free curcumin, showed that it exhibits its antioxidant potential in a concentration-dependent fashion, thereby formulating a bioreactivity profile supporting development of new efficient vanado-pharmaceuticals, targeting (extra)intra-cellular processes under (patho)physiological conditions.

Korbecki, J., Gutowska, I., Wiercioch, M.*, et al.* (2020) Sodium Orthovanadate Changes Fatty Acid Composition and Increased Expression of Stearoyl-Coenzyme A Desaturase in THP-1 Macrophages. *Biological Trace Element Research,* 193(1): 152-161.

Available at: https://link.springer.com/content/pdf/10.1007/s12011-019-01699-2.pdf
Keywords: Desaturase; Fatty acids; Macrophage; Sodium orthovanadate; THP-1; acyl coenzyme A desaturase; acyl coenzyme A desaturase 1; arachidonic acid; docosahexaenoic acid; docosapentaenoic acid; icosapentaenoic acid; linoleic acid; oleic acid; palmitic acid; palmitoleic acid; phorbol 13 acetate 12 myristate; stearic acid; vanadate sodium; Article; controlled study; FADS1 gene; FADS2 gene; gas chromatography; gene; gene expression; human; human cell; in vitro study; lipid composition; real time polymerase chain reaction; SCD gene; THP-1 cell line; upregulation

Abstract:
Vanadium compounds are promising antidiabetic agents. In addition to regulating glucose metabolism, they also alter lipid metabolism. Due to the clear association between diabetes and atherosclerosis, the purpose of the present study was to assess the effect of sodium orthovanadate on the amount of individual fatty acids and the expression of stearoyl-coenzyme A desaturase (SCD or Δ9-desaturase), Δ5-desaturase, and Δ6-desaturase in macrophages. THP-1 macrophages differentiated with phorbol 12-myristate 13-acetate (PMA) were incubated in vitro for 48 h with 1 μM or 10 μM sodium orthovanadate (Na3VO4). The estimation of fatty acid composition was performed by gas chromatography. Expressions of the genes SCD, fatty acid desaturase 1 (FADS1), and fatty acid desaturase 2 (FADS2) were tested by qRT-PCR. Sodium orthovanadate in THP-1 macrophages increased the amount of saturated fatty acids (SFA) such as palmitic acid and stearic acid, as well as monounsaturated fatty acids (MUFA)—oleic acid and palmitoleic acid. Sodium orthovanadate caused an upregulation of SCD expression. Sodium orthovanadate at the given concentrations did not affect the amount of polyunsaturated fatty acids (PUFA) such as linoleic acid, arachidonic acid, eicosapentaenoic acid (EPA), docosapentaenoic acid (DPA), and docosahexaenoic acid (DHA). In conclusion, sodium orthovanadate changed SFA and MUFA composition in THP-1 macrophages and increased expression of SCD. Sodium orthovanadate did not affect the amount of any PUFA. This was associated with a lack of influence on the expression of FADS1 and FADS2. © 2019, The Author(s).

Lu, L.P., Liu, J.H., Cen, S.H.*, et al.* (2019) Discovery of vanadium complexes bearing tridentate schiff base ligands as novel LSD1 inhibitors. *Bioorganic & Medicinal Chemistry Letters,* 29(4): 681-683.
Keywords: Histone Demethylases/antagonists & inhibitors; Humans; Ligands; Molecular Docking Simulation; Schiff Bases/chemistry; Structure-Activity Relationship; Vanadium Compounds/chemistry; Anticancer; LSD1; MAO; Vanadium complex

Abstract:
Lysine specific demethylase (LSD1) plays a pivotal role in epigenetic modulation of gene expression. Abberrant expression of LSD1 was associated with the progress and oncogenesis of multiple human cancers. Herein, we report the preliminary anti-LSD1 evaluation of the synthetic vanadium (V) complexes. Among them, complex 2 showed a moderate inhibitory effect against LSD1 with IC50 value of 19.0muM, as well as good selectivity over MAO-A/B. Complex 2 is the first vanadium based LSD1 inhibitor, which provides a novel scaffold for the development of LSD1 inhibitor.

Ma, W., Liu, J., Xin, Y.*, et al.* (2020) Clinically colorimetric diagnostics of blood glucose levels based on vanadium oxide quantum dots enzyme mimics. *Microchemical Journal,* 153.
Keywords: Detection of H2O2 and glucose; Kinetic study; Peroxidase-like activity; Vanadium oxide quantum dots

Abstract:
The environmental vulnerability of the natural enzyme have always been the most concerned issue in the diagnosis of blood glucose levels, which could be settled by the discovery and application of nanozyme mimics. However, the nanozyme still encountered with the problem of complex preparation process or low enzymatic activities. Herein, peroxidase-like vanadium oxide quantum dots (VOxQDs) were synthesized via a one-step bottom-up solvothermal method using vanadium (Ⅲ) trichloride (VCl3) powder as the precursor. Besides, the most favorable temperature and solvent for VOxQDs synthesis were confirmed. Due to the inherent properties of quantum dots, including larger specific surface areas and more active sites, the as-prepared VOxQDs exhibited 43 times lower value of Km and 32 times higher one of Vmax than those of natural peroxidase using H2O2 as the substrate, indicating the higher affinity and stronger peroxidase-like activity of the VOxQDs nanozymes. Accordingly, a facile and sensitive colorimetric sensor to detect glucose was designed via the integrated enzyme system of VOxQDs and glucose oxidase, which showed wider linear range of 0.005 - 2 mM glucose and lower limit of detection of 1.7 μM compared with those of many other peroxidase-like nanozymes. Especially, the colorimetric sensor was demonstrated with reliable and satisfactory performance in detection of glucose in human serum, which was in good accordance with the clinical results provided from the domestic hospital. © 2019 Elsevier B.V.

Noriega, L., Castro, M.E., Perez-Aguilar, J.M.*, et al.* (2020) Oxidovanadium(V) complexes as promising anticancer photosensitizers. *Journal of Inorganic Biochemistry,* 203.**
Keywords: Anticancer activity; Density Functional Theory calculations; Oxido-vanadium(V) complexes; Photodynamic therapy; Photosensitizer; 1 [[(5 chloro 2 oxidophenyl)imino]methyl]naphthalen 2 olate butoxido oxidovanadium; 1 [[(5 chloro 2 oxidophenyl)imino]methyl]naphthalen 2 olate propoxido oxidovanadium; alcohol; antineoplastic agent; oxygen; photosensitizing agent; Schiff base; triethylammonium 1 [[(5 chloro 2 oxidophenyl)imino]methyl]naphthalene 2 olate di oxido vanadate; unclassified drug; vanadium derivative; water; antineoplastic activity; aqueous solution; Article; density functional theory; electron transport; photochemistry; solvation; solvent effect; surface property; ultraviolet visible spectroscopy

Abstract:
Photodynamic therapy (PDT) is an alternative treatment widely used against cancer. PDT requires molecular systems, known as photosensitizers (PS), which not only exhibit strong absorption at a particular wavelength range, but also need to be selectively accumulated inside cancer cells. PS are activated by specific wavelengths that cause tumor cell death by mechanisms related with oxidative stress. In this paper, three oxidovanadium(V) complexes linked to a Schiff base, which exhibit anticancer activity by displaying desirable accumulation inside malignant cells, are studied using Density Functional Theory (DFT) and Time Dependent-DFT (TD-DFT) methodologies to characterize their structural and photophysical properties as possible PS. The maximum absorption of these complexes in aqueous solution was predicted to be approximately 460 nm presenting a ligand-to-metal charge transfer. Additionally, we describe the photodynamic type reaction that these complexes can undergo when considered as PS candidates. Our results suggest that the system, containing triethylammonium as substituent, is the most suitable complex to act both as PS and as a possible therapeutic candidate in PDT. © 2019 Elsevier Inc.

Rambaran, V.H., Saumya, S.M., Roy, S.*, et al.* (2020) The design, synthesis and in vivo biological evaluations of [V(IV)O(2,6-pyridine diacetatato) (H2O)2] (PDOV): Featuring its

prolonged glucose lowering effect and non-toxic nature. *Inorganica Chimica Acta,* 504: 119448.

Abstract:
The synthesis and characterization of a novel vanadyl complex, [V(IV)O(2,6-pyridine diacetatato)(H2O)2] (PDOV) is reported. The pH-controlled release of the complex from polymer coated mesoporous silica was demonstrated for possible oral administration; results showed that release at pH 2 was significantly lower than that at pH 7.4. The said complex was subsequently screened for possible anti-diabetic activity, via an in vivo dose-response study (intraperitoneal and oral supplementation of PDOV) for 90 days in streptozotocin (STZ) induced diabetic rats. The results revealed that over a 90 day period, intraperitoneal administration of PDOV (at a dose of 75 mg/kgbw) and oral administration of the PDOV (at a dose of 100 mg/kgbw) were effective in suppressing the hyperglycemic state in the diabetic subjects. Exposure to PDOV was found to have little impact on the insulin levels of diabetics; however improved urea, creatinine, AST and ALT levels were noted. ".

Rehder, D. (2012) The potentiality of vanadium in medicinal applications. *Future Medicinal Chemistry,* 4(14): 1823-1837.
Keywords: Animals; Antineoplastic Agents/chemistry/pharmacokinetics/pharmacology/therapeutic use; Blood Glucose/metabolism; Diabetes Mellitus/drug therapy/metabolism; Humans; Hypoglycemic Agents/chemistry/pharmacokinetics/pharmacology/therapeutic use; Insulin/metabolism; Neoplasms/drug therapy/metabolism; Vanadium Compounds/chemistry/pharmacokinetics/pharmacology/therapeutic use

Abstract:
In the early treatment of diabetes with vanadium, inorganic vanadium compounds have been the focus of attention; organic vanadium compounds are nowadays increasingly attracting attention. A key compound is bis(maltolato)oxidovanadium, which became introduced into clinical tests Phase IIa. Organic ligands help modulate the bioavailability, transport and targeting mechanism of a vanadium compound. Commonly, however, the active onsite species is vanadyl (VO(2+)) or vanadate (H(2)VO(4) (-)), generated by biospeciation. The mode of operation can be ascribed to interaction of vanadate with phosphatases and kinases, and to modulation of the level of reactive oxygen species interfering with phosphatases and/or DNA. This operating mode has also been inferred for most cancerostatic vanadium compounds, although some, for example vanadocenes, may directly intercalate with DNA. Novel medicinal potentiality of vanadium compounds is geared towards endemic diseases in tropical countries, in particular leishmaniasis, Chagas' disease and amoebiasis, and viral infections such as Dengue fever, SARS and HIV.

Wang, T., Liu, X., Han, D.*, et al.* (2020) Biomass derived the V-doped carbon/Bi2O3 composite for efficient photocatalysts. *Environmental Research,* 182.
Keywords: Biological extract; Catalyst mechanism; Lignin-based carbon; One-step carbonization; Vanadium-doped; bismuth derivative; bismuth oxide; carbon; lignin; sodium lignosulfonate; unclassified drug; vanadium; catalyst; coating; composite; plant extract; Article; bamboo; biomass; carbon source; carbonization; photocatalysis; priority journal; pulping; pyrolysis; synthesis

Abstract:
This work focused on the utilization of biological extract for the preparation of lignin-based carbon composites materials and used in the field of photocatalysis. A straightforward one-

step carbonization way has been developed to prepare vanadium-doped lignin-based carbon/Bi2O3 composites photocatalyst by using sodium lignosulfonate as the carbon source and catalyst. The application of lignin as the carbon source to form photocatalyst support tends to control the uniform distribution. At the same time, sodium lignosulfonate as the catalyst could break down the BiVO4 during carbonization process. A series of characterizations demonstrated the BiVO4 was transformed into Bi2O3 and vanadium-doped lignin-based carbon. The possible synthesis process was proposed. Moreover, the novel V-doped carbon/Bi2O3 composites photocatalyst displayed higher photocatalytic activity than bare BiVO4. A possible photocatalytic mechanism was also discussed. This work provided new insight into the lignin-based carbon materials. © 2019 Elsevier Inc.

Zhang, T., Li, Z., Hou, W.*, et al.* (2020) Nanomaterials for implantable batteries to power cardiac devices. *Materials Today Nano,* 9: 100070.
Keywords: Implantable batteries; Nanomaterials; Energy density; Energy storage

Abstract:
Batteries have been used in various biomedical devices, such as neurostimulators, cardiac pacemakers, and implantable cardiac defibrillators. Compared to applications in electronics and electric vehicles, those implantable batteries need to be extremely safe and stable as they are placed inside human bodies to play a vital role in curing human diseases. They also need to have high energy density to save volume and weight in the limited space inside organs, such as heart ventricles. Not only that, complete packaging with no leakage possibility and extremely low self-discharge rate are also required to ensure the safe operation of devices without interruption for an 8–10 years battery life. These requirements are considerably demanding, and primary batteries are widely used in biomedical batteries to meet those requirements. Especially for cardiology applications, Li-CFx and Li-SVO (silver vanadium oxide) batteries have been used in industry for decades, and several improvements have been made to push overall battery performance to a theoretical limit. With recent progress made in enhanced treatment methods, such as communication functions among multiple leadless pacemakers for a more accurate sensing mechanism, those devices require even higher power input in order to drive new functions without losing life expectancy. In this review, we reviewed principles and recent progress on using nanomaterials in these battery systems for biomedical applications, such as how to further improve electrochemical performance and increase the reversibility of these battery systems as a potential solution to prolong their longevity inside human bodies. ".

Zhu Haifeng, Wang Yinghou, Liu Dan*, et al.* (2020) Vanadium-Rutin Complex Sensitizes Breast Cancer Cells Via Modulation of P53/bax/bcl2/vegf Correlated with Apoptotic Events. *Acta Poloniae Pharmaceutica,* 77(1): 89-98.
Keywords: apoptosis; breast cancer; DNA binding; in vitro; vanadium-rutin; OXIDATIVE STRESS; FLAVONOIDS; QUERCETIN; DNA; PROLIFERATION; STATISTICS; INTEGRITY; PROFILES; DISEASE; IODINE; Pharmacology & Pharmacy

Abstract:
In pursuit of a novel approach in breast cancer therapy, we explored the ability of vanadium-rutin complex to eradicate cancer by efficiently targeting various apoptotic pathways on human breast cancer cell lines. We provide direct proof of the chemotherapeutic potential of the vanadium-rutin complex by activating p-53 dependent intrinsic apoptosis and modulating the VEGF pathways. The complex was also capable of binding and cleaving CT-DNA at different concentrations. The complex was able to inhibit cell viability at 100 and 150 mu M doses in both MCF7 and MDA-MB-231 cells. Furthermore, the complex successfully

initiated apoptosis in both cell lines by activating the p53 dependent intrinsic apoptotic pathway. In vitro studies also established that the complex modulated p53, Bax, Bcl2 and VEGF expressions and induced DNA fragmentation in both the cell lines.

5. ENVIRONMENTAL EFFECTS in PLANTS and SOIL

Aihemaiti, A., Gao, Y., Meng, Y.*, et al.* (2020) Review of plant-vanadium physiological interactions, bioaccumulation, and bioremediation of vanadium-contaminated sites. *The Science of the Total Environment,* 712: 135637.
Keywords: Bioaccumulation; Bioremediation; Plant physiology; Tolerance; Vanadium

Abstract:
Vanadium is a multivalent redox-sensitive metal that is widely distributed in the environment. Low levels of vanadium elevate plant height, root length, and biomass production due to enhanced chlorophyll biosynthesis, seed germination, essential element uptake, and nitrogen assimilation and utilization. However, high vanadium concentrations disrupt energy metabolism and matter cycling; inhibit key enzymes mediating energy production, protein synthesis, ion transportation, and other important physiological processes; and lead to growth retardation, root and shoot abnormalities, and even death of plants. The threshold level of toxicity is highly plant species-specific, and in most cases, the half maximal effective concentration (EC50) of vanadium for plants grown under hydroponic conditions and in soil varies from 1 to 50 mg/L, and from 18 to 510 mg/kg, respectively. Plants such as Chinese green mustard, chickpea, and bunny cactus could accumulate high concentrations of vanadium in their tissues, and thus are suitable for decontaminating and reclaiming of vanadium-polluted soils on a large scale. Soil pH, organic matter, and the contents of iron and aluminum (hydr)oxides, phosphorus, calcium, and other coexisting elements affect the bioavailability, toxicity, and plant uptake of vanadium. Mediation of these conditions or properties in vanadium-contaminated soils could improve plant tolerance, accumulation, or exclusion, thereby enhancing phytoremediation efficiency. Phytoremediation with the assistance of soil amendments and microorganisms is a promising method for decontamination of vanadium polluted soils.

Ali, A., Pan, J., Yan, J.*, et al.* (2020) Geochemical characteristics and uranium mineralization exploration potential of late Miocene molasse sediments of NW Himalayan foreland basin Pakistan. *Arabian Journal of Geosciences,* 13(3).
Keywords: Geochemical exploration; Paleo-weathering; Provenance; Sandstone; Sediment-recycling; Siwaliks; chemical weapon; chemical weathering; concentration (composition); exploration; foreland basin; geochemistry; igneous rock; mineralization; Miocene; molasse; sediment chemistry; uranium; Pakistan

Abstract:
This study has defined the provenance, tectonic settings, paleo-weathering, sediment-recycling, and sandstone-type uranium mineralization potential of late Miocene mid-Siwalik Dhok Pathan Formation from Surghar-Shingar Range of NW-Himalayan foreland Fold-and-Thrust-belt. Twenty-six sandstone samples were analyzed on XRF and ICP-MS to determine concentrations of different geochemical species. These Himalayan molasse sediments are moderately rich in quartz. The other framework gains include igno-metamorphic and sedimentary lithic fragments (second in abundance after quartz), feldspars, and dominance of ferroan phlogopite (biotite) over white mica. Garnet, epidot, amphibole, magnetite, tourmaline, rutile, zircon, monazite, and uranothorite are present as common accessory minerals. These sandstones are generally classified as lithic arenite, greywacke, and arkose

on the basis of geochemistry. These molasse sediments have recorded the signatures of first-cycle detritus mainly contributed by felsic-igneous rocks in collision-arc tectonic settings. Chemical index of weathering and alteration (CIW and CIA) revealed slight/low weathering of source areas. The REE patterns and Eu/Eu* values are also supporting felsic-igneous provenance for the studied samples. The median high concentrations (ppm) of vanadium (V 79.57), thorium (Th 10.08) and uranium (U 33.05) in sandstone, positive correlation of U with Al2O3 (r = 0.22), deposition in strong anoxic environments are the characteristic features of uranium enrichment/accumulation processes in sandstone-type environments thus signifying good potential for uranium exploration. © 2020, Saudi Society for Geosciences.

Ali, F., Jilani, G., Fahim, R.*, et al.* (2019) Functional and structural roles of wiry and sturdy rooted emerged macrophytes root functional traits in the abatement of nutrients and metals. *Journal of Environmental Management,* 249.**
Keywords: Fibrous-root; Nutrients; Root-traits; Sediments; Thick-root; Toxic-metals

Abstract:
Macrophytes root functional traits (RFTs) play central roles in the cycling of aquatic contaminants, and there is evidence that emerged macrophytes differ in macronutrients (N and P) and heavy metals (Cd, Cr, Cu, Ni, Pb, V, Zn) abatement due to difference in RFTs. However, it remains ambiguous what root type of emerged macrophytes and their RFTs play more significant roles in the mineralization and removal of nutrients and heavy metals in aquatic systems. There is a clear need of intensive investigation on fibrous- and thick-root emerged macrophytes and their diverse RFTs in previous literatures to identify appropriate plants for phytoremediation technology. Morphological, physiological, anatomical, and symbiotic RFTs of fibrous-root emerged macrophytes favour the nutrients and heavy metals uptake. Thick-root emerged macrophytes with greater root rhizomes, lignifications and suberization illustrate tolerance under higher stress. Besides higher removal abilities of fibrous-root macrophytes, their limited lifespan and stress tolerance are the challenges for long-term removal of metals. Thus, it is still infancy to wrap up at once that the fibrous-root macrophytes and their RFTs are equally efficient for removal of heavy metals from aquatic ecosystems. Several advance techniques include cisgenesis intragenesis, symbiotic endophytes, and plant-harboring microbes are emerging to improve the RFTs of plants. These techniques need to be employed in emerged macrophytes to achieve desirable RFTs and targets. Still, these macrophytes require advanced studies on emerging contaminants, such as pharmaceutical and personal care products, organic carbon stability, and mitigation of greenhouse gases emission. © 2019 Elsevier Ltd.

Almeida, M.C., Branco, R. & Morais, P.V. (2020) Response to vanadate exposure in Ochrobactrum tritici strains. *PloS One,* 15(2): e0229359.
Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7039435/pdf/pone.0229359.pdf

Abstract:
Vanadium is a transition metal that has been added recently to the EU list of Raw Critical Metals. The growing needs of vanadium primarily in the steel industry justify its increasing economic value. However, because mining of vanadium sources (i. e. ores, concentrates and vanadiferous slags) is expanding, so is vanadium environmental contamination. Bioleaching comes forth as smart strategy to deal with supply demand and environmental contamination. It requires organisms that are able to mobilize the metal and at the same time are resistant to the leachate generated. Here, we investigated the molecular

mechanisms underlying vanadium resistance in Ochrobactrum tritici strains. The highly resistant strain 5bvl1 was able to grow at concentrations > 30 mM vanadate, while the O. tritici type strain only tolerated < 3 mM vanadate concentrations. Screening of O. tritici single mutants (chrA, chrC, chrF and recA) growth during vanadate exposure revealed that vanadate resistance was associated with chromate resistance mechanisms (in particular ChrA, an efflux pump and ChrC, a superoxide dismutase). We also showed that sensitivity to vanadate was correlated with increased accumulation of vanadate intracellularly, while in resistant cells this was not found. Other up-regulated proteins found during vanadate exposure were ABC transporters for methionine and iron, suggesting that cellular responses to vanadate toxicity may also induce changes in unspecific transport and chelation of vanadate.

Amato-Lourenco, L.F., Ranieri, G.R., de Oliveira Souza, V.C.*, et al.* (2020) Edible weeds: Are urban environments fit for foraging? *Science of the Total Environment,* 698.
Available at:
https://www.sciencedirect.com/science/article/pii/S0048969719339373/pdfft?md5=35170162ad92607fc150fa309e9a44a2&pid=1-s2.0-S0048969719339373-main.pdf
Keywords: Biomonitoring; Edible weeds; Foraging; Traffic pollution; Urban environment; Wild edible plants; Urban planning; Edible plants; Urban environments; Pollution; aluminum; arsenic; barium; cadmium; chromium; cobalt; lead; manganese; nickel; rubidium; vanadium; zinc; heavy metal; concentration (composition); edible species; traffic emission; urban pollution; weed; Amaranthus; Article; Brazil; concentration (parameter); controlled study; edible plant; edible weed; highway; nonhuman; Plantago; Plantago tomentosa; priority journal; Taraxacum officinale; traffic; urban area; chemistry; city; dietary exposure; environmental monitoring; soil; soil pollutant; Sao Paulo [Brazil]; Cities; Metals, Heavy; Plant Weeds; Soil Pollutants

Abstract:
Foraging wild-growing edible plants (WEPs) is a re-emerging practice with increasing popularity worldwide, including in urban areas. However, in cities, this practice raises questions about the safety of foraging these plants for human consumption, due to the potential exposure of plants to higher levels of pollutants. In this study, the concentration of 12 elements (Al, V, Cr, Mn, Co, Ni, Zn, As, Rb, Cd, Ba and Pb) in three different WEPs (Amaranthus spp., Plantago tomentosa and Taraxacum officinale) were determined according to different traffic categories in the municipality of São Paulo. Additionally, plants were sampled within the inner areas of three municipal parks in the same study region. Different gradients of elemental concentrations were obtained according to the traffic categories. Freeways presented higher concentrations of several elements than local roads or parks. For the WEPs collected along freeways and some plants along arterial roads, the concentrations of Pb exceeded safety levels for human consumption. Our data suggest that foraging in large urban centres should be performed preferentially in low-traffic areas. © 2019 Elsevier B.V.

Aullón Alcaine, A., Schulz, C., Bundschuh, J.*, et al.* (2020) Hydrogeochemical controls on the mobility of arsenic, fluoride and other geogenic co-contaminants in the shallow aquifers of northeastern La Pampa Province in Argentina. *Science of the Total Environment,* 715: 136671.
Keywords: Arsenic; Fluoride; Shallow groundwater; La Pampa; Loess sediments; Volcanic ash

Abstract:
Elevated Arsenic (As) and Fluoride (F) concentrations in groundwater have been studied in

the shallow aquifers of northeastern of La Pampa province, in the Chaco-Pampean plain, Argentina. The source of As and co-contaminants is mainly geogenic, from the weathering of volcanic ash and loess (rhyolitic glass) that erupted from the Andean volcanic range. In this study we have assessed the groundwater quality in two semi-arid areas of La Pampa. We have also identified the spatial distribution of As and co-contaminants in groundwater and determined the major factors controlling the mobilization of As in the shallow aquifers. The groundwater samples were circum-neutral to alkaline (7.4 to 9.2), oxidizing (Eh ~0.24 V) and characterized by high salinity (EC = 456–11,400 μS/cm) and Na+–HCO3– water types in recharge areas. Carbonate concretions ("tosca") were abundant in the upper layers of the shallow aquifer. The concentration of total As (5.6 to 535 μg/L) and F (0.5 to 14.2 mg/L) were heterogeneous and exceeded the recommended WHO Guidelines and the Argentine Standards for drinking water. The predominant As species were arsenate As(V) oxyanions, determined by thermodynamic calculations. Arsenic was positively correlated with bicarbonate (HCO3−), fluoride (F), boron (B) and vanadium (V), but negatively correlated with iron (Fe), aluminium (Al), and manganese (Mn), which were present in low concentrations. The highest amount of As in sediments was from the surface of the dry lake. The mechanisms for As mobilization are associated with multiple factors: geochemical reactions, hydrogeological characteristics of the local aquifer and climatic factors. Desorption of As(V) at high pH, and ion competition for adsorption sites are considered the principal mechanisms for As mobilization in the shallow aquifers. In addition, the long-term consumption of the groundwater could pose a threat for the health of the local community and low cost remediation techniques are required to improve the drinking water quality. ".

Bai, X., Wang, J., Ding, X.*, et al.* (2020) Proteomic alteration of albumen by dietary vanadium in commercial egg-type layers. *Poultry Science,* 99(3): 1705-1716.
Available at:
https://www.sciencedirect.com/science/article/pii/S0032579119491761/pdfft?md5=dd4a3cb0c6e0bd3fc19ba9192d9b6d4b&pid=1-s2.0-S0032579119491761-main.pdf
Keywords: albumen; vanadium; quantitative proteomic

Abstract:
Vanadium (V) is an ultratrace metal with the insulin-tropic properties and is often researched as the diabetes drug. However, in animals, V has been reported to have toxic effects on the development, immunity, oxidation–reduction equilibrium, gastrointestinal function, and so forth. Especially in poultry, supplementation of more than 10 mg of V/kg in the layer diets has been shown to adversely affect the egg production and egg quality. In this study, we supplemented 0 mg of V/kg, 5 mg of V/kg, and 10 mg of V/kg in the layer diets for 35 D and examined the quantitative proteomics of albumen for finding the possible target signaling pathway and mechanism of V action and made the preliminary verification. In contrast to the control group, V resulted in a significant drop in the albumen height, and in oviduct ampulla, the activity of total antioxidant capacity and glutathione peroxidase significantly decreased (P = 0.01, P = 0.02), the content of malonic dialdehyde significantly increased (P = 0.01), and the apoptosis rate significantly increased in the 5-mg V/kg and 10-mg V/kg treatment groups ($P < 0.01$). V affected 36 differentially accumulated proteins in albumen, with 23 proteins upregulated and 13 proteins downregulated. The expressions of innate protein albumen lysozyme (Q6LEL2), vitellogenin-2 (P02845), and the F1NWD0 protein in albumen belonged to the P53 family were significantly reduced, in contrast to the control ($P < 0.05$), and the expression of riboflavin-binding protein (P02752) was significantly improved ($P < 0.05$). The Hippo signaling pathway-fly, which is suitable for the key protein P53 as the most significantly affected network, might be important for discriminating V. ".

Bakir, O. & Agar, G. (2020) Ameliorating Effect of Boric Acid Against Vanadium Toxicity in Wheat (Triticum aestivum L.). ***Arabian Journal for Science and Engineering,*** **45: 113-120.**
Keywords: Antioxidant enzyme; Boric acid; Genomic template stability; Vanadium

Abstract:
Heavy metal pollution, which is one of the most important environmental problems, has a significant effect on plant productivity. Vanadium (V) is considered one of the most important elements of the twenty-first century due to its high consumption in industries. Morphological and physiological measurements have been performed in V studies, but there are deficiencies in molecular studies. The purpose of the present work was to elucidate the effects of V on enzymes activity, DNA damage levels and genomic template stability (GTS%) in *Triticum aestivum* L., as well as to investigate whether boric acid (BA) has preventive effects on these changes. Antioxidant enzyme activities were determined by SOD (superoxide dismutase), POD (peroxidase) and MDA (malondialdehyde) level. The inter-simple sequence repeats polymerase chain reaction (ISSR-PCR) assay was used to determine the genotoxic effects of V on DNA. According to the obtained results, while V stress increased MDA level and POD enzyme activity, SOD enzyme activity decreased. When V and BA were applied together, MDA level decreased and SOD and POD enzyme activities increased. All doses of V (4.4, 6.6, 8.8 mM) resulted in DNA damage and decreased GTS%. On the other hand, different concentrations of BA (4 and 8 mM) combined with V decreased the toxic effects of V. The results suggested that V could also have negative effects on wheat plants by increasing DNA damage and lipid peroxidation, and BA has an antagonistic effect against V toxicity. BA may be an alternative to reduce genetic damage in plants.

Chen, L., Zhu, Y.-., Luo, H.-*, et al.* (2020) Characteristic of adsorption, desorption, and co-transport of vanadium on humic acid colloid. ***Ecotoxicology and Environmental Safety,*** **190.**
Keywords: Adsorption; Co-transport; Desorption; humic acid colloid; Vanadium; functional group; ground water; humic acid; colloid; concentration (composition); environmental fate; porous medium; transport process; Article; concentration response; Fourier transform infrared spectroscopy; ionic strength; pH; pollution transport; scanning electron microscopy; soil; temperature dependence

Abstract:
Understanding the interactions between humic acid colloid (HAC) and vanadium (V) in soils is of great importance in forecasting the behaviors and fates of V in the soil and groundwater systems. This study investigated the characteristics and factors that affect V adsorption-desorption by the HAC; meanwhile, we also explored the co-transport of the HAC and V in a saturated porous media. Scanning Electronic Microscopy micrographs showed the variation of morphological features on the surface of the HAC before and after V adsorption. Fourier transform infrared spectroscopy spectra revealed that the presence of hydroxyl, carboxyl, carbonyl, carbon-carbon double bond, amino, and aromatic ring on the HAC participated in V adsorption. The adsorption isotherms were well described by the Langmuir model, and the adsorption kinetics of the HAC was better described by the pseudo-first-order kinetic models. The adsorption-desorption was strongly dependent on the initial V concentration, solution pH, and temperature. The maximum adsorption amount was 861.17 mg g−1 by 200 mg L−1 HAC at the initial V concentration of 500 mg L−1, and the corresponding desorption amount was 15.13 mg g−1. These results showed that the HAC had high fixation capacity of V in soil. In addition, the HAC sped up the mobility of V; however, it decreased mass of migration of V in the saturated quartz sand column. These

results are expected to provide insight into the potential impact of HAC on geochemical behaviours of V in vulnerable ecosystems. © 2019 Elsevier Inc.

Davila, R.B., Fontes, M.P.F., Pacheco, A.A.*, et al.* (2020) Heavy metals in iron ore tailings and floodplain soils affected by the Samarco dam collapse in Brazil. *Science of the Total Environment,* 709.
Keywords: Doce River; Environmental pollution; Health risk assessment; Mariana disaster; Mine waste; Sequential extraction; Banks (bodies of water); Contamination; Disasters; Extraction; Floods; Health risks; Heavy metals; Iron ores; Ore tailings; Positive ions; Risk assessment; Risk perception; Rivers; Sediments; Soils; BCR sequential extraction; Environmental pollutions; Flood-plain soils; Heavy metal contents; Hydroelectric plant; Mine wastes; Soils and sediments; River pollution; arsenic; barium; chromium; cobalt; copper; heavy metal; nickel; vanadium; zinc; dam failure; floodplain; health risk; iron ore; tailings; adult; Article; Brazil; cancer risk; child; controlled study; dam (barrier); health hazard; human; mine tailings; pollution; priority journal; risk algorithm; sediment; soil pollution; structure collapse; Minas Gerais

Abstract:
In November 2015, the Fundão Dam collapsed releasing about 35 million m− 3 of iron ore tailings into the environment, which covered approximately 15 km2 of floodplain soils. Four years later, there is still great concern and controversy regarding contamination by heavy metals in the affected areas. Thus, the present study sought to evaluate the heavy metal contents and its distribution in tailings and non-affected soils. Tailings samples were collected in the stretch between Bento Rodrigues and the Candonga hydroelectric plant, in addition to a sample inside the Fundão Dam. Non-affected soils and river sediments from the same region were also collected as a control group. The heavy metal contents in the tailings were lower than in non-affected samples from the same area, discarding the hypothesis of contamination by the tailings mud. The non-affected samples presented high levels of As, Ba, Co, Cr, Cu, Ni and Zn, with at least one sample exceeding the quality reference values (QRV's) established for Minas Gerais state, which indicated a scenario of pre-disaster contamination for the Doce River watershed. Most of the elements (As, Cr, Cu, Ni, V and Zn) were extracted in the residual fraction of the BCR sequential extraction, presenting low risk of release in nature. The health risk assessment for As estimated that all the non-affected soils and sediments from Gualaxo do Norte, Carmo and Doce rivers have carcinogenic risk higher than the acceptable value for children. From our results, it is more likely to conclude that the deposited tailings are not a time-bomb for heavy metals contamination in the region. © 2018.

Di Carlo, E., Boullemant, A. & Courtney, R. (2020) Ecotoxicological risk assessment of revegetated bauxite residue: Implications for future rehabilitation programmes. *Science of the Total Environment,* 698: 134344.
Available at:
https://www.sciencedirect.com/science/article/pii/S0048969719343359/pdfft?md5=3e05d87ac7b3c30b4c6d1bd10edf9c6f&pid=1-s2.0-S0048969719343359-main.pdf
Keywords: Elements bioavailability; Mine tailings; Phytotoxkit™; Remediation; RHIZOtest; Alkalinity; Alumina; Aluminum oxide; Biogeochemistry; Bioremediation; Chemical contamination; Gypsum; Organic compounds; pH; Revegetation; Seed; Soil conservation; Tailings; Trace elements; Ecotoxicological risk assessment; Ecotoxicological risks; Implications for futures; Phytotoxkit; Rehabilitation strategy; Trace element uptake; Risk assessment; aluminum; arsenic; bauxite residue; calcium sulfate; chromium; organic matter; trace element; unclassified drug; vanadium; bauxite; bioavailability; concentration

(composition); ecotoxicology; environmental risk; mine waste; phytoremediation; phytotoxicity; Article; bioassay; concentration (parameter); controlled study; germination; Lepidium sativum; nonhuman; perennial ryegrass; plant development; plant stress; priority journal; seedling; Sinapis alba; soil rehabilitation; soil treatment; sorghum; analysis; chemistry; ecosystem restoration; microbiology; salinity; Sinapis; soil; soil pollutant; toxicity; Animalia; Lolium perenne; Sorghum bicolor bicolor; Biodegradation, Environmental; Environmental Restoration and Remediation; Soil Microbiology; Soil Pollutants

Abstract:
Around 3 billion tonnes of bauxite residue (BR), the by-product of alumina extraction, have been produced and stockpiled worldwide, representing a potential risk for the environment due to the high alkalinity and the presence of relatively high concentrations of trace elements. Phytoremediation (or simply revegetation) is regarded as the most promising in situ remediation option to mitigate the environmental risk that might arise from the land-disposal of BR. Rehabilitation strategies (including the incorporation of amendments such as gypsum and organic matter) have been employed to address the main limitations to plant establishment and growth on BR, typically the high alkalinity, salinity and sodicity. However, the potential for trace element uptake and phytotoxicity have been largely unreported in revegetated BRs. In order to assess the ecotoxicological risk, samples of previously revegetated BR were collected from the field, characterized in the laboratory, and used to conduct ex-situ plant bioassays (Phytotoxkit™ and the RHIZOtest). Without rehabilitation, fresh BR severely inhibits seed germinationand root/shoot development in test species Lepidium sativum, Sinapis alba and Sorghum saccharatum. Plant uptake for Al, As, Cr, V was assessed with RHIZOtest bioassay trials with Lolium perenne and demonstrated that plants exposed to fresh BR take up and translocated trace elements to their shoots at concentrations (As = 4.13 mg/kg dm; Cr = 3.29 mg/kg dm; V = 85.66 mg/kg dm) exceeding phytotoxic levels (vanadium) or maximum levels specified for animal feed (arsenic), showing visible stress symptoms in the seedlings. Conversely, revegetated BR show improved chemical properties, allow seed germination, and permits seedling growth with no evidence of trace element phytotoxicity. However, Na can be taken up at concentrations that could elicit phytotoxicity and impair the success of revegetation. For future rehabilitation programmes, direct revegetation on BR after the incorporation of amendments such as gypsum and organic matter is recommended. © 2019 Elsevier B.V.

Elbehiry, F., Elbasiouny, H., El-Ramady, H.*, et al.* (2019) Mobility, distribution, and potential risk assessment of selected trace elements in soils of the Nile Delta, Egypt. *Environmental Monitoring and Assessment,* 191(12).
Keywords: Kafrelsheikh; Nile Delta; Risk assessment; Spatial distribution; Trace elements; Biochemistry; Ecosystems; Pollution; Soils; Ecological health; Ecological risk assessment; Environmental pollutions; Nile delta , Egypt; Pollution sources; Productive soils; antimony; molybdenum; strontium; trace element; vanadium; heavy metal; bioavailability; concentration (composition); delta; mobility; pollutant source; soil pollution; agroecosystem; Article; concentration (parameter); Egypt; extraction; geographic distribution; pollution control; soil acidity; soil analysis; chemistry; ecosystem; environmental monitoring; human; soil; soil pollutant; Kafr ash Shaykh; Biological Availability; Environmental Pollution; Humans; Metals, Heavy; Soil Pollutants

Abstract:
Environmental pollution has received considerable attention over the last 50 years. Recently, there has been an increasing interest in pollution of the Nile Delta, Egypt, which is one of the longest settled deltaic systems in the world. Pollution in the delta is increasingly

recognized as a serious health concern that requires proper management of ecosystems. Therefore, this project aimed to study the distribution and assess the risk associated with selected trace elements (TEs) in different soils (i.e., marine, fluvial, and lacustrine parent materials) in the northern Nile Delta. Mehlich-3 extraction was used to determine the availability of antimony, vanadium, strontium, and molybdenum in agro-ecosystems in this area and their spatial distributions were investigated. Five indices were used to assess ecological risk. Results showed that TEs were higher in the southern part of the study area because it is affected by multiple pollution sources. The available concentrations of TEs were Sr < V < Sb < Mo. The bioavailability of Sr was highest among the studied TEs. The studied indices suggested the study area was moderately polluted by Sr and Sb. Furthermore, the results showed that marine soils had higher TE levels then lacustrine and fluvial soils. The ecological risk assessment indicated that V and Mo were of natural origin, while Sr and Sb were anthropogenically linked. Therefore, the situation calls for planning to reduce pollution sources, especially in the protected north Nile Delta, so these productive soils do not threaten human and ecological health. © 2019, Springer Nature Switzerland AG.

Ettler, V., Mihaljevič, M., Jarošíková, A.*, et al.* (2020) Vanadium-rich slags from the historical processing of Zn–Pb–V ores at Berg Aukas (Namibia): Mineralogy and environmental stability. *Applied Geochemistry,* 114.

Keywords: Berg aukas; Leaching; Mineralogy; Slag; Vanadium; Zinc; Costs; Deionized water; Kilns; Metal recovery; Metals; Ores; Silicate minerals; Slags; Solubility; Average concentration; Environmental conditions; Environmental stability; Geochemical investigations; Orders of magnitude; Reducing conditions; Static leaching test; Iron compounds; clinopyroxene; environmental effect; geoaccumulation; historical perspective; lead; soil pollution; Namibia

Abstract:
The historical mining and processing of Zn–Pb–V ores at Berg Aukas in northern Namibia left large amounts of various wastes. This study focuses on the mineralogical and geochemical investigation of the V-rich slags issued from the processing of the local ores in the Waelz kiln, which was operational between 1968 and 1980 and left ca. 500 kt of slag deposited on the adjacent dump. A combination of mineralogical methods, bulk chemistry, leaching tests and speciation-solubility modeling was used to understand the binding of the major contaminants (Zn, Pb, V) in the solid phase and their potential release under the changing environmental conditions. The average concentrations of the metal(loid) contaminants in the slags are 3.78 wt% Zn, 3370 mg/kg Pb, 5880 mg/kg V, 767 mg/kg Cu, 578 mg/kg As and 92 mg/kg Sb. The mineralogy is dominated by high-temperature silicates (clinopyroxene, melilite, olivine-family phases) and Zn-bearing phases (willemite, zincite). All the primary silicates and oxides are Zn-rich, but vanadium is mainly concentrated in clinopyroxene (up to 5 wt% V2O3). Metallic Fe inclusions, formed under highly reducing conditions in the kiln, are highly weathered. Secondary Fe(III) (hydr)oxides, corresponding to the main weathering products in the slag, efficiently sequester the metal(loid)s (mainly As and Sb). The EU regulatory leaching tests indicated that the release of the metal(loid) contaminants is quite low at the natural pH (deionized water extract: 8.5–10.4) obtained by extraction in the deionized water and only Sb in all the slag samples exceeds the EU limits for the landfilling of inert waste. The pH-static leaching tests revealed up to 5 orders of magnitude higher release of Pb and Zn under acidic conditions (up to 38% and 63% of their total concentration, respectively), compared to the natural pH. In contrast, V exhibits relatively flat pH-dependent leaching patterns with only <1.6% of the total V leached. Using the slag re-processing costs by acidic (bio)leaching and the current metal prices, the recovery of V,

being the most important critical metal in the Berg Aukas slags, seems to be non-economical. © 2019 Elsevier Ltd.

Fierros-Romero, G., Gómez-Ramírez, M., Sharma, A.*, et al.* (2020) czcD gene from Bacillus megaterium and Microbacterium liquefaciens as a potential nickel–vanadium soil pollution biomarker. *Journal of Basic Microbiology,* 60(1): 22-26.
Keywords: biomarkers; Bacillus megaterium; Microbacterium liquefaciens; czcD; nickel–vanadium resistance

Abstract:
Abstract Metals are among the most prevalent pollutants released into the environment. For these reasons, the use of biomarkers for environmental monitoring of individuals and populations exposed to metal pollution has gained considerable attention, offering fast and sensitive detection of chemical stress in organisms. There are different metal resistance genes in bacteria that can be used as biomarkers, including cation diffusion facilitators carrying metal ions; the prototype is the cobalt?zinc?cadmium transporter (czcD). The present study reports the expression changes in the czcD gene in Bacillus megaterium and Microbacterium liquefaciens under nickel and vanadium exposure by real-time polymerase chain reaction. The nickel?vanadium-resistant strains of B. megaterium and M. liquefaciens used in this study were isolated from mine tailings in Guanajuato, Mexico. The czcD gene showed high expression under exposure to 200?ppm of Ni and 200?ppm of V during the logarithmic growth phase of M. liquefaciens in PHGII liquid media. In contrast, no changes were observed in B. megaterium during logarithmic and stationary growth, perhaps due to the gene having differential expression during the growth phases. The expression profiles obtained for czcD show the possibility of using this gene from M. liquefaciens as a biomarker of nickel and vanadium pollution in microorganisms.

Gan, C., Liu, M., Lu, J.*, et al.* (2020) Adsorption and Desorption Characteristics of Vanadium (V) on Silica. *Water, Air, & Soil Pollution,* 231(1): Article number: 10.

Abstract:
With the extensive mining of vanadium (V) ore, much attention has been focused on soil V pollution and its hazards. This study was conducted to investigate the adsorption-desorption properties of V on silica under various conditions, such as initial vanadate (V(V)) concentration, reaction time, pH, ionic strength, and temperature. The Langmuir and Freundlich isotherm models were applied to describe the adsorption of V(V) on silica and the results indicate that the adsorption was mainly monolayer adsorption. The kinetic studies show that the mechanisms of V adsorption on and desorption from silica were different from one another. The main adsorption-desorption-controlling step was chemical reaction, whereas V adsorption on silica also involved the diffusion. The adsorption-desorption procedure was highly dependent on the initial V(V) concentration and solution pH. Adsorption of V(V) increased with an increase in initial concentration and the maximum adsorption capacity was observed at solution pH 3.0–5.0. At 29.1 mg L^{-1} initial V(V), and silica dosage 36.4 g L^{-1} at 25 °C, the adsorption amount reached maximum of 82.7 mg kg^{-1} and the corresponding desorption rate was 5.44%. Therefore, silica is an effective adsorbent which can fix V in the soil.

Garvin, M.C., Schijf, J., Kaufman, S.R.*, et al.* (2020) A survey of trace metal burdens in increment cores from eastern cottonwood (Populus deltoides) across a childhood cancer cluster, Sandusky County, OH, USA. *Chemosphere,* 238.

Available at:
https://www.sciencedirect.com/science/article/pii/S0045653519317527/pdfft?md5=1d44d75fbf11fd7368a875bdc5562489&pid=1-s2.0-S0045653519317527-main.pdf
Keywords: Cancer cluster; Dendrochemistry; Eastern cottonwood; Scan statistic; Trace metals; Cotton; Diseases; Forestry; Groundwater; Metals; Surveys; Trace analysis; Scan statistics; Trace metal; Trace elements; arsenic; cadmium; chromium; cobalt; lead; nickel; vanadium; trace element; aerosol; bioaccumulation; cancer; concentration (composition); core analysis; dendroecology; microwave radiation; spatial analysis; statistical data; wood; annual ring; Article; childhood cancer; concentration (parameter); inductively coupled plasma mass spectrometry; method detection limit; Ohio; Populus; Populus deltoides; chemistry; child; environmental monitoring; human; neoplasm; questionnaire; soil; tree; Sandusky County; United States; Humans; Neoplasms; Surveys and Questionnaires; Trees

Abstract:
A dendrochemical study of cottonwood trees (Populus deltoides) was conducted across a childhood cancer cluster in eastern Sandusky County (Ohio, USA). The justification for this study was that no satisfactory explanation has yet been put forward, despite extensive local surveys of aerosols, groundwater, and soil. Concentrations of eight trace metals were measured by ICP-MS in microwave-digested 5-year sections of increment cores, collected during 2012 and 2013. To determine whether the onset of the first cancer cases could be connected to an emergence of any of these contaminants, cores spanning the period 1970–2009 were taken from 51 trees of similar age, inside the cluster and in a control area to the west. The abundance of metals in cottonwood tree annual rings served as a proxy for their long-term, low-level accumulation from the same sources whereby exposure of the children may have occurred. A spatial analysis of cumulative metal burdens (lifetime accumulation in the tree) was performed to search for significant 'hotspots', employing a scan statistic with a mask of variable radius and center. For Cd, Cr, and Ni, circular hotspots were found that nearly coincide with the cancer cluster and are similar in size. No hotspots were found for Co, Cu, and Pb, while As and V were largely below method detection limits. Whereas our results do not implicate exposure to metals as a causative factor, we conclude that, after 1970, cottonwood trees have accumulated more Cd, Cr, and Ni, inside the childhood cancer cluster than elsewhere in Sandusky County. © 2019 The Authors.

Hou, M., Huo, Y., Yang, X.*, et al.* (2020) Chemical form and subcellular distribution of vanadium in corn seedlings. *Microchemical Journal,* 153: 104468.
Keywords: Corn seedlings; Vanadium; Subcellular distribution; Chemical form

Abstract:
The subcellular distribution and chemical forms of corn seedlings under different concentrations of V(V) stress were investigated by hydroponics. The results of subcellular distribution showed that the cell wall and soluble fraction were the main binding sites for vanadium (V). Root cell wall played a major binding role in regulating response to V, and only a small amount of V was transported to leaves. Similarly, the chemical form of V in corn seedlings comprised small molecular pigments and amino acids in leaves which had a stronger binding affinity to V, in addition to acidic polar substances with low activity, inert substances, and polysaccharides in the cell wall. The content of binding V was highest in roots cell wall. Further analysis of the cell wall showed that V were highly soluble in the active low HCl and less soluble in the active high H2O. The V interacted mainly with cellulose and pectin in the cell wall. The combination with cellulose and pectin in the cell wall may be one of the important detoxification mechanisms of corn. ".

Liao, Y. & Yang, J. (2020) Remediation of vanadium contaminated soil by nano-hydroxyapatite. *Journal of Soils and Sediments,* 20(3): 1534-1544.
Keywords: Nano-hydroxyapatite; Plant growth; Soil; Soil amendment; Stabilization; Vanadium; Brassica oleracea var. capitata; Brassica rapa subsp. chinensis

Abstract:
Purpose: Vanadium (V) contamination in soil can cause diverse damage to soil ecosystem and has attracted research interests in exploring soil V stabilization methods, but only a few materials were proposed and studied. Here, a pot experiment was firstly conducted to estimate the efficiency of nano-hydroxyapatite (n-HAP) in stabilizing V in soil. To verify the impact of n-HAP on soil V bioavailability and phytotoxicity, cabbages (Brassica chinensis L.) were grown in V-spiked soils after n-HAP amendment. Materials and methods: Soils were sampled from a farmland in China, and the n-HAP was prepared in the laboratory. In each pot of soil spiked with 0, 75, 150, 300, and 600 mg/kg V, 2% n-HAP was amended for 30 days, while soils without n-HAP amendment were set as controls. The stabilization effect of n-HAP on V in soil was estimated by the water-extractable and bioavailable V concentrations in soils. Cabbages were grown in pots subsequently. The V(V/IV) concentrations in cabbage leaves and roots, the organic bound V concentrations in cabbage roots, and the chlorophyll concentrations in leaves were determined. Bioconcentration factor and translocation factor were calculated. The composition of organic bound V in leaf was characterized by fluorescence excitation–emission matrix. Results and discussion: In soils spiked with 150 mg/kg V, n-HAP amendment yielded the highest stabilization rates of 51.0% and 42.4% for water-extractable and bioavailable V, respectively. In 75, 150, and 300 mg/kg V-spiked soil, the plant weight, plant height, and root length of cabbage after 60-day growing decreased 54.6%/89.6%, 30.9%/45.5%, and 41.5%/51.4% in groups with/without n-HAP, respectively. Cabbage leaf chlorophyll concentrations descend firstly then ascend with rising soil V concentration. Leaf V speciation analysis revealed that less leaf V was reduced to V(IV) in groups amended with n-HAP than groups without n-HAP amendment. In 150 and 300 mg/kg V-spiked soil, n-HAP effectively reduced the V content and the V bioconcentration factor of cabbage root. Tyrosine-like and humic acid-like analogues composed the principal part of V complex. Conclusions: In general, n-HAP amendments are potential to decrease the mobility of V in soils, as well as inhibit the bioavailability and phytotoxicity of V to cabbage. In V-spiked soils, n-HAP amendment can alleviate the toxicity of V to the cabbage. Overall, 2% n-HAP is efficient for the amendment of slight V-polluted (150–300 mg/kg) soils to alleviate the soil V stress to cabbage. © 2019, Springer-Verlag GmbH Germany, part of Springer Nature.

Lieberman, R.N., Izquierdo, M., Córdoba, P.*, et al.* (2020) The geochemical evolution of brines from phosphogypsum deposits in Huelva (SW Spain) and its environmental implications. *Science of the Total Environment,* 700.
Keywords: Brine; Evaporation pond; Hazardous waste; Heavy metals; Phosphogypsum; Brines; Chlorine compounds; Deposits; Evaporation; Fluorine compounds; Geochemistry; Lakes; Pollution; Sulfur compounds; Environmental conditions; Environmental implications; Hazardous wastes; Laboratory conditions; Local weather conditions; Precipitation sequence; Steady-state condition; Gypsum; arsenic; calcium sulfate; chloride; chromium; copper; fertilizer; fluoride; fluorine; nickel; phosphate; sulfate; unclassified drug; uranium; vanadium; zinc; concentration (composition); heavy metal; phosphorus; slurry; time dependent behavior; weathering; agricultural slurry; Article; controlled study; dissolution; environmental enrichment; geochemical analysis; liquid waste; mineralogy; pollutant; pond; precipitation; priority journal; sampling; seasonal variation; Spain; weather; Andalucia; Huelva [Andalucia]

Abstract:
The present study focuses on the geochemistry of large phosphogypsum deposits in Huelva (SW Spain). Phosphogypsum slurry waste from fertiliser production was disposed in large ponds containing aqueous waste (i.e. brines) and exposed to weathering. These evaporation ponds were found to be dynamic environments far from attaining steady state conditions where a number of trace pollutants are subjected to temporal variations in response to changing environmental conditions. Chemical, mineralogical and morphological data were used to improve our understanding on the dynamics of a large number of elements in the phosphogypsum-brine-evaporation deposits system. Weekly sampling of brines over the course of 1 yr indicated a substantial enrichment in potentially harmful elements (e.g. As, Cr, Cu, F, Ni, U, V, Zn) present in time-dependent concentrations. The evaporation deposits formed multi-layered precipitates of chlorides, sulphates, phosphates and fluorides containing a large number of pollutants in readily soluble forms. The precipitation sequence revealed a time-dependent composition reflecting alternating precipitation and re-dissolution processes associated with seasonal changes in the local weather conditions. Concatenation of precipitation/re-dissolution stages was found to progressively enrich the brines in pollutants. These findings were supported by the observations from a tank experiment simulating the phosphogypsum-brine-evaporation deposits system under laboratory conditions. Given the substantially high concentrations of pollutants present in mobile forms in the brine-salt system, actions to abate these compounds should be implemented. © 2019 Elsevier B.V.

Naumov, V.D., Kamennyh, N.L., Lebedev, A.V.*, et al.* (2020) Heavy metals in sod-podzolic soils under forest stands of Moscow. *IOP Conference Series: Earth and Environmental Science,* 421(6).
Available at: https://iopscience.iop.org/article/10.1088/1755-1315/421/6/062036/pdf
Keywords: Biotechnology; Environmental technology; Forestry; Heavy metals; Nickel; Soils; Trace elements; Vanadium; Environmental pollutions; Forest stand; Large cities; Maximum permissible concentration; Podzolic soil; Soil profiles; Soil pollution

Abstract:
In large cities, soil pollution occurs with heavy metals. Forest stands react to environmental pollution by a decrease in growth and an increase in mortality. A typical object for the city of Moscow is the Timiryazev Academy Forest Experimental District. A comparison of the content of gross forms with the clark content of trace elements in the soil profile revealed a significant excess for the following chemical elements: copper, zinc, lead, arsenic. The content of chromium, nickel, vanadium is lower than the clark content. Comparison of the content of gross forms of trace elements with maximum permissible concentrations showed that the content of nickel, vanadium, cobalt is lower than the maximum permissible concentration. The distribution of the gross forms of the elements along the soil profile is heterogeneous. The maximum content in the profile of sod-podzolic soils falls on the humus horizon, which is associated with the biogenic accumulation of these elements. © 2019 IOP Publishing Ltd. All rights reserved.

Olise, F.S., Ogundele, L.T., Olajire, M.A.*, et al.* (2019) Biomonitoring of environmental pollution in the vicinity of iron and steel smelters in southwestern Nigeria using transplanted lichens and mosses. *Environmental Monitoring and Assessment,* 191(11).
Keywords: Airborne particulates; Biomonitors; PMF; XRF

Abstract:
This study identified specific emission sources of atmospheric pollution in the vicinity of two

secondary iron and steel smelting factories in Osun state, southwestern Nigeria, using transplanted biomonitors. A total of 120 biomonitors consisting of lichen and moss were grown under a controlled environment and later transplanted to the surroundings of each factory for monitoring of air pollutants for 3 months in both wet and dry seasons. The elemental contents (K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb and Sr) of the biomonitors were determined by X-ray florescence (XRF) spectroscopy. The source identification was performed by applying positive matrix factorization (PMF) receptor modelling approach using the elemental data set from the two smelters. Among the measured elements, Fe had the highest average concentration in the lichen and moss samples as well as in both seasons. The average concentrations of Co, Ni, Cu, Zn, As and Br were low. The varying average elemental concentrations of lichen and moss reflect the pattern of impact of smelting on atmospheric airborne pollution around the factories. The four factors resolved by PMF and their respective contributions were metal processing (39.0%), Fe source (28.0%), crustal/soil (22.0%) and road dust (11.0%) for moss and Fe source (34.0%), crustal/soil (26.0%), coal combustion (25.0%) and road dust (15.0%) for lichen. The study showcases lichen and moss as cheaper and yet efficient uninterrupted monitoring tools of air pollution sources associated with iron and steel smelting industrial activities.

Rutigliano, F.A., Marzaioli, R., De Crescenzo, S.*, et al.* (2019) Human health risk from consumption of two common crops grown in polluted soils. *Science of the Total Environment,* 691: 195-204.
Keywords: Bio-accumulation factor; Health risk index; Lettuce; Soil contamination; Trace elements; Zucchini

Abstract:
Contamination of agricultural soils by trace elements is a recurrent hazard for human health because of the possibility of pollutants entering the food chain. Aim of this study was to assess the human health risk from consumption of the common leafy (Lactuca sativa L.) and fruit (Cucurbita pepo L.) crops, in an agricultural area of Southern Italy. Along with agricultural practices, a major pollutant source is recurrent flooding from the highly polluted Solofrana river. Soil samples and edible parts of crops from 14 sites (10 flooded and 4 not flooded) were analyzed for total amounts of As, Cd, Co, Cr, Cu, Ni, Pb, V, Zn. The bio-accumulation factor (BAF) and Health Risk Index (HRI) were calculated for each element, crop and site and as average values of all sites (BAFmean and HRImean). Moreover, the Hazard Index (HI) was determined for each site, as the sum of HRI for all elements. Cr and Cu, mostly derived from river flooding and agricultural practices, respectively, were the only elements whose levels exceeded law thresholds and/or the natural background of the study area. Of the two considered crops, L. sativa accumulated more Cd, Cr and Ni, whereas C. pepo was a more effective bioaccumulator of Zn. Both HRImean (for As, Cd, Cr and Ni) and HI were higher for L. sativa than for C. pepo. A low health risk was associated to major soil pollutants (Cr and Cu) found in the study area; in contrast, combined data on soil pollution and plant bio-accumulation points to accumulation of Cd and As, mainly in lettuce, as a potential risk for human health. The results suggest that soil pollution data alone is not sufficient to assess health risk.

Samuel-Nakamura, C., Hodge, F.S., Sokolow, S.*, et al.* (2019) Metal(loid)s in Cucurbita pepo in a Uranium Mining Impacted Area in Northwestern New Mexico, USA. *International Journal of Environmental Research and Public Health,* 16(14): 10.3390/ijerph16142569.
Available at: https://www.mdpi.com/1660-4601/16/14/2569/pdf

Keywords: Adult; Aged; Aged, 80 and over; Arsenic/analysis; Cucurbita/chemistry; Drinking Water/standards; Female; Humans; Male; Metals, Heavy/analysis; Middle Aged; Mining; New Mexico; Selenium/analysis; Soil; Soil Pollutants/analysis; United States; United States Environmental Protection Agency; Uranium/analysis; Water Pollutants, Chemical/analysis; American Indian; Dine; Navajo; cadmium; food chain; irrigation water; lead; squash

Abstract:
More than 500 unreclaimed mines and associated waste sites exist on the Navajo Nation reservation as a result of uranium (U) mining from the 1940s through the 1980s. For this study, the impact of U-mine waste on a common, locally grown crop food was examined. The goal of this site-specific study was to determine metal(loid) concentration levels of arsenic (As), cadmium (Cd), cesium (Cs), molybdenum (Mo), lead (Pb), thorium (Th), U, vanadium (V) and selenium (Se) in Cucurbita pepo Linnaeus (squash), irrigation water, and soil using inductively coupled plasma-mass spectrometry. The concentrations of metal(loid)s were greatest in roots > leaves > edible fruit (p 30 years) for V ($p = 0.001$), As ($p < 0.001$), U ($p = 0.002$), Cs ($p = 0.012$), Th ($p = 0.040$), Mo ($p = 0.047$), and Cd ($p = 0.042$). Lead and Cd crop irrigation water concentrations exceeded the United States Environmental Protection Agency (USEPA) Maximum Contaminant Levels for drinking water for those metals. Edible squash concentration levels were 0.116 mg/kg of As, 0.248 mg/kg of Pb, 0.020 mg/kg of Cd, and 0.006 mg/kg of U. Calculated human ingestion of edible squash did not exceed Provisional Tolerable Weekly Intake or Tolerable Upper Limit levels from intake based solely on squash consumption. There does not appear to be a food-ingestion risk from metal(loid)s solely from consumption of squash. Safer access and emphasis on consuming regulated water was highlighted. Food intake recommendations were provided. Continued monitoring, surveillance, and further research are recommended.

Stafilov, T. & Šajn, R. (2019) Spatial distribution and pollution assessment of heavy metals in soil from the Republic of North Macedonia. ***Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering,*** **54(14): 1457-1474.**
Keywords: geogenic and anthropogenic distributions; multi-element mapping; multivariate analysis; Republic of North Macedonia; Soil; Chemical analysis; Heavy metals; Inductively coupled plasma; Mass spectrometry; Multivariant analysis; Soil pollution; Soils; Spatial distribution; Sulfur compounds; Atomic emission spectrometry; Geogenic; Macedonia; Multi variate analysis; Multi-element; Quaternary volcanisms; Regional distribution; Statistical parameters; Soil surveys; antimony; barium ion; bismuth; cadmium; calcium ion; cerium; cobalt; cuprous ion; heavy metal; hydrofluoric acid; iron; lanthanum; lead; lithium ion; manganese; molybdenum; nickel; potassium ion; rubidium ion; scandium; sodium ion; strontium; thallium; thorium; tin; titanium; uranium; vanadium; zinc ion; zirconium; Article; biological monitoring; cluster analysis; comparative study; factor analysis; geochemical analysis; Greece; inductively coupled plasma atomic emission spectrometry; inductively coupled plasma mass spectrometry; Mesozoic; quality control; soil analysis; chemistry; environmental monitoring; geographic and geological phenomena; human; soil pollutant; Geological Phenomena; Humans; Metals, Heavy; Soil Pollutants

Abstract:
The purpose of the study was to determine the spatial distribution and pollution assessment of 39 chemical elements in soil from the Republic of North Macedonia. From the whole territory of the country top soil samples (0–30 cm) were collected from 995 locations with a grid of 5 × 5 km distance between the sampling locations. Two analytical techniques were used for the analysis of soil samples: inductively coupled plasma–atomic emission spectrometry and inductively coupled plasma–mass spectrometry. Based on a comparison of

statistical parameters, spatial distribution of particular elements and results of cluster and factor analysis, four main geochemical associations were identified: (1) association connected with the Neogene and Quaternary volcanism (Ba, Be, Ce, Hf, K, La, Rb, Th, Tl, U and Zr); (2) association of siderophile elements (Co, Cu, Fe, Mn, Sc, Ti and V); (3) association connected with ophiolites and Mesozoic ultrabasic magmatic rocks of Vardar zone (Cr and Ni) and (4) chalcophile (sulphide) elements (As, Bi, Cd, Pb, Sb, Sn and Zn). The regional distribution was prepared according to the eight statistical regions in Macedonia, distribution according to 15 most common geological formation and distribution according to 13 pedological units.

Vural, A. (2020) Investigation of the relationship between rare earth elements, trace elements, and major oxides in soil geochemistry. ***Environmental Monitoring and Assessment,*** **192(2).**

Keywords: Environmental geochemistry; Exploration geochemistry; Gümüşhane; Rare earth elements (REEs); Trace/heavy metal elements; Exploratory geochemistry; Magnesia; Manganese oxide; Principal component analysis; Rare earth elements; Rare earths; Silica; Soils; Correlation coefficient; Descriptive statistics; Negative correlation; Positive correlations; Principle component analysis; Trace/heavy metals; Trace elements; arsenic; barium; cesium; cobalt; gallium; gold; hafnium; lanthanide; magnesium oxide; nickel; niobium; oxide; potassium oxide; rubidium; scandium; silicon dioxide; silver; tantalum; thorium; tin; trace element; tungsten; unclassified drug; uranium; vanadium; zinc; zirconium; heavy metal; organic compound; correlation; geochemical cycle; mineral exploration; mineralization; rare earth element; Article; geochemistry; soil chemistry; statistical analysis; environmental monitoring; procedures; soil; soil pollutant; Metals, Heavy; Metals, Rare Earth; Organic Chemicals; Oxides; Soil Pollutants

Abstract:
Investigation on the behavior of elements in the soil is important both in exploration and environmental geochemistry studies. Rare earth elements (REEs) are the most useful among all trace elements. REE studies have shown that they have important applications in igneous, sedimentary, and metamorphic petrology. This work aims to investigate the relationship of these elements with one another and the behavior of the major oxides and trace elements with REEs. Soil samples were obtained from the alteration site possibly related to mineralization and were analyzed for major oxides, trace elements, and REEs. The relationships between the major oxide–trace element/heavy metal and REE were investigated by statistical methods, such as descriptive statistics, correlation coefficient, and principle component analysis. According to the correlation coefficient matrix, light REEs (LREEs) showed weak to moderate negative correlation with MgO and MnO and moderately positive correlation with SiO2 and K2O. No association was detected between the heavy REEs (HREEs) and the main oxides, but a strong positive correlation with LREEs was observed. For the trace elements, LREE showed a weak positive correlation with Ba and Sn and moderate to strong positive correlation with As, Hf, Nb, Rb, Ta, Th, U, W, and Zr. They also displayed weak to moderate correlation with Sc, Co, Zn, Ni, and V. HREE showed weak to moderate positive correlation with Ni, Cs, Ga, Hf, Th, Zr, As, and LREE. Although REEs exhibited no direct correlation with Au and Ag, they showed a good correlation with some trace elements that are related to hydrothermally altered products. This study showed that REEs can also be used in exploration and environmental geochemistry studies by exploiting the relationship between REEs and other trace/heavy metal elements.

Wang, L., Lin, H., Dong, Y.*, et al.* (2020) Effects of endophytes inoculation on rhizosphere and endosphere microecology of Indian mustard (Brassica juncea) grown in vanadium-contaminated soil and its enhancement on phytoremediation. *Chemosphere,* 240: 124891.
Keywords: Bacteria/classification/drug effects/growth & development/metabolism; Biodegradation, Environmental; Endophytes/growth & development; Mustard Plant/drug effects/metabolism/microbiology; Plant Development/drug effects; Plant Roots/drug effects/metabolism/microbiology; Rhizosphere; Soil Microbiology; Soil Pollutants/analysis/toxicity; Vanadium/analysis/toxicity; Bacterial community; Endophyte-assisted phytoremediation; Heavy metal speciation; Microbial inoculants; Vanadium

Abstract:
We investigated the effects of endophytes inoculation on ecological factors such as root morphology, rhizosphere soil properties, heavy metal speciation, and rhizosphere and endophytic bacterial communities and their role on phytoremediation. Indian mustards were grown for two months in V-contaminated soil with three treatments (control, inoculation with Serratia PRE01 or Arthrobacter PRE05). Inoculation with PRE01 and PRE05 increased organic matter content by 6.94% and 4.6% respectively and significantly increased bioavailability of heavy metals in rhizosphere soils. Despite the endophyte inocula failed to flourish as stable endophytes, they significantly affected the specific composition and diversity of endophytic bacterial communities in roots, with no significant effect on rhizosphere bacterial communities. The test strains could greatly increase plant growth promotion-related biomarkers in the endosphere, especially those associated with Pseudomonas and Microbacterium genera. PICRUSt analysis predicted high relative abundances of functional genes related to environmental information processing especially in the endophytic microbiota. More biomass production (12.0%-17.4%) and total metals uptake (24.2%-32.0%) were acquired in inoculated treatments. We conclude that endophyte PRE01 or PRE05 inoculation could effectively enhance phytoremediation of V-contaminated soil by improving the rhizosphere and endosphere microecology without causing any ecological damage.

Wang, S., Zhang, B., Li, T.*, et al.* (2020) Soil vanadium(V)-reducing related bacteria drive community response to vanadium pollution from a smelting plant over multiple gradients. *Environment International,* 138: 105630.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412019339741/pdfft?md5=17d2a45e5e8f10ffb96816da28b1f8ab&pid=1-s2.0-S0160412019339741-main.pdf
Keywords: Community response; Core microbiome; Soil microorganisms; Vanadium pollution; Vanadium(V)-reducing related bacteria

Abstract:
The mining and smelting of navajoite has resulted in a serious vanadium pollution in regional geological environments and significant influence on soil microorganisms. However, the core microbiome responsible for adjusting community response to vanadium pollution and the driving pattern have been kept unclear. In this study, a suite of surface and profile soil samples over multiple gradients were collected in four directions and distances of 10-2000 m from a vanadium smelting plant in Panzhihua, China. The indigenous microbial communities and vanadium(V)-reducing related bacteria (VRB) were profiled by 16S rRNA gene high-throughput sequencing technique. Five VRB were detected in the original collected soil samples including Bacillus, Geobacter, Clostridium, Pseudomonas and Comamonadaceae based on high-throughput sequencing data analysis, and their abundances were significantly related with the content of vanadium. Low vanadium

concentration promoted the growth of VRB, while high vanadium concentration would inhibit VRB multiplication. The Gaussian equation could be used to quantitatively describe the nonlinear relationship between VRB and vanadium. Network analysis demonstrated that the microbial communities were significantly influenced by VRB assemblage, and 1.32-52.77% of microbes in the community showed a close association with VRB. A laboratory incubation experiment also confirmed the core role of VRB to drive community response to vanadium pressure.

Yu, X., Kang, X., Li, Y.*, et al.* (2019) Rhizobia population was favoured during in situ phytoremediation of vanadium-titanium magnetite mine tailings dam using Pongamia pinnata. *Environmental Pollution,* 255.**
Keywords: Microbial communities; Mine tailings; Phytoremediation; Pongamia pinnata; Rhizobia

Abstract:
Mine tailings contain toxic metals and can lead to serious pollution of soil environment. Phytoremediation using legumes has been regarded as an eco-friendly way for the rehabilitation of tailings-laden lands but little is known about the changes of microbial structure during the process. In the present study, we monitored the dynamic change of microbiota in the rhizosphere of Pongamia pinnata during a 2-year on-site remediation of vanadium-titanium magnetite tailings. After remediation, overall soil health conditions were significantly improved as increased available N and P contents and enzyme activities were discovered. There was also an increase of microbial carbon and nitrogen contents. The Illumina sequencing technique revealed that the abundance of taxa under Proteobacteria was increased and rhizobia-related OTUs were preferentially enriched. A significant difference was discovered for sample groups before and after remediation. Rhizobium and Nordella were identified as the keystone taxa at genus rank. The functional prediction indicated that nitrogen fixation was enhanced, corresponding well with qPCR results which showed a significant increase of nifH gene copy numbers by the 2nd year. Our findings for the first time elucidated that legume phytoremediation can effectively cause microbial communities to shift in favour of rhizobia in heavy metal contaminated soil. © 2019 Elsevier Ltd The main findings throw light on the changes of rhizobia community in mine tailings during its phytoremediation using Pongamia pinnat. © 2019 Elsevier Ltd.

Yu, Y., Luo, H., Tang, W.*, et al.* (2020) Mechanism of vanadium(IV) resistance of the strains isolated from a vanadium titanomagnetite mining region. *Ecotoxicology and Environmental Safety,* 195: 110463.
Keywords: Resistant mechanism; Vanadium(IV); Biosorption; Bioabsorption; Bioadsorption; Biotransformation

Abstract:
Microbial treatment for vanadium contamination of soils is a favorable and environment-friendly method. However, information of the resistant mechanism of the strains in soils to vanadium, especially to tetravalent vanadium [vanadium(IV)], is still limited. Herein, potential of the vanadium(IV) biosorption and biotransformation of the strains (4K1, 4K2, 4K3 and 4K4) which were capable of tolerating vanadium(IV) was determined. For biosorption, the bioadsorption and the bioabsorption of vanadium(IV) occur on the bacterial cell wall and within the cell, respectively, were taken into consideration. Comparison of the vanadium(IV) adsorbed on the bacterial cell walls and remained in the cells after sorption indicated the major bacterial vanadium(IV) sorption role of the bioadsorption which was at least one order of magnitude higher than the bioabsorption amount. Isotherm study using

various isotherm models revealed a monolayer and a multilayer vanadium(IV) biosorption by 4K2 and the others (4K1, 4K3 and 4K4), respectively. Higher biosorption was observed in acidic conditions than in alkaline conditions, and the maximum biosorption was 2.41, 9.35, 7.76 and 8.44 mg g−1 observed at pH 6 for 4K1, at pH 3 for 4K2, and at pH 4 for 4K3 and 4K4, respectively. At the present experimental range of the initial vanadium(IV) concentration, optimal biosorption capacity of the bacteria was observed at the vanadium(IV) level of 100–250 mg L−1. Different biotransformation level of vanadium(IV) in soils by the stains was observed during a 28-d pot incubation of the soils mixed with the strains, which can be attributed to the discrepancy of both soil properties and bacterial species. Present study can help to fill up the gaps of the insufficient knowledge of the vanadium(IV) resistant mechanism of the strains in soils. ".

Zakir, H.M. & Arafat, M.Y. (2020) Contamination Level of Different Chemical Elements in Top Soils of Barapukuria Coal Mine Area in Dinajpur, Bangladesh. *Asian Journal of Water Environment and Pollution,* 17(1): 59-73.
Keywords: Contamination; major and trace elements; Barapukuria coal mine; Bangladesh; POLLUTION; METALS; VANADIUM; BIOAVAILABILITY; ENVIRONMENT; SEDIMENTS; SYSTEMS; PLANTS; Environmental Sciences & Ecology

Abstract:
The contents and contamination level of 17 different chemical elements (Rb, Cs, Sr, Ba, Y, Zr, Co, Ni, V, Nb, Sn, Nd, Ce, La, Pr, Sb and Th) along with major elemental composition in 19 top soils and three canal sediment samples of the Barapukuria coal mine area were studied by X-ray Fluorescence spectroscopy (XRF). The study results revealed that SiO2, TiO2, Fe2O3, MgO, CaO and P2O5 were within the limit of normal soil, while Al2O3, Na2O and K2O in soil, and MnO and Na2O in sediment samples exceeded the maximum level of normal soil. Among the metals, the contents of Rb, Cs, Zr, Sn, Ce, La, Nd, Pr and Th in most of the top soils were higher compared to Earth's crust average, while Y and Sb contents were comparatively higher in sediment samples. Mine water discharge canal sediment samples had EFc values for Sb ranged from 24.72 to 57.09, indicating very severe to extremely severe contamination due to mining activities. Similarly, EFc values varied from 5 to 5 in several soil sampling locations indicating moderately severe contamination level in the study area. The study concluded that high EFc values indicate enrichment of metals, which might be originated from geogenic sources due to coal mining and coal based power generation related activities at the study area.

6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

Almalki, A.M., Ajarem, J., Allam, A.A.*, et al.* (2019) Use of spilopelia senegalensis as a biomonitor of heavy metal contamination from mining activities in riyadh (Saudi Arabia). *Animals,* 9(12).
Available at: https://www.mdpi.com/2076-2615/9/12/1046/pdf
Keywords: Biomonitoring; Heavy metals; Mining; Oxidative stress; Pollution

Abstract:
Environmental pollution with heavy metals (HMs) is of serious ecological and public health concern worldwide. Mining is one of the main sources of HMs and can impact the environment, species diversity, and human health. This study assessed the value of Spilopelia senegalensis as a biomonitor of environmental contamination with metal(loid)s caused by mining activities. S. senegalensis was collected from a gold mining site and a

reference site, and metal(loid)s and biochemical parameters were determined. Lead, cadmium, mercury, vanadium, arsenic, copper, zinc, and iron were significantly increased in the liver, kidney, and lung of S. senegalensis from the mining site. Serum transaminases, alkaline phosphatase, creatinine, and urea were significantly elevated in S. senegalensis from the mining site. Lipid peroxidation and nitric oxide were increased, whereas glutathione and antioxidant enzymes were diminished in the liver and kidney of S. senegalensis from the mining site. In addition, multiple histological alterations were observed in the liver, kidney, and lung of S. senegalensis. In conclusion, mining activities provoke the accumulation of metal(loid)s, oxidative stress, and tissue injury in S. senegalensis. Therefore, S. senegalensis is a valuable biomonitor of environmental pollution caused by mining activities and could be utilized in epidemiological avian studies of human health.

Gupta, P.K., Vaswani, S., Kumar, V.*, et al.* (2020) Investigations on Modulating Effect of Vanadium Supplementation on Growth and Metabolism Through Improved Immune Response, Antioxidative Profile and Endocrine Variables in Hariana heifers. *Biological Trace Element Research,* 194(2): 379-389.

Keywords: Antioxidant; Endocrine; Growth; Hariana; Immunity; Vanadium; DIABETIC-RATS; BROWN-ALGAE; VANADATE; LIVER; PERFORMANCE; OXIDATION; TOXICITY; ELEMENTS; HORMONE; METALS; Biochemistry & Molecular Biology; Endocrinology & Metabolism

Abstract:
This study was conducted to investigate the effect of vanadium (V) supplementation on growth, metabolism, antioxidant, and immunological and endocrine variables in Hariana heifers. Eighteen indigenous Hariana heifers (body weight 130.0 +/- 3.0 kg; age 10.0 +/- 2.0 months) were randomly blocked into three groups, each comprising of six animals. All the animals were on same dietary plan except that the respective groups were additionally supplemented with 0.0, 2.5, and 5.0 mg of V/kg dry matter (DM), during the experimental period of 90 days. There was a linear increase (p 0.05) of V supplementation were observed on hemato-biochemical attributes, the mean plasma V concentration showed dose-dependent increase ($p < 0.001$) on V supplementation. The activity of SOD was significantly higher ($p < 0.001$), whereas mean values of LPO decreased linearly ($p < 0.05$) in V-supplemented groups. Plasma total antioxidant status (TAS) also increased linearly ($p < 0.05$) in V-supplemented groups. Plasma IgG levels increased linearly ($p < 0.05$). Plasma IGF-1 concentrations showed significant effect ($p < 0.05$) of V supplementation. Plasma T4 concentration increased linearly ($p < 0.05$). The results suggest that V supplementation may play a role in modulating the immunity and antioxidant status of growing Hariana heifers.

Miroshnikov, S.A., Skalny, A.V., Zavyalov, O.A.*, et al.* (2020) The Reference Values of Hair Content of Trace Elements in Dairy Cows of Holstein Breed. *Biological Trace Element Research,* 194(1): 145-151.

Keywords: Dairy cow; Hair; Holstein; Reference interval; Trace elements; arsenic; boron; cadmium; chromium; cobalt; copper; iodine; iron; lead; lithium; manganese; mercury; selenium; silicon; strontium; tin; trace element; vanadium; zinc; Article; concentration (parameter); dairy cattle; dietary intake; hair analysis; Holstein cattle; inductively coupled plasma mass spectrometry; lactation; nutritional requirement; reference value; Russian Federation

Abstract:
The objective of this study was to assess trace element content in hair of Holstein dairy cows bred in the Leningrad Region of Russia and to calculate the site-specific reference intervals.

Hair content of arsenic, boron, cadmium, cobalt, chromium, copper, iron, mercury, iodine, lithium, manganese, lead, selenium, silicon, tin, strontium, vanadium, and zinc in 148 cows during first (n = 50), second (n = 48), and third (n = 50) lactation periods of life was determined using inductively coupled plasma mass spectrometry. Dietary intake of trace elements corresponded to the adequate values according to national and international recommendations. Comparative analysis did not reveal any significant differences in hair content of main essential elements on the animals depending on the number of lactation. At the same time, the first-lactation cows had significantly ($P < 0.05$) lower concentration of lead in hair as compared to the third-lactation cows and a higher level of mercury as compared to the second-lactation cows. The reference intervals and 90% confidence intervals for the lower and upper limits were calculated in agreement with the American Society for Veterinary Clinical Pathology Quality Assurance and Laboratory Standard Guidelines.

Picone, M., Corami, F., Gaetan, C.*, et al.* (2019) Accumulation of trace elements in feathers of the Kentish plover Charadrius alexandrinus. *Ecotoxicology and Environmental Safety,* 179: 62-70.
Keywords: Bioaccumulation; Cadmium; Mercury; Ptilochronology; Selenium; Water birds conservation

Abstract:
A non-invasive study of trace element accumulation in tail feathers of the Kentish plover (Charadrius alexandrinus) was performed along the coastline of the northern littoral strip of the Venice Lagoon, with the aim to verify whether contamination may be a factor affecting conservation status of Kentish plover populations. Body burdens in feathers of 11 trace elements including toxic metals/metalloids and essential elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) were quantified by ICP-MS, then concentrations were normalized to feather's age calculated using ptilochronology in order to obtain daily deposition rates. Mercury emerged as a major threat to the conservation of the species, since average feather concentration was clearly above the adverse-effect threshold associated with impairment in the reproductive success in a number of bird species. Also Cd and Se occurred at levels that may impact on the conservation status of the studied species at local scale, even if to a lesser extent than Hg. Gender-related differences in trace element accumulation emerged only for As, although for this element the risks associated to environmental exposure seem to be negligible. © 2019 Elsevier Inc.

7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS

Awan, R.S., Liu, C., Gong, H.*, et al.* (2020) Paleo-sedimentary environment in relation to enrichment of organic matter of Early Cambrian black rocks of Niutitang Formation from Xiangxi area China. *Marine and Petroleum Geology,* 112.
Keywords: Biogenic; Hydrothermal activity; Kerogen type index; Niutitang Formation; Paleoclimate; Redox conditions; Trace elements; Upwelling; Biogeochemistry; Feldspar; Kerogen; Oil shale; Organic carbon; Productivity; Pyrites; Quartz; Sea level; Sedimentology; Structural geology; Kerogen type; Paleoclimates; Redox condition; Sedimentary rocks; Cambrian; hydrothermal fluid; maceral; organic matter; paleoenvironment; trace element; transgression-regression cycle; China; Hunan; Xiangxi

Abstract:
Early Cambrian organic-rich black rocks are extensively distributed in the southern China. In this study, we have discussed the relation of paleo-sedimentary environments with

enrichment of organic matter. Based on TOC data, we divided the Niutitang Formation into three parts (Upper, Middle, and Lower). The amount of total organic carbon in the Lower (1.55 wt %) and the Upper part (1.35 wt %) of Niutitang Formation is significantly smaller than the Middle part (8.0 wt %) which suggest initial transgression, and regression stages of the sea level respectively. The Middle part from both sections (Longbizui and Sancha) contains higher TOC content, which is a clue of intense transgression stage of sea level with high bio-productivity. Kerogen type index (KTI) using different macerals specify the organic matter in these black rock series is mainly type-I with a minor amount of type-II1. Moreover, these black rocks were deposited in weak to moderately restricted hydrographic conditions. The heterogenic mineral composition was also observed in these black rocks, including quartz, clay, gypsum, pyrite, barite, dolomite, and plagioclase. Quartz content in the Middle part is relatively higher than the Upper, and the Lower part displays a strong positive relation with TOC which suggests the main source of quartz during deposition of the Middle part was biogenic quartz. During Early Cambrian period due to extension between the Yangtze and the Cathaysian plate, the hydrothermal fluids rich in uranium, vanadium, molybdenum, zinc, barium, etc. from the deeper part of the earth crust and entered the ocean basin through extensional remnant fissures and cracks, and due to upwelling phenomena entered to the shelf area. These nutrient-rich deep crustal fluids at the surface of the sea enhanced the evolution and breeding of planktons and other marine life; meanwhile, it upsurges the bio-productivity. Additionally, it creates bottom water hypoxia, which is favourable for the preservation of organic matter in the sedimentary rocks. The main factors responsible for the enrichment of organic matter in these Early Cambrian black rock series of Niutitang Formation were a hydrographic restriction, hydrothermal activities, and paleo-redox conditions, respectively. © 2019 Elsevier Ltd.

Cammilleri, G., Galluzzo, P., Pulvirenti, A.*, et al.* (2020) Toxic mineral elements in Mytilus galloprovincialis from Sicilian coasts (Southern Italy). *Natural Product Research,* 34(1).
Available at:
https://iris.unimore.it/retrieve/handle/11380/1178801/223953/Toxic%20mineral%20elements%20in%20Mytilus%20galloprovincialis%20from%20Sicilian%20coasts%20Southern%20Italy.pdf
Keywords: Mussels; biomarkers; metallothioneins; toxic mineral elements

Abstract:
We assessed the relationship between V, Cr, Mn, Hg, As, Cd, Sn, Sb and Pb concentrations in Mytilus galloprovincialis samples from the coasts of Sicily and the expression of metallothioneins. Toxic mineral elements assessment was carried out by A.A. Spectrometry and ICP-MS. The metallothioneins expression was performed by q-PCR method. Low metals' levels were found in the mussel samples examined, in comparison with what was reported in literature. The highest mean values of toxic mineral elements were found in Gela (Cr 0.178 +/- 0.03 mg/Kg, Mn 4.325 +/- 0.012 mg/Kg, As 3.706 +/- 0.009 mg/Kg, Sn 0.148 +/- 0.014 mg/Kg, Sb 0.009 +/- 0.004 mg/Kg e Pb 0.364 +/- 0.01 mg/Kg). Significant levels of Hg were found in samples from Catania (0.014 +/- 0.005 mg/Kg). Only vanadium and lead concentrations showed significant differences between sampling areas ($p < 0.05$). Molecular analysis verified a basal expression of Mt1 and the absence of over-expression of Mt2, confirming the low mineral's concentrations found in the samples examined.

Condesso de Melo, M.T., Shandilya, R.N., Silva, J.B.P.*, et al.* (2020) Volcanic glass leaching and the groundwater geochemistry on the semi-arid Atlantic island of Porto Santo. *Applied Geochemistry,* 114.
Keywords: Arid; Arsenic; Bicarbonate; Boron; Fluoride; Geochemistry; Glass; Groundwater;

Model; Sodium; Vanadium; Volcanics; Weathering; Alkalinity; Aquifers; Carbon dioxide; Diffusion in solids; Fluorine compounds; Groundwater resources; Hydrochemistry; Hydrogeology; Ion exchange; Leaching; Models; pH; Residence time distribution; Seawater; Sodium bicarbonate; Volcanoes; Geochemical modeling; Groundwater chemistry; Groundwater residence time; Solid-state diffusion; Groundwater geochemistry; aquifer pollution; arid region; calcarenite; climate conditions; diffusion; geochemical survey; volcanic glass; Atlantic Ocean; Madeira; Porto Santo; Portugal

Abstract:
The groundwater chemistry of the semi-arid volcanic island of Porto Santo, part of the Madeira archipelago, Atlantic Ocean, was investigated. Generally, the groundwater was brackish, containing 2–10 mol % seawater. Groundwater with up to 20 mM alkalinity and a Na enrichment of up to 30 mM, as compared to the Na concentration predicted by the seawater Na/Cl ratio, was found in the main aquifer. Also notable are the high concentrations of F (up to 0.3 mM), B (up to 0.55 mM), As (up to 0.35 µM), all in excess of WHO recommendations, as well as up to 6 µM V. Geochemical modeling, using the PHREEQC code, was used to explore different scenarios that could explain the genesis of the observed bulk groundwater chemistry. First, a model for aquifer freshening with the displacement of resident seawater from the aquifer by infiltrating freshwater, was tested. This scenario leads to the development of NaHCO3 waters as observed in many coastal aquifers. However, the measured alkalinity concentration in the groundwater was far higher than the concentration predicted by the freshening model. In addition, the behavior of modelled pH and PCO2 were at variance with their distributions in the field data. The second model explored the possible effect of volcanic glass leaching on the groundwater chemistry. Using insight derived from studies of volcanic glass surface alteration as well as experimental work on water-volcanic glass interactions, a geochemical model was developed in which the exchange of H+ for Na+ on the volcanic glass surface is the main mechanism but the exchange of other cations on the volcanic glass surface is also included. The uptake of H+ by the glass surface causes the dissociation of carbonic acid, generating bicarbonate. This model is consistent with the local geology and the field data. It requires, however, volcanic glass leaching to occur in the unsaturated zone where there is an unlimited supply of CO2. The exchange reaction of H+ for Na+ is confined to the surface layer of volcanic glass as otherwise the process becomes limited by slow solid state diffusion of H+ into the glass and Na+ out of the glass. Therefore, volcanic ash deposits, with their high volcanic glass surface areas and matrix flow, are the aquifers where this type of high NaHCO3 waters can be expected, rather than in basalts, which predominantly feature fracture flow. The trace components F, B, As and V are believed to originate from hyaloclastites, consisting of predominantly (90%) of trachy-rhyolite volcanic glass. Although stratigraphically older than the main calcarenite aquifer, topographically they are often located at higher altitudes, above the phreatic level and located along the main recharge flow path. In addition, the semi-arid climate conditions provide a long groundwater residence time for the reactions as well as limited aquifer flushing. © 2019 Elsevier Ltd.

Dahms-Verster, S., Nel, A., van Vuren, J.H.J.*, et al.* (2020) Biochemical responses revealed in an amphibian species after exposure to a forgotten contaminant: An integrated biomarker assessment. *Environmental Toxicology and Pharmacology,* 73.
Available at:
https://www.sciencedirect.com/science/article/pii/S1382668919301462/pdfft?md5=b1cc64fe07fc8e851abb895668b11db2&pid=1-s2.0-S1382668919301462-main.pdf
Keywords: Amphibians; Biomarkers; Integrated biomarker response v2; Metal toxicity; Reactive oxygen species; Vanadium pentoxide; acetylcholinesterase; biological marker;

carbonyl derivative; catalase; glucose; glutathione; lipid; malonaldehyde; metallothionein; reactive oxygen metabolite; superoxide dismutase; adaptation; animal experiment; animal tissue; Article; biochemical response; biochemistry; cell energy; cellular energy allocation; concentration (parameter); controlled study; energy balance; energy consumption; intermethod comparison; liver tissue; long term exposure; muscle tissue; nonhuman; priority journal; tissue level; water pollution; water quality; Xenopus laevis

Abstract:
Vanadium is a metal whose toxicity towards terrestrial and aquatic species has been under-reported to date. The biochemical responses of vanadium in amphibian species have not been determined. To establish the effects of vanadium (V) on exposed adult Xenopus laevis, acute and chronic exposures were conducted, and biomarker analyses were performed on liver and muscle tissues from exposed frogs. Biomarkers of exposure, such as acetylcholinesterase (AChE) and metallothioneins (MT), were analysed. Biomarkers of effect were also analysed to determine possible increases in reactive oxygen species (ROS), and the effect of the exposure on the energy balance in the organisms. These included superoxide dismutase (SOD), catalase (CAT), reduced glutathione (GSH), protein carbonyls (PC), malondialdehyde (MDA), and cellular energy allocation (CEA) (energy available, energy consumption, lipids, proteins and glucose). In acute exposures, the energy balances in organisms were distinctly affected, possibly due to insulin mimetic properties of V. In chronic exposures, MT, AChE, SOD, CAT and GSH responses were more pronounced. Although AChE is generally inhibited by pollutant exposure, in this study, it was stimulated. There were significant inhibitions of SOD and CAT, previously observed in frog species. PC levels increased in the highest acute exposure concentration, indicating protein damage. The IBR.v2 revealed the biochemical responses of V more effectively than traditional statistical analysis. © 2019 Elsevier B.V.

Dane, H. & Şişman, T. (2020) A morpho-histopathological study in the digestive tract of three fish species influenced with heavy metal pollution. *Chemosphere,* 242.
Keywords: Biological parameters; Cyprinidae; Digestive tract; Histopathology; Karasu river; Water pollution; Digestive system; Fish; Heavy metals; Integrated circuits; Manganese removal (water treatment); Rivers; Sediments; Biological parameter; Contaminated sites; Environmental stress; Freshwater fishes; Heavy metal pollution; River pollution; bromide; chromium; cobalt; heavy metal; iron; lead; manganese; river water; selenium; strontium; titanium; vanadium; zinc; condition factor; cyprinid; freshwater ecosystem; health status; Alburnus mossulensis; animal experiment; animal model; animal tissue; Article; Capoeta capoeta; cell vacuole; concentration (parameter); controlled study; degeneration; hyperplasia; intestinal fibrosis; nonhuman; river; sediment; Squalius cephalus; swelling; animal; chemistry; environmental monitoring; gastrointestinal tract; metabolism; pollution; procedures; turkey (bird); water pollutant; Erzurum [Turkey]; Karasu River [Turkey]; Turkey; Chalcalburnus mossulensis; Leuciscus cephalus; Animals; Environmental Pollution; Geologic Sediments; Metals, Heavy; Water Pollutants, Chemical

Abstract:
In this study, the digestive tract of three freshwater fish species (Capoeta capoeta, Alburnus mossulensis and Squalius cephalus) was examined using a morpo-histopathological technique. Sediment and fish samples were taken from selected four stations in the Karasu River (Erzurum, Turkey) between June and September in 2015–2016. In water and sediment samples, the concentrations of some metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr and Pb) were determined. Histopathological changes in digestive tract were determined by histopathological alterations index (HAI). Intestinal coefficient (IC) and condition factor (CF),

which are general indicators of exposure to environmental stress, were calculated for each fish. The highest CF was observed at the least contaminated site of the gradient. C. capoeta showed the highest values of IC among species. The detected abnormalities were infiltration, swelling, gastric degenerations, vacuolization, congestion, epithelial degenerations, hyperplasia, fibrosis and fusion at polluted site fish. It was also observed that the HAI and IC values in fish varied significantly from site to site. The results showed that the content of heavy metals in the river water and sediment may affect the health status of the fish species. © 2019 Elsevier Ltd.

Davila, R.B., Fontes, M.P.F., Pacheco, A.A.*, et al.* (2020) Heavy metals in iron ore tailings and floodplain soils affected by the Samarco dam collapse in Brazil. *Science of the Total Environment,* 709.
Keywords: Doce River; Environmental pollution; Health risk assessment; Mariana disaster; Mine waste; Sequential extraction; Banks (bodies of water); Contamination; Disasters; Extraction; Floods; Health risks; Heavy metals; Iron ores; Ore tailings; Positive ions; Risk assessment; Risk perception; Rivers; Sediments; Soils; BCR sequential extraction; Environmental pollutions; Flood-plain soils; Heavy metal contents; Hydroelectric plant; Mine wastes; Soils and sediments; River pollution; arsenic; barium; chromium; cobalt; copper; heavy metal; nickel; vanadium; zinc; dam failure; floodplain; health risk; iron ore; tailings; adult; Article; Brazil; cancer risk; child; controlled study; dam (barrier); health hazard; human; mine tailings; pollution; priority journal; risk algorithm; sediment; soil pollution; structure collapse; Minas Gerais

Abstract:
In November 2015, the Fundão Dam collapsed releasing about 35 million m− 3 of iron ore tailings into the environment, which covered approximately 15 km2 of floodplain soils. Four years later, there is still great concern and controversy regarding contamination by heavy metals in the affected areas. Thus, the present study sought to evaluate the heavy metal contents and its distribution in tailings and non-affected soils. Tailings samples were collected in the stretch between Bento Rodrigues and the Candonga hydroelectric plant, in addition to a sample inside the Fundão Dam. Non-affected soils and river sediments from the same region were also collected as a control group. The heavy metal contents in the tailings were lower than in non-affected samples from the same area, discarding the hypothesis of contamination by the tailings mud. The non-affected samples presented high levels of As, Ba, Co, Cr, Cu, Ni and Zn, with at least one sample exceeding the quality reference values (QRV's) established for Minas Gerais state, which indicated a scenario of pre-disaster contamination for the Doce River watershed. Most of the elements (As, Cr, Cu, Ni, V and Zn) were extracted in the residual fraction of the BCR sequential extraction, presenting low risk of release in nature. The health risk assessment for As estimated that all the non-affected soils and sediments from Gualaxo do Norte, Carmo and Doce rivers have carcinogenic risk higher than the acceptable value for children. From our results, it is more likely to conclude that the deposited tailings are not a time-bomb for heavy metals contamination in the region. © 2018.

Diana, Z., Sawickij, N., Rivera, N.A.,Jr*, et al.* (2020) Plastic pellets trigger feeding responses in sea anemones. *Aquatic Toxicology (Amsterdam, Netherlands),* 222: 105447.
Keywords: Anemone; Feeding; Lead; Metals; Plastic; Pre-production pellets

Abstract:
Multiple mechanisms for plastic consumption by marine animals have been proposed based on the feeding cues and behavior of the animal studied. We investigated plastic

consumption in sea anemones. We found that anemones readily consumed pristine National Institute of Standards and Technology low-density polyethylene and high-density polyethylene II and III pre-production pellets. Anemone weight, crown area, and number of tentacles were measured before and after 12 days of daily pellet consumption. Crown area significantly increased for control anemones only. Fresh anemones were then sequentially fed consumed and egested pellets from two of the earlier daily trials to measure feeding retention time, which decreased over three to four feedings. The concentrations of elements in anemones (zinc, iron, arsenic, manganese, chromium, copper, vanadium, selenium, nickel, cadmium, and cobalt) were similar to control anemones that were not exposed to pellets. Lead concentrations were significantly higher in anemones fed HDPE III pellets as compared to control. Plastic consumption by marine animals might be reduced by reducing the amount of plastic that enters the ocean and understanding the chemical triggers underlying plastic consumption.

Frank, P., Carlson, R.M.K., Carlson, E.J.*, et al.* (2020) Biological sulfur in the blood cells of Ascidia ceratodes: XAS spectroscopy and a cellular-enzymatic hypothesis for vanadium reduction in the ascidians. *Journal of Inorganic Biochemistry,* 205: 110991.

Keywords: X-ray absorption spectroscopy; Sulfur; Vanadium; Reduction mechanism; Vanadium oxido-reductase

Abstract:

Two samples of living blood cells and of cleared blood plasma from the Phlebobranch tunicate Ascidia ceratodes from Bodega Bay, California, and one of fresh Henze solution from A. ceratodes of Monterey Bay, California, have been examined using sulfur K-edge x-ray absorption spectroscopy (XAS). Biological sulfur included sulfate esters, sulfate and bisulfate ions, benzothiazole, thianthrene, epi-sulfide, thiol and disulfide. Glutathione dominated reduced sulfur, from which an average intracellular Voltage of −0.21 V was calculated. Sulfate-bisulfate ratios yielded blood cell pH values of 2.0 and 2.8. Total blood cell [sulfur] was 373±9 mM or 296±73 mM from $BaSO_4$ gravimetry. Two plasma samples (pH 6.9 or 7.0; [S] = 33±6 mM or 26±4 mM) were dominated by sulfate and disulfide. Fresh Henze solution evidenced a sulfur inventory similar to blood cells, with calculated pH = 2.7. A V(III)-sulfonate fraction varied systematically with intracellular pH across six independent blood cell samples, implying a vanadium mobilization pathway. Bodega Bay and Monterey Bay A. ceratodes appear to maintain alternative suites of low-valent sulfur. The significance of the vanabins to vanadium metabolism is critically examined in terms of known protein – V(IV) biochemistry. Finally, a detailed hypothesis for the reduction of $[VO_4]^{3-}$ to V(III) in ascidians is introduced. A vanadium oxido-reductase is proposed to span the signet ring membrane and to release V(III) into the inner acidic vacuole. The V(V) to V(III) reduction is predicted require an inner-sphere mechanism, a thiol reductant, 7-coordinate V(III), a biologically accessible Voltage, and proton-facilitated release of V(III). ".

Guo, Y., Li, H.Y., Yuan, Y.H.*, et al.* (2020) Microemulsion extraction: An efficient way for simultaneous detoxification and resource recovery of hazardous wastewater containing V(V) and Cr(VI). *Journal of Hazardous Materials,* 386: 121948.

Keywords: Cr(VI); Microemulsion extraction; Recovery; V(V); Wastewater

Abstract:

Vanadium (V) metallurgy industry produces significant amount of ammonium polyvanadate (APV) wastewater containing V(V) and Cr(VI), thereby polluting the ecological environment and adversely affecting human health and wasting natural resources. Herein, an efficient method for separating V and chromium (Cr) from APV wastewater is proposed based on an artful pretreatment of the selective transformation of Cr(VI) using microemulsion extraction

to realize harmless treatment of the wastewater and recycling of V and Cr resources. The influence of various factors on the V and Cr extraction efficiencies has been investigated, including the extractant concentration, aqueous phase-to-microemulsion volume ratio, contact time, and temperature. Furthermore, the principle of Cr transformation and microemulsion extraction and stripping has been illustrated and the recyclability of the microemulsion has been evaluated. Under optimum conditions, 96.29 % of V(V) and 95.56 % of Cr(VI) were separately recovered from the AVP wastewater, confirming the efficient separation and recovery of V and Cr. This study highlights a new approach for the separate recovery of V(V) and Cr(VI) from hazardous wastewater and provides new insights into the simultaneous detoxification and resource utilization of industrial hazardous wastes.

He, W., Liao, W., Yang, J.*, et al.* (2020) Removal of vanadium from aquatic environment using phosphoric acid modified rice straw. *Bioremediation Journal,* 24(1): 1-10.
Keywords: Adsorption; aquatic environment; modified rice straw; vanadium

Abstract:
Vanadium (V) is a toxic metal, which dominantly exists as V^{5+} in an aquatic environment. Rice straw, which is an abundant agricultural by-product throughout China was used to treat V^{5+} containing wastewater as an adsorbent after phosphoric acid treatment. The effects of initial V^{5+} concentration, solution temperature, pH and reaction time on V removal by phosphoric acid modified rice straw (AcM) were systematically assessed. A pH range of 2.0–3.0 was favorable for V removal and the adsorption capacity of V by AcM increased with elevated solution temperature. The maximum adsorption capacity for water containing 500 mg V^{5+} L^{-1} was 24.70 mg V g^{-1} dry matter under the optimum operation (3.33 g L^{-1} AcM, pH = 2.0, 50 °C, and 200 rpm for 4 h). Adsorption experiment data fitted well to pseudo-second-order kinetic and Langmuir adsorption isotherm models. In the presence of coexisting ions, Na^{+}, Cu^{2+}, NO_3^{-} and Cl^{-} had no significant ($P > 0.05$) effect on V removal. These results indicated that AcM derived from agricultural waste was effective to remove V^{5+} from aqueous solution.

Kay, M.L., Wiklund, J.A., Remmer, C.R.*, et al.* (2020) Evaluating temporal patterns of metals concentrations in floodplain lakes of the Athabasca Delta (Canada) relative to pre-industrial baselines. *The Science of the Total Environment,* 704: 135309.
Keywords: Alberta oil sands; Aquatic ecosystem monitoring; Environmental impact assessment; Paleolimnology; River sediment quality; Wood Buffalo National Park

Abstract:
Sediment quality monitoring is widely used to quantify extent of river pollution, but requires knowledge of pre-disturbance conditions in the potentially altered landscape. This has long been identified as a critical aspect to develop for addressing concerns of river pollution in the Alberta Oil Sands Region. Here, we use analyses of sediment cores from eight floodplain lakes spanning a 67 river-km transect across the Athabasca Delta to define pre-1920 (pre-industrial) baseline concentrations for vanadium and five primary pollutants. We then evaluate if sediment metals concentrations have become enriched above baseline since onset of oil sands development and other industrial activities. Results demonstrate no enrichment of metals concentrations (except zinc at one lake) and absence of consistent temporal increases above pre-industrial baselines. Thus, natural processes continue to dominate metal deposition in floodplain lakes of the Athabasca Delta -- an important finding to inform stewardship decisions. The pre-1920 metals concentrations baselines offer a useful tool for ongoing sediment monitoring in aquatic ecosystems of the Athabasca Delta.

Li, K., Liu, Z., Shi, X.*, et al.* (2020) Novel in situ method based on diffusive gradients in thin-films with lanthanum oxide nanoparticles for measuring As, Sb, and V and in waters. ***Journal of Hazardous Materials,*** **383**.
Keywords: As; Diffusive gradients in thin-films; Monitoring; Sb; V; Alkalinity; Antimony; Arsenic; Deterioration; Diffusion in solids; Ionic strength; Lanthanum oxides; Nanoparticles; Oxide films; Sodium nitrate; Thin films; Vanadium; Competition effects; Concentration ratio; Diffusive gradients in thin films; Field deployment; Long-term storage; Oxide nanoparticles; Performance characteristics; Performance deterioration; Antimony compounds; lanthanum oxide; metal nanoparticle; water; diffusivity; environmental gradient; film; in situ measurement; long-term change; methodology; nanoparticle; performance assessment; pollution monitoring; sampling; water treatment; Article; diffusion; gel; pH; storage; China; Yangtze River

Abstract:
Lanthanum oxide nanoparticles (nano-La2O3) was used to develop a novel binding gel within an in situ passive sampler based on diffusive gradients in thin-films technique (NL-DGT) for measuring As(V), Sb(V), and V(V). Performance characteristics of NL-DGT were independent of pH (pH: 3.1–7.9 for As, 3.1–8.5 for V, and 3.1–6.5 for Sb) and ionic strength (0.1–500 mmol L−1 for As and V, and 0.1–200 mmol L−1 for Sb). No obvious competition effects among As, Sb, and V with different concentration ratios were found for NL-DGT measurement. Long term storage (8–188 d) of the nano-La2O3 gels in 0.01 mol L−1 NaNO3 at 4 °C did not affect their performance. During the field deployments in Yangtze and Jiuxiang River, NL-DGT measured concentrations of As and V were similar to those measured by the grab samples, while some differences were found for Sb between DGT and grab sampling because higher pH (∼8.0) in the studied rivers caused the performance deterioration of NL-DGT. Generally, the newly developed NL-DGT is suitable for monitoring As and V in freshwater from acidic to light alkaline and Sb in acidic and neutral water. © 2019 Elsevier B.V.

Lin, X., Meng, G., Pan, H.*, et al.* (2019) Continental-scale stream sediment geochemical mapping in southern China: An insight into surface processes and tectonic framework. ***Journal of Geochemical Exploration,*** **207**.
Keywords: 76-GEM; Compositional data; Stream sediments; Surface processes; Tectonic framework; Bismuth alloys; Chromium compounds; Economic geology; Exploratory geochemistry; Hematite; Lithology; Manganese compounds; Mapping; Mineral resources; Mineralogy; Nickel compounds; Process control; Rare earth elements; Rare earths; Sediments; Tectonics; Tin alloys; Titanium compounds; Topography; Weathering; Surface process; Vanadium compounds; chemical composition; chemical weathering; mineral resource; rare earth element; sediment chemistry; sedimentation; trace element; Cathaysia Block; China; Yangtze Platform

Abstract:
Continental-scale stream sediment geochemical data from the 76-element GEochemical Mapping (76-GEM) project covering southern China were analyzed in this contribution. 5244 composite stream sediment samples at the scale of ca. 1 sample per 500 km2 were used. The focus has been directly put on element associations of: (1) Light Rare Earth Elements (LREEs, i.e. La, Ce, Pr, Nd, Sm and Eu); (2) Heavy Rare Earth Elements (HREEs, i.e. Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y); (3) Iron Group Elements (IGEs, Ti, V, Cr, Mn, total Fe2O3 (FeT), Co and Ni); (4) Platinum Group Elements (PGEs, i.e. Ru, Rh, Pd, Os, Ir and Pt) and (5) Mo, Sn, W and Bi. Given that geochemical data are typical of compositional (closed) data, the five associations were represented by the sum values of centered logratio (clr) transformed data

of elements in the predefined groups. It presents the first-time the continental-scale patterns of representative element associations in southern China. Maps were compared to independent datasets of lithology, tectonics and topography to discover processes governing the distribution. The five element associations could reflect the processes of: (1) weathering of dominantly felsic intrusive rocks (LREEs and HREEs); (2) weathering of mafic/ultramafic rocks (IGEs and PGEs); (3) weathering of dominantly felsic intrusives and hosted mineralization (Mo-Sn-W-Bi) and (4) anthropogenic and possible geogenic additions (Mo-Sn-W-Bi and PGEs). A general good agreement was found between maps of element associations and maps of surface geology and tectonics. The clr patterns are interpretable geologically and respond reasonably well to the processes such as lithological control and secondary transportation. As indicated by the clr patterns, two prominent tectonic units with controversial boundary in southern China, i.e. the Yangtze and Cathaysia blocks can be geochemically demarcated by the spatial patterns of REEs, IGEs and PGEs at this scale. The distinct patterns across the Jiangshan-Shaoxing and Pingxiang-Chaling faults (or the Shi-Hang Belt) suggested a felsic end-member to the southeast and a mafic end-member to the northwest. The spatial patterns of IGEs, PGEs and Mo-Sn-W-Bi also reflected that lithology is in dominant control of the distribution rather than local mineralization at this scale. Future studies of this dataset regarding single elements and certain element associations of particular interests (e.g., Cd, Ni and REEs) are also needed, which may provide new insights into environmental issues, mineral resources and tectonic framework in southern China.

Lüders, K., Dahmke, A., Fiedler, M.*, et al.* (2020) Temperature influence on mobilisation and (re)fixation of trace elements and heavy metals in column tests with aquifer sediments from 10 to 70 °C. *Water Research,* 169.

Keywords: Geothermal applications; Groundwater quality; Hydrogeochemistry; Reversibility; Trace elements and heavy metals; Underground thermal energy storage; Aquifers; Geothermal energy; Groundwater; Groundwater resources; Heat storage; Heavy metals; Hydrochemistry; Sediments; Temperature; Thermal energy; Water quality; Environmental consequences; Hydro geochemistries; Hydrochemical conditions; Increased temperature; Temperature influence; Temperature variation; Trace elements; aluminum; arsenic; barium; calcium ion; chloride; chromium; cobalt; copper; ground water; heavy metal; lead; lithium; magnesium ion; manganese; molybdenum; nickel; oxygen; selenium; silicon; sodium ion; strontium; thallium; tin; trace element; uranium; vanadium; zinc; concentration (composition); energy storage; mobilization; temperature effect; Article; dissolution; heating; oxidation; priority journal; sediment; temperature sensitivity; environmental monitoring; heat; water pollutant; Geologic Sediments; Hot Temperature; Metals, Heavy; Water Pollutants, Chemical

Abstract:
The operation of seasonal underground thermal energy storages (UTES) as part of renewed heat supply systems can cause amplified temperature variations in the urban subsurface. Therefore, long-term environmental consequences for water extractions by trace elements and heavy metals (TEHMs) are a key point of concern regarding temperature effects on aquifer hydrogeochemistry. To address this issue, we report the results of flow-through and circular-flow column tests conducted with 4 anoxic northern German aquifer sediments, tempered to 10, 25, 40 and 70 °C and analysed for 20 TEHMs. Increased temperatures in column tests caused increasing Li, As, Mo, Sb and Ba concentrations and decreasing Ni concentrations in all of the sediments with a sediment-specific extent, whereas effects on V, Mn, Co, Tl and U concentrations varied sediment-specifically. Apart from Ba, all these components were released as a pulse in the initial heating phase, indicating a temperature

dependent, finite, elutable pool. Re-cooling of the previously heated circular-flow column tests to 10 °C caused reversals of concentration changes by 30–95%. This indicates a return to initial hydrochemical conditions after termination of heat storage operation and downstream from heat storages during the operations. The latter was approximated for As with a simplified analytical 1-dimensional approach, presuming transferability from a laboratory to a field scale. This reversal in concentration changes enables active cooling as a countermeasure in cases of unexpected, adverse TEHM progression. From the perspective of our findings, TEHM concentration changes appear to be temporally and spatially limited.

Montoya-Mendoza, J., Alarcón-Reyes, E., Castañeda-Chávez, M.R.*, et al.* (2019) Heavy metals in muscle tissue of pterois volitans from the veracruz reef system national park, mexico. *International Journal of Environmental Research and Public Health,* 16(23).
Available at: https://www.mdpi.com/1660-4601/16/23/4611/pdf
Keywords: Lionfish; Reef; Trace metals; cadmium; lead; vanadium; zinc; concentration (composition); fish; health risk; heavy metal; muscle; trace metal; animal tissue; Article; atomic absorption spectrometry; concentration (parameter); controlled study; dry weight; health hazard; Mexico; muscle tissue; nonhuman; Pterois volitans; Scorpaeniformes; Mexico [North America]; Pterois

Abstract:
Concentrations of cadmium (Cd), lead (Pb), vanadium (V), and zinc (Zn) were measured in the muscle of 30 specimens of Pterois volitans, captured on April 2018, in the Veracruz Reef System National Park (VRSNP), Veracruz, Mexico. Concentrations, in the samples, were quantified with atomic absorption spectrophotometry (AAS), after microwave digestion. Results of the mean concentration, in descending order were V = 7.3 ± 0.7; Pb = 0.66 ± 0.07; Zn = 0.43 ± 0.14; and Cd = 0.03 ± 0.01 mg kg^{-1} dry weight. These values did not exceeded limits established in the Mexican National Standard (NOM-242-SSA1-2009), of Cd and Pb (0.5 mg kg^{-1}) wet weight. This means that consumption of lionfish from this site does not pose a potential risk for human health. © 2019 by the authors. Licensee MDPI, Basel, Switzerland.

Owca, T.J., Kay, M.L., Faber, J.*, et al.* (2020) Use of pre-industrial baselines to monitor anthropogenic enrichment of metals concentrations in recently deposited sediment of floodplain lakes in the Peace-Athabasca Delta (Alberta, Canada). *Environmental Monitoring and Assessment,* 192(2).
Available at: https://link.springer.com/content/pdf/10.1007/s10661-020-8067-y.pdf
Keywords: Alberta oil sands; Aquatic ecosystem monitoring; Environmental impact assessment; Paleolimnology; River sediment quality; Wood Buffalo National Park; Aluminum; Aquatic ecosystems; Environmental impact; Environmental impact assessments; Floods; Lakes; Oil sands; Petroleum transportation; Sand; Surficial sediments; Ecosystem monitoring; Environmental stewardship; Industrial development; Monitoring frameworks; Peace-athabasca deltas; River sediments; Rivers; beryllium; cadmium; chromium; copper; floodwater; lead; metal; nickel; river water; unclassified drug; vanadium; water; zinc; aquatic ecosystem; concentration (composition); enrichment; environmental monitoring; floodplain; lacustrine deposit; oil sand; surficial sediment; Alberta; Article; concentration (parameter); controlled study; environmental enrichment; flooding; lake sediment; pollution transport; river sediment; sediment; tar sand; water analysis; Canada; Peace-Athabasca Delta

Abstract:
Well-designed monitoring approaches are needed to assess effects of industrial

development on downstream aquatic environments and guide environmental stewardship. Here, we develop and apply a monitoring approach to detect potential enrichment of metals concentrations in surficial lake sediments of the Peace-Athabasca Delta (PAD), northern Alberta, Canada. Since the ecological integrity of the PAD is strongly tied to river floodwaters that replenish lakes in the delta, and the PAD is located downstream of the Alberta oil sands, concerns have been raised over the potential transport of industry-supplied metals to the PAD via the Athabasca River. Surface sediment samples were collected in September 2017 from 61 lakes across the delta, and again in July 2018 from 20 of the same lakes that had received river floodwaters 2 months earlier, to provide snapshots of metals concentrations (Be, Cd, Cr, Cu, Ni, Pb, V, and Zn) that have recently accumulated in these lakes. To assess for anthropogenic enrichment, surficial sediment metals concentrations were normalized to aluminum and compared to pre-industrial baseline (i.e., reference) metal-aluminum linear relations for the Athabasca and Peace sectors of the PAD developed from pre-1920 measurements in lake sediment cores. Numerical analysis demonstrates no marked enrichment of these metals concentrations above pre-1920 baselines despite strong ability (> 99% power) to detect enrichment of 10%. Measurements of river sediment collected by the Regional Aquatics- and Oil Sands-Monitoring Programs (RAMP/OSM) also did not exceed pre-1920 concentrations. Thus, results presented here show no evidence of substantial oil sands-derived metals enrichment of sediment supplied by the Athabasca River to lakes in the PAD and demonstrate the usefulness of these methods as a monitoring framework.

Paradis, C.J., Johnson, R.H., Tigar, A.D.*, et al.* (2020) Field experiments of surface water to groundwater recharge to characterize the mobility of uranium and vanadium at a former mill tailing site. *Journal of Contaminant Hydrology,* 229: 103581.
Keywords: Groundwater; Surface water; Uranium; Vanadium

Abstract:
Characterizing the mobility of uranium and vanadium in groundwater with a hydraulic connection to surface water is important to inform the best management practices of former mill tailing sites. In this study, the recharge of river water to the unsaturated and saturated zones of a uranium-contaminated alluvial aquifer was simulated in a series of forced-gradient single- and multi-well injection-extraction tests. The injection fluid (river water) was traced with natural and artificial tracers that included halides, fluorobenzoates, lithium, and naphthalene sulfonate to characterize the potential mass transport mechanisms of uranium and vanadium. The extraction fluid (river water/groundwater mixture) was analyzed for the tracers, uranium, and vanadium. The results from the tracers indicated that matrix diffusion was likely negligible over the spatiotemporal scales of the tests as evident by nearly identical breakthrough curves of the halides and fluorobenzoates. In contrast, the breakthrough curves of lithium and naphthalene sulfonate indicated that sorption by cation exchange and sorption to organic matter, respectively, were potential mass transport mechanisms of uranium and vanadium. Uranium was mobilized in the saturated zone containing gypsum (gypsum-rich zone), the vadose zone (vadose-rich zone), and the saturated zone containing organic carbon (organic-rich zone) whereas vanadium was mobilized only in the saturated gypsum-rich zone. The mechanisms responsible for the mobilization of uranium and vanadium were likely dissolution of uranium- and vanadium-bearing minerals and/or desorption from the gypsum-rich zone, flushing of uranium from the vadose-rich zone, and desorption of uranium from the organic-rich zone due to the natural contrast in the geochemistry between the river water and groundwater. The experimental design of this study was unique in that it employed the use of multiple natural and artificial tracers coupled with a direct injection of native river water to groundwater.

These results demonstrated that natural recharge and flooding events at former mill tailing sites can mobilize uranium, and possibly vanadium, and contribute to persistent levels of groundwater contamination.

Qiao, J., Zhu, Y., Jia, X.*, et al.* (2020) Distributions of arsenic and other heavy metals, and health risk assessments for groundwater in the Guanzhong Plain region of China. *Environmental Research,* 181.**
Keywords: Groundwater; Health risk assessment; Heavy metal; aluminum; arsenic; cadmium; chromium; cobalt; copper; ground water; iron; lead; manganese; molybdenum; nickel; vanadium; zinc; concentration (composition); health risk; risk assessment; water quality; China; health hazard; human; monsoon climate; precipitation; priority journal; statistics; water pollution; water sampling; Guanzhong Plain; Shaanxi

Abstract:
We assessed the quality of groundwater in the Guanzhong Plain region of China, where we evaluated the levels of As and 12 other heavy metals. © 2019 Elsevier Inc. The aim of this study was to evaluate the quality of shallow groundwater and deep groundwater in the Guanzhong Plain region of China, as well as the related health risk to humans. In total, 130 groundwater samples were collected comprising 116 from shallow groundwater (dug wells) and 14 from deep groundwater (drilled wells). The water samples were analyzed to determine the levels of As and 12 other heavy metals (Al, Cd, Mn, Cr, V, Fe, Ni, Cu, Zn, Co, Pb, and Mo). The results showed that the concentrations of As and other heavy metals in the deep groundwater samples were lower than the safe limits, but the Cr concentrations in some shallow groundwater samples exceeded the safe limits. The heavy metal pollution index and heavy metal evaluation index both showed that As and other heavy metals were pollutants at low levels in all of the shallow and deep groundwater sample. Health risk assessments showed that the deep groundwater samples had no associated non-carcinogenic health risks, whereas the shallow groundwater samples had non-carcinogenic health risks due to contamination with Cr and As. Some shallow groundwater samples had associated carcinogenic health risks due to contamination with Cr and As, whereas the deep groundwater samples only had carcinogenic health risks because of contamination with Cr. These results suggest that local residents and government departments should be made aware of Cr and As pollution in shallow groundwater. © 2019 Elsevier Inc.

Roche, K., Kuta, J., Sedlacek, I.*, et al.* (2019) Concentrations of Thirteen Trace Metals in Scales of Three Nototheniid Fishes from Antarctica (James Ross Island, Antarctic Peninsula). *Biological Trace Element Research,* 191(1): 214-223.
Keywords: Antarctic peninsula; Bioaccumulation; Czech Antarctic Station; Notothenioidei; Trace metal contaminants; Shallow coastal waters; KING-GEORGE ISLAND; URANIUM BIOACCUMULATION; CLIMATE-CHANGE; HEAVY-METALS; ELEMENTS; TISSUE; VARIABILITY; ECOSYSTEM; MERCURY; HABITS; Biochemistry & Molecular Biology; Endocrinology & Metabolism

Abstract:
In this study, we assessed concentrations of 13 trace metals in the scales of Notothenia coriiceps, Trematomus bernacchii and Gobionotothen gibberifrons caught off the coast of James Ross Island (Antarctic Peninsula). Overall, our results for scales broadly match those of previous studies using different fish and different organs, with most metals found at trace levels and manganese, aluminium, iron and zinc occurring at high levels in all species. This suggests that scales can serve as a useful, non-invasive bioindicator of long-term contamination in Antarctic fishes. High accumulation of manganese, aluminium, iron and

zinc is largely due to high levels in sediments associated with nearby active volcanic sites. Manganese, vanadium and aluminium showed significant positive bioaccumulation in T. bernacchii (along with non-significant positive accumulation of iron, zinc, cobalt and chromium), most likely due to greater dietary specialisation on sediment feeding benthic prey and higher trophic species. Levels of significance in bioaccumulation regressions were strongly affected by large-scale variation in the data, driven largely by individual differences in diet and/or changes in habitat use and sex differences associated with life stage and reproductive status. Increased levels of both airborne deposition and precipitation and meltwater runoff associated with climate change may be further adding to the already high levels of manganese, aluminium, iron and zinc in Antarctic Peninsula sediments. Further long-term studies are encouraged to elucidate mechanisms of uptake (especially for aluminium and iron) and possible intra- and interspecific impacts of climate change on the delicate Antarctic food web.

Schuth, S., Brüske, A., Hohl, S.V.*, et al.* (2019) Vanadium and its isotope composition of river water and seawater: Analytical improvement and implications for vanadium isotope fractionation. *Chemical Geology,* 528.**

Keywords: Isotopes; River water; Seawater; Vanadium; Yangtze River Basin; Dissolution; Hot springs; Iron oxides; Oceanography; Oxygen; Particles (particulate matter); Resins; Rivers; Submarine geology; Watersheds; Analytical uncertainty; Isotope fractionation; Lower yangtze rivers; Particulate fraction; Redox-sensitive metals; Theoretical calculations; adsorption; isotopic composition; isotopic fractionation; marine sediment; oxidation; water chemistry; China; Hubei; Three Gorges Dam; Yangtze Basin

Abstract:
Investigation of redox variations in recent and paleo-oceans has been of particular scientific interest to elucidate the rise and variations of the atmospheric oxygen level by analyses of isotopic signatures of redox-sensitive elements like Fe, Mo, and U. Vanadium is another redox-sensitive metal that has become the target of stable isotope research during the last decade. During the last decade, research of the oceanic V cycle revealed a rather complex interplay of riverine V as a major V source to the oceans on one side with V deposition in sediments and at hydrothermal vents as major sinks on the other. The balance between these major V pools is sensitive to the ocean water oxygen level and chemistry. However, the data set of stable V isotope signatures of seawater is still very small, but indicates already subtle variation of the V isotope signatures in the marine environment. However, the V isotopes of marine sediments and particularly the riverine V isotope composition of dissolved and particulate V, i.e. the major source of V in modern marine environments, has not been constrained at all so far. In this study, we present a new method for efficient V separation from seawater that allows multiple analyses of the V isotope composition of a single sample. To separate V from large amounts (volume ≥2 L) of seawater samples, we employ the Bio-Rad® Chelex-100 resin and conventional cation and anion resins to yield a high V recovery of ≥90% from an UV-irradiated sample. Non-irradiated samples were marked by lower V recovery rates of ca. 75%, which was also observed in earlier studies. Further tests however revealed that even such reduced V yields do not incur significant V isotope fractionation within analytical uncertainty. Our δ51VAA value of +0.27‰ ±0.14 (2s.d., n = 3) for the NASS-6 seawater reference solution perfectly matched earlier results. In addition, seawater collected in the Wadden Sea at the German North Sea coast is marked by a δ51VAA signature of around +0.02‰ ±0.19 (2s.d., n = 17), which is slightly lower than those of the great oceans, and may be related to an influx of river water, bioactivity, or a tide-induced V mobilization. To characterize the V isotope composition of the major V source to the oceans, we determined for the first time V isotope signatures of 13 selected rivers (dissolved and particulate fractions of source water, tributary rivers, and the Yangtze

River) in the Yangtze River Basin, China. A large variation of dissolved V (ca. 0.07 to 6.0 μg/L) and particulate-bound V (ca. 0.03 to 17 μg/L) was found for the sample suite. The obtained δ51VAA values of the dissolved V pool span a range of −0.76‰ (±0.18; 2s.d.) to −0.10‰ (±0.22, 2s.d.), whereas particulate-bound V extends to lower δ51V signatures between −2.13‰ (±0.30, 2s.d.) and −0.11‰ (±0.11, 2s.d.). Notably, dissolved V from the river sources and small tributaries scatters between ca. −0.4‰ to −0.7‰, and agrees well with the predicted average δ51VAA value of −0.6‰ ±0.3 for continental run-off by Wu et al. (2019). For the lower Yangtze River, however, the dissolved δ51VAA signatures increase from the Three-Gorges Dam towards the estuary from −0.76‰ to −0.10‰, suggesting V isotope fractionation due to adsorption to abundant particulate Fe oxides, but may also reflect an input of anthropogenic V. The low δ51VAA of particulate V largely follow this trend, and thus indicate ongoing V isotope fractionation during riverine V transport to the ocean. Our first results of stable V isotope investigation of river waters show that V isotope signatures can indeed carry their host rock signature, but are also sensitive to adsorption-driven fractionation in oxidized environments. The latter strongly depends, as predicted from earlier theoretical calculations, on the presence of particulate Fe-(oxyhydr)oxides and highlights gradual V isotope fractionation during riverine V transport to the ocean.

Shaheen, S.M., El-Naggar, A., Antoniadis, V.*, et al.* (2020) Release of toxic elements in fishpond sediments under dynamic redox conditions: Assessing the potential environmental risk for a safe management of fisheries systems and degraded waterlogged sediments. *Journal of Environmental Management,* 255: 109778.

Keywords: Controlling factors; Degraded waterlogged sediments; Redox potential; Risk assessment; Trace elements; aromatic compound; arsenic; chloride ion; cobalt; copper; fatty acid; molybdenum; nickel; organic carbon; phospholipid; selenium; sulfate; sulfur; trace element; vanadium; zinc; environmental risk; fishery management; freshwater sediment; redox conditions; sediment chemistry; toxicity; waterlogging; Article; ecotoxicity; Egypt; environmental management; factor analysis; fish; fishery; microcosm; nonhuman; oxidation reduction potential; pH; pond; risk; sampling; sediment; soil; solubility; environmental monitoring; oxidation reduction reaction; soil pollutant; water pollutant; Fisheries; Geologic Sediments; Oxidation-Reduction; Soil Pollutants; Water Pollutants, Chemical

Abstract:
Waterlogged soils and sediments contaminated with potentially toxic elements (PTEs) constitute a complicated case of degraded areas; their management requires understanding of the dynamic redox-driven PTE mobilization. Such studies about PTE redox-induced dynamics in fishpond sediments are still scarce, but of great importance concerning environmental and human health risk. We studied the redox potential (EH)-induced impacts on the solubility of As, Co, Cu, Mo, Ni, Se, V, and Zn in the sediments of a fish farm in the Nile Delta, Egypt, using an automated apparatus of biogeochemical microcosm. We assessed the fate of elements as affected by the EH-induced changes in pH, Fe, Mn, SO4 2−, Cl−, and the dissolved aliphatic (DOC) and aromatic (DAC) organic carbon. Sediment redox ranged from −480 mV to +264 mV. Flooding the sediments caused a significant decrease in pH from 8.2 to 5.7. Dissolved concentrations of As, Co, Ni, Se, and Zn, as well as DOC, Fe, and Mn increased under the reducing acidic conditions. The release of As, Co, Ni, Se, and Zn could be attributed to the decrease of EH and the subsequent decrease of pH, as well as to the increase of DOC, and/or the dissolution of Fe–Mn oxides caused by redox reactions. Dissolved concentrations of Cu, Mo, and V increased under oxic conditions and were significantly positive correlated with EH, pH, DAC, and SO4 2−. This enhancement might be caused by the EH-dependent increase of pH under oxic conditions (particularly for Mo and

V), which also led to DAC increase. Sulfide oxidation and the release of the associated elements may have also had a contribution, particularly in the release of Cu. Therefore, the release dynamics of dissolved Cu, Mo, and V in the sediments were controlled, to a certain extent, by the changes of EH/pH, DAC, and sulfur chemistry. We conclude that the biogeochemical differences in the behaviour of the studied elements under variable redox regimes substantially affected the fishponds via possible enhancement of PTE mobilization. Our work shows that the potential environmental risks related to PTE mobilization and fish food security should be taken into consideration for the management of degraded aquaculture systems and waterlogged soils and sediments. © 2019 Elsevier Ltd.

Smolen, S., Kowalska, I., Halka, M.*, et al.* (2020) SelectedAspects of Iodate and Iodosalicylate Metabolism in Lettuce Including the Activity of Vanadium Dependent Haloperoxidases as Affected by Exogenous Vanadium. *Agronomy-Basel,* 10(1): 1.
Keywords: beneficial elements; iodobenzoates; iodosalicylates; plant-derived thyroid hormone analogs; T3; thyroid hormone; triiodothyronine; vanadium-dependent haloperoxidases; IODINE BIOFORTIFICATION; LAMINARIA-DIGITATA; GROWTH; IODOPEROXIDASE; TOXICITY; BROMOPEROXIDASE; MOLYBDENUM; INHIBITORS; NUTRITION; FEATURES; Agriculture; Plant Sciences

Abstract:
In marine algae, vanadium (V) regulates the cellular uptake of iodine (I) and its volatilization as I-2, the processes catalyzed by vanadium-dependent haloperoxidases (vHPO). Relationships between I and vanadium V in higher plants, including crop plants, have not yet been described. Little is known about the possibility of the synthesis of plant-derived thyroid hormone analogs (PDTHA) in crop plants. The activity of vHPO in crop plants as well as the uptake and metabolism of iodosalicylates in lettuce have not yet been studied. This studyaimed to determine the effect of V on the uptake and accumulation of various forms of I, the metabolism of iodosalicylates and iodobenzoates and, finally, on the accumulation of T3 (triiodothyronine-as example of PDTHA) in plants. Lettuce (Lactuca sativa L. var. capitata 'Melodion' cv.) cultivation in a hydroponic NutrientFilm Technique (NFT) system was conducted with the introduction of 0 (control), 0.05, 0.1, 0.2, and 0.4 mu M V doses of ammonium metavanadate (NH4VO3) in four independent experiments. No iodine treatment was applied in Experiment No. 1, while iodine compounds were applied at a dose of 10 mu M (based on our own previous research) as KIO3, 5-iodosalicylic acid (5-ISA) and 3,5-diiodosalicylic acid (3,5-diISA) in Experiment Nos. 2, 3 and 4, respectively. When lettuce was grown at trace amount of I in the nutrient solution, increasing doses of V contributed to the increase of (a) I content in roots, (b) I uptake by whole lettuce plants (leaves + roots), and (c) vHPO activity in leaves (for doses 0.05-0.20 mu M V). Vanadium was mainly found in roots where the content of this element increased proportionally to its dose. The content of V in leaves was not modified by V introduced into the nutrient solution. We found that5-ISA, 3,5-diISA and T3 were naturally synthesized in lettuce and its content increased when 5-ISA, 3,5-diISA were applied. Quantitative changes in the accumulation of organic metabolites (iodosalicylates and iodobenzoates) accumulation were observed, along with increased T3 synthesis, with its content in leaves exceeding the level of individual iodosalicylates and iodobenzoates. The content of T3 was not affected by V fertilization. It was concluded that iodosalicylates may participate in the biosynthesis pathway of T3-and probably of other PDTHA compounds.

Snow, J.T., Holdship, P. & Rickaby, R.E.M. (2020) Antagonistic co-limitation through ion promiscuity – On the metal sensitivity of Thalassiosira oceanica under phosphorus stress. *Science of the Total Environment,* 699.

Keywords: Nutrients; Phosphorus; Elevated concentrations; Fundamental principles; Intracellular accumulation; Microbial communities; Multiple resources; Nutrient limitations; Oceanic Anoxic Event; Primary productivity; Vanadium compounds; arsenic; arsenic acid; molybdenum; molybdic acid; phosphate; vanadic acid; vanadium; metal; antagonism; arsenate; community response; concentration (composition); environmental stress; ion; molybdate group; nutrient limitation; phytoplankton; vanadate group; animal cell; Article; cell communication; cell size; cell volume; chemical phenomena; concentration (parameter); controlled study; growth inhibition; homeostasis; ion promiscuity; nonhuman; priority journal; Thalassiosira; Thalassiosira oceanica; diatom; physiology; sea; toxicity; water pollutant; Diatoms; Metals; Oceans and Seas; Water Pollutants, Chemical

Abstract:
Nutrient limitation of primary producers is a fundamental principle in biogeochemical oceanography and has been used with great success in prescribing understanding to patterns of marine primary productivity. In recent years the paradigm of nutrient limitation has expanded from single nutrient limitation towards concepts of co-limitation by multiple resources. Interactive effects between multiple limiting resources are now thought commonplace in marine microbial communities. Here we investigate the response exhibited by phosphate-limited Thalassiosira oceanica to elevated concentrations of the phosphate analogs vanadate, arsenate and molybdate. Enrichments in external arsenate and vanadate to phosphate-limited cultures act to suppress growth rates entirely, an effect not seen in phosphate replete conditions. Retardation of growth rates is attributed to mistaken uptake through ion promiscuity as evidenced by observations of significant intracellular accumulation of both arsenic and vanadium under phosphate limited conditions. We describe this novel co-limitation scenario as dependent antagonistic co-limitation (DAC), and suggest that this phenomenon of non-deliberate intracellular accumulation could be used as both a proxy of phosphate stress in the modern ocean and a possible marker of phosphate depletion limiting the duration of oceanic anoxic events. © 2019.

Tzafriri-Milo, R., Benaltabet, T., Torfstein, A.*, et al.* (2019) The Potential Use of Invasive Ascidians for Biomonitoring Heavy Metal Pollution. *Frontiers in Marine Science,* 6: 611.
Keywords: benthic ecology; metal accumulation; biomonitoring Programs; tunicates; Red Sea; Mediterranean Sea; REPRODUCTIVE MECHANISMS; STYELA-PLICATA; TRACE-METALS; BIOACCUMULATION; VANADIUM; ACCUMULATION; CD; CU; CONTAMINATION; BIOINDICATOR; Environmental Sciences & Ecology; Marine & Freshwater Biology

Abstract:
Heavy metal (HM) inputs into marine environments and their effect on marine organisms are of major concern. Here, we examined the potential use of two invasive ascidian species, Phallusia nigra and Microcosmus exasperatus, as bio-indicators of 11 HMs in the Mediterranean and Red Sea coasts of Israel. Individuals were collected on a seasonal basis from three sites over 1 year, and analysis was carried out separately for the tunic and the body. Both species accumulated high levels of HMs, which varied seasonally and spatially. In M. exasperatus the majority of HMs were found in the tunic, and in P. nigra in the body, suggesting the need to analyze total individuals in future studies. Hepato-Somatic Index values for M. exasperatus were significantly lower at the polluted site. Investigation of a popular public beach revealed high levels of certain dissolved HMs in both the water and in the ascidians. The wide geographic distribution and high filtration capacity of invasive ascidians offer great potential for their use in monitoring metal pollution in marine environments.

Wang, J., Peng, W., Wang, S.*, et al.* Establishment of geochemical baseline and multiple assessment of vanadium pollution in sediment cores from the two cascade reservoirs, North China. *Environmental Science and Pollution Research,*
Keywords: Vanadium (V); Panjiakou-Daheiting reservoir; Sediments; Geochemical baseline; Environmental impact assessment model; Health risk assessment; 3 GORGES RESERVOIR; HEAVY-METAL CONTAMINATION; WATER-LEVEL-FLUCTUATION; HEALTH-RISK ASSESSMENT; SURFACE SEDIMENTS; RIVER; SOILS; LAKE; ACCUMULATION; ELEMENTS; Environmental Sciences & Ecology

Abstract:
Vanadium (V) is a potential toxic pollutant, and thus, V pollution in reservoir sediment should be scientifically evaluated because reservoirs are the main source of drinking water in China. However, the pollution assessment of V in reservoir sediment is often overestimated or underestimated due to the limitation for selecting local background values. In this study, the selection of the V background value in sediments was based on regional geochemical baseline (RGB) model. Multiple methods including geo-accumulation index (I-geo), potential ecological risk index (EI), and health risk assessment were applied to evaluate V pollution in sediment cores collected from the Panjiakou-Daheiting Reservoirs (PDR). The results show that the mean value of V concentrations in the PDR sediment cores was 92.86 mg/kg (57.69-141.19 mg/kg), which is higher than the soil background in Hebei Province and stream sediment values in China. V concentrations in the Panjiakou Reservoir were higher than those in the Daheiting Reservoir. The RGB value of V was 96.33 mg/kg in the PDR sediments. A comparison of the V concentrations and RGB values in the sampling sites indicated that half of these sites are impacted by anthropogenic inputs. Among the sites influenced by human activity, the average anthropogenic contribution was 9.9%, suggesting that majority of V in the PDR sediments originated from natural source. The pollution assessments of V were evaluated using I-geo and EI with RGB as the background value, and results indicated that the sediments in the PDR were not polluted with V. The environmental impact assessment model was also established for calculating V accumulation in fish due to sediment resuspension. Then, health risk assessment model was applied to further calculate the health risk to residents due to fish consumption. The evaluated target hazard quotient demonstrated that local fish consumption produced no adverse effect on human health during sediment disruption.

Yavar Ashayeri, N. & Keshavarzi, B. (2019) Geochemical characteristics, partitioning, quantitative source apportionment, and ecological and health risk of heavy metals in sediments and water: A case study in Shadegan Wetland, Iran. *Marine Pollution Bulletin,* 149.
Keywords: Distribution coefficients; Environmental assessment; Heavy metals; MLR-APCS; Shadegan Wetland (Iran); Ecology; Health risks; Linear regression; Sediments; Wetlands; Distribution coefficient; Geochemical characteristic; Heavy metal concentration; Multiple linear regressions; Partition coefficient; Risk assessment; antimony; arsenic; cadmium; cobalt; copper; heavy metal; lead; molybdenum; nickel; selenium; vanadium; water; zinc; mercury; ecological approach; geochemistry; health risk; human activity; marine pollution; partitioning; quantitative analysis; sediment pollution; source apportionment; wetland; adult; Article; child; concentration (parameter); controlled study; ecological risk; environmental enrichment; environmental impact; health hazard; human; Iran; risk; sediment; water pollution; China; environmental monitoring; water pollutant; Khuzestan; Shadegan Marshes; Geologic Sediments; Metals, Heavy; Water Pollutants, Chemical

Abstract:
Heavy metal concentrations were investigated in water and sediments of Shadegan Wetland southwest of Iran to assess the fate, partitioning, and risk assessment and also to quantify the sources of heavy metals using MLR-APCS (multiple linear regression of absolute principal component scores) receptor model. The relatively high values of Kd (partition coefficient) for Pb, Zn, Ni, As, and V revealed their affinity for being enriched in sediments while Sb, Mo, and Se exhibited greater partitioning towards water. Enrichment factors of Se, Cd, Pb, Mo, Co, Zn, and Cu revealed significant to moderate contamination and should be of some concern. Application of the modified ecological risk index (MRI) revealed sediments moderate to high risk. Hazard index values for Hg were found less than the safe level. MLR-APCS model indicated that anthropogenic sources in sediments were responsible for 80.9%, 73.2%, 73.1%, 88.6% and 74.2% of Se, Mo, Hg, Pb, and Zn, respectively. © 2019 Elsevier Ltd.

Youssef, M., El-Sorogy, A., Osman, M.*, et al.* (2020) Distribution and metal contamination in core sediments from the North Al-Wajh area, Red Sea, Saudi Arabia. *Marine Pollution Bulletin,* 152.
Keywords: Al-Wajh area; Core sediments; Heavy metals; Red Sea; Saudi Arabia; Cluster analysis; Hierarchical systems; Metal analysis; Multivariant analysis; Principal component analysis; Sediments; Atomic absorption spectrophotometer; Heavy metal contamination; Hierarchical cluster analysis; Multivariate statistical analysis; Vertical distributions; Soil pollution; aluminum; cadmium; cobalt; copper; heavy metal; iron; lead; manganese; mercury; nickel; organic matter; strontium; total organic matter; unclassified drug; vanadium; concentration (composition); enrichment; sediment core; sediment pollution; vertical distribution; Article; atomic absorption spectrometry; contamination factor; enrichment factor; environmental aspects and related phenomena; geoaccumulation index; geographic distribution; metal industry; sea; sediment; soil pollution index; urban area; water contamination; water sampling; Al Wajh; Indian Ocean; Red Sea [Indian Ocean]; Tabuk [Saudi Arabia]

Abstract:
Forty-one bottom sediment samples were collected from three cores at the mouth of Wadi Haramel, Wadi Antar, Wadi Dumaygh, north of Al-Wajh, Red Sea, Saudi Arabia, to evaluate the levels of heavy metal contamination, using the enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (Cf), soil pollution index (SPI), and multivariate statistical analysis (hierarchical cluster analysis and principal component analysis). Fe, Al, Pb, Mn, Cu, Ni, Co, Cd, Sr, V, Hg, and Total Organic Matter (TOM%) were quantified by Atomic Absorption Spectrophotometer. The vertical distribution of the heavy metals concentrations increased upwards indicating high heavy metals input. The results of enrichment factor and soil pollution index calculations indicate a strong anthropogenic supply of Cd and Sr (SPI = 1.10, 2.70, EF = 18.25, 17.99 respectively) while Cu and Ni show moderate anthropogenic input from urban, industrial activities and some new projects in the northern coast of Saudi Arabia. © 2020 Elsevier Ltd.

Zhang, B., Jiang, Y., Zuo, K.*, et al.* (2020) Microbial vanadate and nitrate reductions coupled with anaerobic methane oxidation in groundwater. *Journal of Hazardous Materials,* 382.
Keywords: Bio-reduction; Bioremediation; Groundwater; Methane; Vanadate; Groundwater pollution; Nitrates; Oxidation; Reaction intermediates; Vanadium compounds; Anaerobic methane oxidations; Bio reductions; Groundwater environment; Metabolite analysis; Methane oxidizing bacterium; Microbial community structures; Volatile fatty acids (VFAs); Volatile fatty acids; ground water; nitrate; vanadic acid; vanadium derivative; volatile fatty

acid; anoxic conditions; bacterium; biotransformation; community structure; fatty acid; metabolite; microbial activity; microbial community; precipitation (chemistry); reduction; vanadium; Article; Methylomonas; nonhuman; reduction (chemistry)

Abstract:
Vanadate contaminant in groundwater receives increasing attentions, but little is known on its biogeochemical transformation with gaseous electron donors. This study investigated bio-reduction of vanadate coupled with anaerobic methane oxidation and its relationship with nitrate reduction. Results showed 95.8 ± 3.1% of 1 mM vanadate was removed within 7 days using methane as the sole electron donor. Tetravalent vanadium compounds were the main reduction products, which precipitated naturally in groundwater environment. The introduction of nitrate inhibited vanadate reduction, though both were reduced in parallel. Accumulations of volatile fatty acids (VFAs) were observed from methane oxidation. Preliminary microbial community structure and metabolite analyses indicated that vanadate was likely reduced via Methylomonas coupled with methane oxidation or through synergistic relationships between methane oxidizing bacteria and heterotrophic vanadate reducers with VFAs served as the intermediates. © 2019 Elsevier B.V.

8. MISCELLANEOUS

Bernardin, M., Masle, A.L., Bessueille-Barbier, F.*, et al.* (2020) Comprehensive two-dimensional liquid chromatography with inductively coupled plasma mass spectrometry detection for the characterization of sulfur, vanadium and nickel compounds in petroleum products. *Journal of Chromatography A,* 1611.
Keywords: Heavy oils; ICP-MS/MS; Organic matrices; Peak capacity; SECxRPLC; Speciation; Crude oil; Gasoline; Heavy oil production; Inductively coupled plasma mass spectrometry; Liquids; Mass spectrometers; Molecular weight; Nickel compounds; Petroleum industry; Separation; Size exclusion chromatography; Vanadium compounds; Organic matrix; Liquid chromatography; asphalthene; nickel; petroleum; petroleum derivative; sulfur; unclassified drug; vanadium; Article; chemical analysis; chemical composition; chromatography by separation mechanism; comparative study; controlled study; dilution; elution; flow rate; hydrophobicity; mathematical computing; petrochemical industry; priority journal; process optimization; reversed phase liquid chromatography; two dimensional liquid chromatography

Abstract:
The petroleum industry is increasingly concerned with the conversion of vacuum residues as a consequence of decreased conventional crude oil availability. The compositional analysis of heavy oil products has become a key step in conversion processes, but the complexity of these oil matrices tends to increase with their boiling point. In this study, comprehensive two-dimensional liquid chromatography (LCxLC) coupled to inductively coupled mass spectrometry (ICP-MS/MS) is considered with a view to meet new requirements and to bring additional information regarding the species present in these matrices. In search for a high degree of orthogonality, two separation techniques involving two different retention mechanisms were evaluated: Size Exclusion Chromatography (SEC) and Reverse Phase Liquid Chromatography (RPLC). In SEC, the analytes are separated according to their molecular weight while according to their hydrophobicity in RPLC. The separation power of both individual separation techniques was first evaluated. Off-line and on-line LCxLC were compared on the basis of an optimization approach. It is shown that off-line SECxRPLC can provide, for the same analysis time of 150 min, a higher peak capacity (2600 vs 1700) than on-line RPLCxSEC while a similar dilution factor (close to 30) but also requires far fewer

fractions to be analyzed (12 vs 400). Asphaltenes which constitute the heaviest fraction of crude oils (obtained from petroleum industry) were analyzed by the developed off-line SECxRPLC method. The resulting 2D-contour plots show that co-elutions could be removed leading, for the first time, to new information on high molecular weight species containing sulfur and vanadium. © 2019.

Chen, A.S.C., Wang, L., Sorg, T.J*., et al.* (2020) Removing arsenic and co-occurring contaminants from drinking water by full-scale ion exchange and point-of-use/point-of-entry reverse osmosis systems. *Water Research,* 172: 115455.
Keywords: Ion exchange; Reverse osmosis; Arsenic; Nitrate; Natural organic matter; Co-occurring contaminants

Abstract:
This study investigated the performance of two full-scale ion exchange (IX) systems, one point-of-entry (POE) reverse osmosis (RO) system and nine point-of-use (POU) RO units for simultaneous removal of arsenic and several co-occurring contaminants from drinking water. The study was performed as part of the U.S. Environmental Protection Agency's Arsenic Treatment Demonstration Program. The IX systems, with strong base anionic (SBA) resins, effectively removed arsenic (As), nitrate (NO3−) and uranium (U) to below respective maximum contaminant levels and vanadium (V) and molybdenum (Mo) to below 2 μg/L. The useful run length, as determined by either 10-mg/L (as N) nitrate or 10-μg/L arsenic breakthrough, was approximately 400 bed volumes (BV) initially. However, it was decreased over time, e.g., by 15% in 13 months at one site and 33% in 7 months at another site, apparently caused by resin fouling due to the presence of 2-mg/L natural organic matter (NOM) in source waters. The use of dual resins – an acrylic SBA resin underlain by a polystyrene SBA resin – effectively removed NOM and allowed the system to perform at its baseline level through the 13-month study. Arsenic and nitrate peaking occurred when the resins were not regenerated timely. The removal of contaminants appeared to follow a selectivity sequence: U, Mo > V > SO42− > HAsO42− > NO3− > HCO3−. RO effectively removed arsenic, nitrate, antimony, uranium and vanadium, mostly with a >99% rejection rate. The POE RO coupled with dual plumbing (only treating a fraction of water for potable use) and POU RO in individual homes could be used as low-cost alternatives to traditional RO treatment. ".

Dong, Y., Lin, H., Liu, Y*., et al.* (2020) Blank roasting and bioleaching of stone coal for vanadium recycling. *Journal of Cleaner Production,* 243: UNSP 118625.
Keywords: Stone coal; Vanadium; Bioleaching; Compound mutagenesis; Blank roasting; EXTRACTING VANADIUM; TECHNOLOGY; ARTP; Science & Technology - Other Topics; Engineering; Environmental Sciences & Ecology

Abstract:
The recovery and utilization of vanadium from stone coal is of great significance because it is an important metal. In the present study, a cleaner metal extraction method to recover vanadium from low-grade stone coal using a novel strain of Bacillus mucilaginosus (BM) and an enhanced bioleaching procedure was explored. The efficient leaching bacteria of BM-5070 were obtained by the atmospheric and room temperature plasma (ARTP)-hydroxylamine hydrochloride compound mutagenesis technique. The results show that BM-5070 had the highest V leaching rate. After a 20-day bioleaching period, the V leaching rate of BM-5070 was 5.5 percentage points higher than that of the original bacteria. Moreover, the pretreatment of stone coal by blank roasting without any additives can further promote the vanadium dissolution, and the V leaching rate reached 85% after bioleaching for 20 days,

which was 57 percentage points higher than that of without roasting. This is due to the decrease in the content of V (III) and the increase in the V (V) and V (IV) content after blank roasting, which is beneficial to the leaching of vanadium. The bioleaching behavior was elucidated through the bacteria-mineral contact leaching and non-contact leaching test. The results show that the V leaching rate (81.0%) in the contact mode was much higher than that in the non-contact leaching mode (64.4%), indicating that the bioleaching of vanadium occurs with direct action and indirect action. The results of our study could significantly contribute to a green method for recovering vanadium from stone coal.

Guan, H., Zhang, D., Yang, Y.*, et al.* (2019) A Novel Method for Notable Reducing Phase Transition Temperature of VO2 Films for Smart Energy Efficient Windows. *Nanomaterials (Basel, Switzerland),* 10(1): 10.3390/nano10010058.
Keywords: phase transition temperature; ultra-thin heavy Cr-doped layer; vanadium dioxide

Abstract:
Although Vanadium dioxide (VO2) has a potential application value for smart energy efficient windows because of its unique phase transition characteristic, there are still many obstacles that need to be overcome. One challenge is to reduce its high transition temperature (zetac = 68 degrees C) to near room temperature without causing its phase transition performance degradation. In this paper, a novel method was employed that covered a 3 nm ultra-thin heavy Cr-doped VO2 layer on the pure VO2 films. Compared with the as-grown pure VO2, obviously, phase transition temperature decreasing from 59.5 degrees C to 48.0 degrees C was observed. Different from previous doping techniques, almost no phase transition performance weakening occurred. Based on the microstructure and electrical parameters measurement results, the mechanism of zetac reducing was discussed. The upper ultra-thin heavy Cr-doped layer may act as the induced role of phase transition. With temperature increasing, carrier concentration increased from the upper heavy Cr-doped layer to the bottom pure VO2 layer by diffusion, and induced the carrier concentration reach to phase transition critical value from top to bottom gradually. The present method is not only a simpler technique, but also avoids expensive alloy targets.

Huang, Q., Xiang, J., Wang, X.*, et al.* Dissolution kinetics of calcium vanadates in sulfuric acid: a fundamental study for the vanadium extraction process. *Journal of Chemical Technology and Biotechnology.*
Keywords: vanadium; calcium vanadates; dissolution; kinetics; SLAG; MECHANISM; CHROMIUM; RECOVERY; Biotechnology & Applied Microbiology; Chemistry; Engineering

Abstract:
BACKGROUND The dissolution behavior of calcium vanadates is vital for the vanadium extraction process, as well as the utilization of calcium vanadates based function materials. Therefore, the dissolution kinetics study of calcium vanadates (CaV2O6, Ca2V2O7, and Ca3V2O8) in sulfuric acid are presented. The effects of stirring speed, solid/liquid ratio, pH, and temperature on the dissolution rate of calcium vanadates were determined. The mineralogical and microstructure of the residue after dissolution are also performed. RESULTS The results showed that the dissolution rate of calcium vanadates significantly increased with the increase of temperature from 30 to 70 degrees C. Under the conditions with solid/liquid ratio of 1:150 g mL(-1), temperature range of 30 to 70 degrees C, and pH of 4, the rate of Ca3V2O8 dissolution is the fastest, followed by Ca2V2O7 and CaV2O6, especially at low temperature. CONCLUSION The mineralogical analyses results showed that the main products for the dissolution of Ca2V2O7 and Ca3V2O8 are needle-like CaSO4

center dot 0.5H(2)O, whereas for CaV2O6 are undissolved CaV2O6 and hydrolyzed V2O5. The dissolution kinetics indicate that the dissolution of CaV2O6 follows second-order pseudo-homogeneous model, whilst Ca2V2O7 and Ca3V2O8 follow the diffusion through the product or ash layer model. The apparent activation energies for the dissolution of CaV2O6, Ca2V2O7, and Ca3V2O8 were determined as 46.44, 38.72, and 23.50 kJ mol(-1), respectively. (c) 2020 Society of Chemical Industry.

Intrakamhaeng, V., Clavier, K.A. & Townsend, T.G. (2020) Hazardous waste characterization implications of updating the toxicity characteristic list. ***Journal of Hazardous Materials,*** **383.**

Keywords: Hazardous waste; Leaching; Risk assessment; Toxicity characteristic (TC) limits; Toxicity characteristic leaching procedure (TCLP); Electric batteries; Fossil fuels; Hazards; Municipal solid waste; Petroleum reservoir evaluation; Potable water; Toxicity; Wood; Attenuation factors; Drinking water standards; Fossil fuel combustion; Hazardous wastes; Metal concentrations; Municipal solid waste incineration ash; Toxicity characteristic leaching procedures; Toxicity characteristics; Waste incineration; antimony; arsenic; barium; beryllium; cadmium; chromium; cobalt; copper; drinking water; fossil fuel; lead; lithium; mercury; molybdenum; nickel; selenium; silver; tap water; thallium; vanadium; zinc; combustion; concentration (composition); incineration; Article; ash; comparative study; dilution; dilution attenuation factor; e-waste; elemental analysis; evaluation study; toxic concentration; toxicity and intoxication; toxicity characteristic leaching procedure; United States; water standard

Abstract:
In the US, the toxicity characteristic leaching procedure (TCLP) determines if a waste is toxicity characteristic (TC) hazardous based on leached concentrations of specific chemicals. The TC limits were originally derived from drinking water standards (DWS) adjusted by a dilution attenuation factor of 100. The TC limits have not been updated along with DWS revisions. This research examines potential implications of updating the TC limits to account for new DWS thresholds and elements, as well as tap-water risk thresholds; this allows a further expanded evaluation of elements that might be regulated as drinking water standards in the future. Fossil fuel combustion residues, batteries, electronic wastes, municipal solid waste incineration (MSWI) ashes, and treated wood were examined with TCLP and the leached metal concentrations were compared to revised TC thresholds. The two wastes most affected by updated TC limits would be batteries and MSWI ashes. Thallium and antimony, which were not included on the original TC list, exceeded the TC thresholds for batteries and MSWI ash, respectively. Copper, a chemical used in current preserved wood formulations, did not cause currently marketed treated wood to be hazardous waste, but arsenic did for older wood products. © 2019 Elsevier B.V.

Ji, J., He, E., Qiu, H.*, et al.* (2020) Effective Modeling Framework for Quantifying the Potential Impacts of Coexisting Anions on the Toxicity of Arsenate, Selenite, and Vanadate. ***Environmental Science & Technology,*** **54(4): 2379-2388.**

Abstract:
Hardly any study has focused on the quantitative modeling of the toxicity of anionic metal(loid)s and their mixtures in the presence of potentially competing anions. Here, we designed a univariate experiment (420 treatments) to investigate the influence of various anions (phosphate, sulfate, carbonate, and OH(-)) on the toxicity of single anionic metal(loid)s (arsenate, selenite, and vanadate) and a full factorial mixture experiment (196 treatments) to examine the interactions and toxicity of As-Se mixtures at 4 phosphate levels.

Standard root elongation tests with wheat (Triticum aestivum) were performed. A modeling framework, resembling the biotic ligand model (BLM) for cationic metals, was developed, extended, and applied to explain anion competitions and mixture effects. Carbonate significantly alleviated the toxicity of all three metal(loid)s. The toxicity of As was significantly mitigated by phosphate, while V toxicity was significantly relieved by OH(-). The BLM-like model successfully explained more than 93% of the observed variance in toxicity. With the parameters derived from single-metal(loid) exposures, the developed BLM-toxic unit model reached an overall prediction performance of 78% in modeling the toxicity of As-Se mixtures at varying phosphate levels, validating the effectiveness of the model framework. It is concluded that by taking possible anion competitions and interactions into account, the BLM-type approaches can serve as promising tools for the risk assessment of single and mixed metal(loid)s contamination.

Jin, Q., Shen, Y., Cai, Y.*, et al.* (2020) Resource utilization of waste V2O5-based deNOx catalysts for hydrogen production from formaldehyde and water via steam reforming. *Journal of Hazardous Materials,* 381.
Keywords: Formaldehyde; Harmless disposal; Hydrogen production; Steam reforming; Waste V2O5(WO3)/TiO2 deNOx catalysts; Catalysts; Hydrogen bonds; Nickel oxide; Tungsten compounds; Vanadium pentoxide; Waste disposal; Water resources; Catalyst carrier; Catalytic performance; De-NOx catalysts; Hydroxyl groups; Hydroxyl species; Impregnation methods; Reaction steps; Resource utilizations; ammonium vanadate; carbon dioxide; formic acid; hydrogen; hydroxyl group; titanium dioxide; unclassified drug; vanadium derivative; vanadium oxide; water; catalysis; catalyst; chemical reaction; inorganic compound; Article; chemical interaction; dehydrogenation; hydrogen bond; water vapor

Abstract:
The harmless disposal of abandoned and toxic V2O5(WO3)/TiO2 (VWT) deNOx catalysts has become a worldwide great demand, a new resource path for hydrogen production from steam reforming of formaldehyde and water using the waste VWT deNOx catalysts as catalyst carriers was proposed. The waste V2O5-based catalysts supported NiO (N/VWT) catalysts prepared by impregnation method were comparatively studied for hydrogen production. The H2 and CO selectivity of the optimum N/VWT separately reached 100% and 72.5%, and the formaldehyde conversion of the N/VWT reached 86.3% at 400 ℃ and higher than 93.0% at 450–600 ℃. Analysis showed that the hydroxyl species played the most important role, and its richness determined the catalytic performance directly. The high acid sites and excellent redox properties were beneficial to enhance the catalytic performance. The in situ DRIFT study verified that the hydrogen bonds between formate species and hydroxyl groups reduced reaction steps, which accelerated the progress of the reaction. The adsorbed formaldehyde transformed to formate species firstly, and then produced H2 and CO2 (or CO) by dehydrogenation. Ultimately, the resource utilization path not only completely solved the harmless problems of the waste V2O5-based deNOx catalysts and formaldehyde, but also contributed to the hydrogen production. © 2019 Elsevier B.V.

Li, M., Zhang, B., Zou, S.*, et al.* (2020) Highly selective adsorption of vanadium (V) by nano-hydrous zirconium oxide-modified anion exchange resin. *Journal of Hazardous Materials,* 384.
Keywords: Anion exchange resin; Hydrous zirconium oxide; Nanocomposite; Selective adsorption; Vanadium (V); Adsorption; Chlorine compounds; Dyes; Groundwater; Groundwater pollution; Ion exchange resins; Nanocomposites; Negative ions; Oxides; Potable water; Sulfur compounds; Thermodynamics; Water pollution control; Water treatment; Zirconium compounds; Adsorption thermodynamics; Anion exchange resins;

Contaminated groundwater; Drinking water sources; Inner-sphere complexation; Modified anion-exchange resin; Pseudo-second order model; Vanadium compounds; chloride; drinking water; ground water; ion exchange resin; nanomaterial; nitrate; phosphate; sulfate; vanadium; zirconium oxide; ion exchange; nanoparticle; oxide; resin; zirconium; China; contact time; inductively coupled plasma mass spectrometry; pH; synthesis; waste component removal; waste water management; Panzhihua; Sichuan

Abstract:
Adsorption is widely used in removal of toxic vanadium (V) [V(V)] from water streams, and a fit-for-purpose adsorbent plays a vital role in this process. Herein HZrO@D201, an adsorbent with decoration of nanosized hydrous zirconium oxide (HZrO) on anion exchange resin D201, is fabricated for efficient V(V) removal. Compared to pristine D201, HZrO@D201 excelled in V(V) removal with a maximum adsorption capacity of 118.1 mg/g, due to potential formation of inner sphere complexation between V(V) and HZrO. HZrO@D201 could also functioned well in a wide pH range (3.00 to 9.00) and exhibited outstanding selective V(V) adsorption under the presence of competing anions (chloride, nitrate, sulfate, and phosphate). The adsorption thermodynamics was in accordance with the Langmuir model, while adsorption kinetics followed the Pseudo-Second-Order model. When treating actual vanadium contaminated groundwater from Panzhihua region (China), HZrO@D201 indicated a satisfactory lifespan in the column experiment for V(V) removal (2.41 times longer than D201), and the treated groundwater could meet the vanadium standard of drinking water source in China (less than 50 μg/L). Regeneration of HZrO@D201 was easily achievable with negligible capacity loss. Results from this work suggests a promising application potential of HZrO@D201 in vanadium pollution control. © 2019 Elsevier B.V.

Liu, F., Ma, S., Ren, K.*, et al.* (2020) Mineralogical phase separation and leaching characteristics of typical toxic elements in Chinese lignite fly ash. *Science of the Total Environment,* 708.**
Keywords: Leaching characteristic; Lignite fly ash; Mineralogical phase separation; Toxic element; Cadmium; Fly ash; Iron compounds; Leaching; Lignite; Magnetic separation; Microbeads; Mullite; Sodium Aluminate; Column leaching tests; Distribution characteristics; Dry magnetic separation; Embedded relationships; Leaching characteristics; Structural characteristics; Toxic elements; Phase separation; aluminum; arsenic; chromium; cobalt; copper; lead; manganese; mercury; molybdenum; nickel; silicon; tungsten; vanadium; zinc; mineralogy; separation; silicate; toxic substance; adsorption; Article; controlled study; ignite fly ash; inductively coupled plasma mass spectrometry; measurement accuracy; particle size; physical chemistry; priority journal; scanning electron microscopy; trend study; X ray diffraction
Abstract:
To investigate the distribution characteristics of typical toxic elements in different mineralogical phases of fly ash is of significance when fly ash is comprehensively utilized. In this study, lignite fly ash can be preliminarily separated into three mineralogical phases: unburned lignite, iron microbeads and aluminate-silicate microbeads by two methods namely screening and dry magnetic separation. Then, the aluminate-silicate microbeads were subjected to two-step leaching. The first step was to investigate whether toxic elements migrated easily in the environment by column leaching test. In the second step, the aluminate-silicate microbeads were stripped from the surface of the particles to the internal by the acid-base combined leaching method, then the structural characteristics of the product and the trend of toxic elements content were explored. The results showed that there were few toxic elements in unburned lignite and the toxic elements Cr, Ni, Mo and Cd had a relatively high proportion in the iron microbeads. Column leaching results showed that

the toxic elements V, Cr, Mn, Co, Cu, Hg and Pb had higher leaching rates, which proved that these elements were significantly enriched on the surface of the particles and easily migrated in the environment. Cr, Mo, Cd and W were highly enriched in the quartz-mullite mixture. Mn, Co, Ni, Cu, Zn and As were highly enriched in the amorphous component. The toxic elements exhibited different leaching rules during the acid-base combined leaching process revealing the complex embedded relationship with constant elements. © 2019 Elsevier B.V.

Marchetti, I., Ricardi-Branco, F., Callefo, F.*, et al.* (2019) Fossildiagenesis and ontogenetic insights of crocodyliform bones from the Adamantina Formation, Bauru Basin, Brazil. ***Journal of South American Earth Sciences,*** **96**.
Keywords: Cretaceous; Crocodile; Montealtosuchus; Paleohistology; REEs; crocodilian; diagenesis; fossil assemblage; fossil record; histology; rare earth element; Vertebrata

Abstract:
The histological analysis of fossil bones allows a taphonomic approach, especially to fossildiagenesis. We studied the femur, vertebra, and osteoderm of the crocodyliform Montealtosuchus arrudacamposi (Adamantina Formation; Late Cretaceous), to make inferences of the sequence of the diagenetic processes. Cross-sections of the bones and the rock matrix that fills the medullar cavity were analyzed under a scanning electron microscopy with compositional analysis (SEM/EDS) and μ-X-Ray fluorescence (μ-XRF). The microstructural pattern of the femur and vertebra was similar, with a transition from vascularized fibrolamellar internal cortex, with reticular and longitudinal canals to zonal lamellar in the outer, and a medullary cavity portion filled with quartz and other mineral grains. The osteoderm, however, presented a less vascularized cortex. In all samples were found the External Fundamental System (EFS), secondary osteons in the internal cortex and spongy tissue, and the transition from a fibrolamellar to a lamellar tissues, indicating that the individual reached ontogenetic maturity (adult/senescent) before they died. The compositional results showed that the samples mainly comprised calcium and phosphorus, which were homogeneously distributed. However, we inferred that these elements occurred during the formation of recrystallized and authigenic minerals. Iron, vanadium, and cerium are the elements found that occurred in the composition of the fossil remains during early diagenesis, and this process was observed to extend to the late diagenesis. Cerium was homogeneously distributed and incorporated to authigenic apatite. Iron and vanadium were restricted to the cortex. The presence of authigenic apatite and Rare Earth Elements (REEs) in the samples supported that the diagenetic environment of the Adamantina Formation was alkaline. Furthermore, it suggested an association with a groundwater environment that have allowed and facilitated the well preservation of fossil vertebrates in this geological formation. © 2019 Elsevier Ltd.

Maurya, M.R., Tomar, R., Avecilla, F., et al. (2020) Trinuclear vanadium(iv) and vanadium(v) complexes derived from 2,4,6-triacetylphloroglucinol and study of their peroxidase mimicking activity. Dalton Transactions, 49(8): 2589-2609.
Keywords: Amines; Catalysts; Catalytic oxidation; Cyclic voltammetry; Energy dispersive X ray analysis; Ligands; Neurophysiology; Reaction kinetics; Single crystals; X ray diffraction analysis; Catalyst precursors; Catalytic potential; Ligand precursors; Phenolate oxygen; Single crystal X-ray analysis; Square-pyramidal geometry; Trinuclear complex; X-ray diffraction studies; Vanadium dioxide

Abstract:
Novel dibasic Schiff bases with three tridentate sites were obtained from the condensation

of the triketone 2,4,6-triacetylphloroglucinol (H3ptk) with four different hydrazides, benzoyl hydrazide (bhz), furoyl hydrazide (fah), isonicotinoyl hydrazide (inh) and nicotinoyl hydrazide (nah): H6ptk(bhz)3I, H6ptk(fah)3II, H6ptk(inh)3III and H6ptk(nah)3IV. These ligand precursors I-IV, each being an ONO donor, are tricompartmental building blocks able to form trinuclear complexes having C3 symmetry. The reaction of I-IV with [VIVO(acac)2] leads to the formation of [{VIVO(H2O)}3(ptk(bhz)3)] 1, [{VIVO(H2O)}3(ptk(fah)3)] 2, [{VIVO(H2O)}3(ptk(inh)3)] 3, and [{VIVO(H2O)}3(ptk(nah)3)] 4. In methanol/aqueous solutions of M2CO3 (M+ = Na+, K+ and Cs+), these complexes are slowly converted into dioxidovanadium(v) compounds, namely, M3[(VVO2)3{ptk(bhz)3}]·6H2O [M+ = K+5, Na+9, Cs+13], M3[(VVO2)3{ptk(fah)3}]·6H2O [M+ = K+6, Na+10, Cs+14], M3[(VVO2)3{ptk(inh)3}]·6H2O [M+ = K+7, Na+11, Cs+15] and M3[(VVO2)3{ptk(nah)3}]·6H2O [M+ = K+8, Na+12, Cs+16]. All ligand precursors and complexes are characterized by various techniques such as FT-IR, UV/Visible, EPR, NMR (1H, 13C and 51V), elemental analysis, thermal studies, cyclic voltammetry (CV) and single-crystal X-ray analysis. X-ray diffraction studies of complexes K2.7[{(VVO2)3ptk(fah)3}]·11.5H2O·MeOH 6a, Cs3[{(VVO2)3ptk(bhz)3}]·7H2O 13a and Cs3[{(VVO2)3ptk(nah)3}]·7.3H2O 16a reveal their distorted square pyramidal geometry by coordinating through phenolate oxygen (of ptk), azomethine nitrogen and enolate oxygen (of hydrazide) atoms. The reactivity of complexes 5-16 and their catalytic potential were screened towards their peroxidase mimetic activity in the oxidation of dopamine to aminochrome driven by H2O2 as an oxidant. The conversion of dopamine to aminochrome with different catalysts was monitored by HPLC showing high activity under mild conditions with good conversions within 1 h. Kinetic studies using compounds 13-16 as catalyst precursors reveal that the reaction follows a Michaelis-Menten-like kinetics. This journal is © 2020 The Royal Society of Chemistry.

Moore, E.K., Hao, J., Spielman, S.J.*, et al.* (2020) The evolving redox chemistry and bioavailability of vanadium in deep time. *Geobiology,* 18(2): 127-138.
Available at:
https://raw.githubusercontent.com/sjspielman/publications/master/2020_Mooreetal_Geobiology.pdf
Keywords: bioavailability; deep time; geochemical modeling; mineral evolution network analysis; redox; vanadium

Abstract:
The incorporation of metal cofactors into protein active sites and/or active regions expanded the network of microbial metabolism during the Archean eon. The bioavailability of crucial metal cofactors is largely influenced by earth surface redox state, which impacted the timing of metabolic evolution. Vanadium (V) is a unique element in geo?bio-coevolution due to its complex redox chemistry and specific biological functions. Thus, the extent of microbial V utilization potentially represents an important link between the geo- and biospheres in deep time. In this study, we used geochemical modeling and network analysis to investigate the availability and chemical speciation of V in the environment, and the emergence and changing chemistry of V-containing minerals throughout earth history. The redox state of V shifted from a more reduced V(III) state in Archean aqueous geochemistry and mineralogy to more oxidized V(IV) and V(V) states in the Proterozoic and Phanerozoic. The weathering of vanadium sulfides, vanadium alkali metal minerals, and vanadium alkaline earth metal minerals were potential sources of V to the environment and microbial utilization. Community detection analysis of the expanding V mineral network indicates tectonic and redox influence on the distribution of V mineral-forming elements. In reducing environments, energetic drivers existed for V to potentially be involved in early nitrogen fixation, while in oxidizing environments vanadate () could have acted as a metabolic

electron acceptor and phosphate mimicking enzyme inhibitor. The coevolving chemical speciation and biological functions of V due to earth's changing surface redox conditions demonstrate the crucial links between the geosphere and biosphere in the evolution of metabolic electron transfer pathways and biogeochemical cycles from the Archean to Phanerozoic.

Mubarak, M.Q.E. & De Visser, S.P. (2019) Second-Coordination Sphere Effect on the Reactivity of Vanadium-Peroxo Complexes: A Computational Study. *Inorganic Chemistry,* 58(23): 15741-15750.

Abstract:
Vanadium-oxo and vanadium-peroxo complexes are common intermediates in biology and are, for instance, found in the catalytic cycle of vanadium haloperoxidases. In biomimetic chemistry synthetic models have been created that mimic the structural features of the coordination environment of these vanadium-oxo and vanadium-peroxo species. Recently, two novel vanadium-oxo complexes were trapped and characterized with a trigonal bipyramidal ligand design with either a solvent exposed vanadium center or the vanadium inside a cage, designated as the bowl-shaped configuration and the dome-shaped structure, respectively. Density functional theory calculations are reported here on these bowl- and dome-shaped structures where we study the reaction with t-butylhydroperoxide to form the vanadium-peroxo species and its reaction with thioanisole. Although the structural features of the vanadate core are close for both structures, the calculations display a strong second-coordination sphere effect of the ligand architecture on the barrier heights of the reaction with a terminal oxidant even though the rate-determining transition states show little structural differences. A similar observation is seen for the reaction of the two vanadium-peroxo species with thioanisole. Overall, the calculations implicate that vanadium-peroxo is an efficient oxidant of sulfoxidation reactions, although it is not as efficient as analogous iron(IV)-oxo heme and nonheme oxidants that react with substantially lower barriers. The reactivity differences are analyzed with thermochemical cycles and valence bond patterns that explain the differences in chemical properties and identify how the ligands affect the chemical reactivity with substrates. © 2019 American Chemical Society.

Noah, N.F.M., Sulaiman, R.N.R., Othman, N.*, et al.* (2020) Extractive continuous extractor for chromium recovery: Chromium (VI) reduction to chromium (III) in sustainable emulsion liquid membrane process. *Journal of Cleaner Production,* 247: 119167.
Keywords: trioctylmethylammonium chloride; Response surface methodology; Continuous emulsion liquid membrane; Chromium; Electroplating wastewater; Palm oil; HEXAVALENT CHROMIUM; WASTE SOLUTION; REMOVAL; ACID; CR(VI); OPTIMIZATION; PERFORMANCE; CARBON; STABILITY; VANADIUM; Science & Technology - Other Topics; Engineering; Environmental Sciences & Ecology

Abstract:
This work reports, for the first time, a detailed investigation on the Chromium (VI) reduction to Chromium (III) in a sustainable continuous emulsion liquid membrane process. This method is used in the treatment of authentic rinse electroplating wastewater containing 40 ppm Chromium (VI) concentration. The liquid membrane phase is composed of palm oil as diluent, Span 80 as surfactant, trioctylmethylammonium chloride as extractant, and acidic thiourea solution as an internal reagent. The statistical experimental design was applied in optimizing the process parameters for the removal of chromium by a sustainable continuous emulsion liquid membrane process. Recovery and enrichment of the less toxic Chromium (III) at optimum process conditions were further studied. Optimization of chromium removal

was investigated using the response surface methodology. Within the range of the selected operating conditions, the optimized values of emulsion to an external feed phase ratio, agitation speed and retention time are found to be 1:5, 342 rpm and 170 s. For instance, 99% of Chromium could be extracted at the optimum process conditions. The recovered species of Chromium (VI) was efficiently stripped into the internal phase (82%) as less-toxic Chromium (III) using 2.0 M thiourea in 2.0 M sulfuric acid as the strippant. In the meantime, up to 200 ppm external feed phase concentration seems to be the best range of condition for the recovery process of chromium from rinse electroplating wastewater.

Peng, H., Yang, L., Wang, L.*, et al.* (2019) Recovery of vanadium with urea in acidic medium. *Environmental Chemistry Letters,* 17(4): 1867-1871.
Keywords: Hydrolysis; Precipitation; Urea; Vanadium

Abstract:
Classical hydrometallurgy methods such as chemical precipitation, ion exchange, solvent extraction and adsorption have been used to recover vanadium from aqueous solutions, but the last step of these methods involves precipitation with ammonium salts, which are harmful to the environment at high concentration. Therefore, here we tested urea as a new precipitant to replace ammonium salts. We studied the effect of various parameters on the precipitation efficiency of vanadium. Results showed that urea is hydrolyzed to form NH4 + in acidic medium at 90 °C. Then, NH4 + reacts with V6O16 2− and precipitates as (NH4)2V6O16. Nearly 95% of the vanadium was precipitated within 120 min in the system containing 2.8 g/L vanadium and n(CON2H4)/n(V) of 0.6. The Avrami model was used to describe crystallization kinetics and analysis of the dimensions of crystal growth. Model results show that the crystalline growth was one-dimensional and that the crystals were shaped in columns. Overall, this study introduced a new way for urea utilization as a new precipitant to recover vanadium. © 2019, Springer Nature Switzerland AG.

Perron, M.M.G., Strzelec, M., Gault-Ringold, M.*, et al.* (2020) Assessment of leaching protocols to determine the solubility of trace metals in aerosols. *Talanta,* 208: 120377.
Keywords: Aerosols; Iron; Leaching protocols; Micronutrients; Solubility; Trace metals

Abstract:
Atmospheric deposition of aerosols to the ocean provides an important pathway for the supply of vital micronutrients, including trace metals. These trace metals are essential for phytoplankton growth, and therefore their delivery to marine ecosystems can strongly influence the ocean carbon cycle. The solubility of trace metals in aerosols is a key parameter to better constrain their potential impact on phytoplankton growth. To date, a wide range of experimental approaches and nomenclature have been used to define aerosol trace metal solubility, making data comparison between studies difficult. Here we investigate and discuss several laboratory leaching protocols to determine the solubility of key trace metals in aerosol samples, namely iron, cobalt, manganese, copper, lead, vanadium, titanium and aluminium. Commonly used techniques and tools are also considered such as enrichment factor calculations and air mass back-trajectory projections and recommendations are given for aerosol field sampling, laboratory processing (including leaching and digestion) and analytical measurements. Finally, a simple 3-step leaching protocol combining commonly used protocols is proposed to operationally define trace metal solubility in aerosols. The need for standard guidelines and protocols to study the biogeochemical impact of atmospheric trace metal deposition to the ocean has been increasingly emphasised by both the atmospheric and oceanographic communities. This lack

of standardisation currently limits our understanding and ability to predict ocean and climate interactions under changing environmental conditions.

Pourret, O. & Hursthouse, A. (2019) It's time to replace the term "heavy metals" with "potentially toxic elements" when reporting environmental research. *International Journal of Environmental Research and Public Health,* 16(22).
Available at: https://www.mdpi.com/1660-4601/16/22/4446/pdf
Keywords: Contaminants; Elements; Heavy metals; Toxic

Abstract:
Even if the Periodic Table of Chemical Elements is relatively well defined, some controversial terms are still in use. Indeed, the term "heavy metal" is a common term used for decades in the natural sciences, and even more in environmental sciences, particularly in studies of pollution impacts. As the use of the term appears to have increased, we highlight the relevance of the use of the term "Potentially Toxic Element(s)", which needs more explicit endorsement, and we illustrate the chemical elements that need to be considered. © 2019 by the authors. Licensee MDPI, Basel, Switzerland.

Qin, J., Hao, C., Wang, D.*, et al.* (2020) Investigation of adsorption, dissociation, and diffusion properties of hydrogen on the V (1 0 0) surface and in the bulk: A first-principles calculation. *Journal of Advanced Research,* 21: 25-34.
Keywords: Adsorption; Diffusion kinetics; Hydrogen separation; Vanadium membrane

Abstract:
To investigate the H2 purification mechanism of V membranes, we studied the adsorption, dissociation, and diffusion properties of H in V, an attractive candidate for H2 separation materials. Our results revealed that the most stable site on the V (1 0 0) surface is the hollow site (HS) for both adsorbed H atoms and molecules. As the coverage range increases, the adsorption energy of H2 molecules first decreases and then increases, while that of H atoms remains unchanged. The preferred diffusion path of atoms on the surface, surface to first subsurface, and first subsurface to second subsurface is HS → bridge site (BS) → HS, BS → BS, and BS → tetrahedral interstitial site (TIS) → BS, respectively. In the V bulk, H atoms occupy the energetically favourable TIS, and diffuse along the TIS → TIS path, which has a lower energy barrier. This study facilitates the understanding of the interaction between H and metals and the design of novel V-based alloy membranes. © 2019.

Steinmann, J.W., Grammer, G.M., Brunner, B.*, et al.* (2020) Assessing the application of trace metals as paleoproxies and a chemostratigraphic tool in carbonate systems: A case study from the "Mississippian Limestone" of the midcontinent, United States. *Marine and Petroleum Geology,* 112.
Keywords: Carbonate geochemistry; Carbonate systems; Chemostratigraphy; Mass spectrometry; Mississippian limestone; Paleoenvironment; Redox proxies; Seawater proxies; Trace metal enrichment; Trace metals; Carbonates; Carbonation; Geochemistry; Inductively coupled plasma mass spectrometry; Lime; Limestone; Metal analysis; Metals; Molybdenum; Seawater; Trace analysis; Carbonate system; Mississippians; Paleo-environment; Trace metal; Trace metal enrichments; Trace elements; enrichment; redox conditions; water chemistry; Midcontinent; United States

Abstract:
Trace metals have been successfully used to reconstruct geochemical seawater conditions of both modern and ancient environments. The majority of these efforts have been limited to

marine shales, with little work on carbonate systems. Applying similar methods of trace metal analysis on carbonate-dominated rocks may provide valuable insight into the paleoseawater chemistry, such as redox state, and productivity, of ancient carbonate systems. This study evaluates the application of trace metals as paleoproxies in carbonate rocks. Middle-ramp wackestones to grainstones from the “Mississippian Limestone” in the Midcontinent were analyzed using inductively-coupled plasma mass spectrometry (ICP-MS) for both the carbonate-fraction and the bulk-fraction trace metal content. Our data show that productivity proxies, such as Cd and P, are captured within the carbonate-fraction and may reflect seawater chemistry of the system. High Cd, and moderate bionutrient (P, Ni, Zn) enrichments indicate primary productivity in the system, though it is difficult to quantify to what extent. Vanadium, Cr, U, and Mo appear to be primarily associated with the bulk-fraction content and correlate well with Al content, indicating a detrital origin. Furthermore, V, U, and Mo show no significant enrichments, and Mo/Fe ratios correlate with those of shales from a modern oxic shelf. This suggests that anoxic or euxinic conditions in the water column were not present. Trace metal content of carbonate rocks have the potential to be used in paleoenvironmental reconstruction of carbonate systems, though challenges exist such as the lack of comparable carbonate trace metal data, bias of trace metal incorporation pathways into carbonates, and diagenetic alteration. © 2019 Elsevier Ltd.

Teng, A. & Xue, X. (2019) A novel roasting process to extract vanadium and chromium from high chromium vanadium slag using a NaOH-NaNO3 binary system. ***Journal of Hazardous Materials,*** **379**.
Keywords: High chromium vanadium slag; Microwave roasting; NaOH-NaNO3 binary system; Water leaching

Abstract:
This paper proposed a novel roasting process of extracting vanadium from high chromium vanadium slag. In this process, the high chromium vanadium slag was treated by NaOH-NaNO3 binary sodium salts, roasted in microwave heating furnace, and leached by water. During the roasting process, the temperature and time took a significant role in the conversion of vanadium and chromium. This novel microwave roasting was able to improve heating speed, accelerate the oxidization and decomposition of slag, and shorten the roasting time, compared with conventional muffle roasting. Under the optimum microwave roasting conditions (1 NaOH/NaNO3 mass ratio, 450 ℃ roasting temperature, and 10 min roasting time), the leaching rates of vanadium and chromium were 94.11% and 90.81%, respectively. In the leaching process, the reaction mechanism for the water leaching process was proposed. The process showed that leaching time and sample size played a significant role, while leaching temperature and liquid-to-solid ratio showed no obvious effect. The leaching residue analysis showed the major mineralogical phases were Fe2O3, Na2TiO3, NaFeSiO4, and a small amount of polymeric substance ((Mn,Ca)x(Fe0.6,Cr0.4)yOz·nSiO2). © 2019 Elsevier B.V.

Wang, L. & Bian, Z. (2020) Photocatalytic degradation of paracetamol on Pd–BiVO4 under visible light irradiation. ***Chemosphere,*** **239**.
Keywords: Degradation mechanism; Paracetamol; Pd-BiVO4; Visible light photocatalysis; Bismuth compounds; Catalysts; Degradation; Electron spin resonance spectroscopy; High resolution transmission electron microscopy; Irradiation; Light; Magnetic moments; Morphology; Nanoparticles; Organic carbon; Particle size analysis; Photocatalytic activity; Photodegradation; Scanning electron microscopy; Tungstate minerals; X ray photoelectron spectroscopy; Nanocrystal particles; Photo catalytic degradation; Photocatalytic systems; Total organic carbon removal; Visible-light irradiation; Visible-light photocatalysis; Palladium

compounds; bismuth; hydroxyl group; hydroxyl radical; palladium nanoparticle; superoxide; vanadic acid; free radical; metal nanoparticle; palladium; absorption; catalysis; dispersion; drug; electron spin resonance; nanoparticle; pollutant removal; visible spectrum; Article; catalyst; density functional theory; kinetic parameters; liquid chromatography-mass spectrometry; mass spectrometry; mineralization; particle size; photocatalysis; total organic carbon; transmission electron microscopy; ultraviolet visible spectroscopy; X ray diffraction; X ray photoemission spectroscopy; chemistry; drug effect; electron microscopy; photolysis; pollutant; radiation response; spectroscopy; Acetaminophen; Environmental Pollutants; Free Radicals; Metal Nanoparticles; Microscopy, Electron; Spectrum Analysis; Vanadates

Abstract:
In this study, Pd–BiVO4 bearing highly dispersed Pd nanoparticles was prepared from pure BiVO4 using an impregnation method. The pure BiVO4 and Pd–BiVO4 catalysts were characterized by X-ray diffraction, scanning electron microscopy, UV–visible diffuse reflection, transmission electron microscopy, and X-ray photoelectron spectroscopy. The results showed that the prepared catalysts had a monoclinic scheelite structure and exhibited a flake-like morphology. Pd–BiVO4 showed a distinct response in the visible light region, with an extended absorption edge at 550 nm. According to the Scherrer formula, the nanocrystal particle sizes of the BiVO4 and Pd–BiVO4 catalysts were 35 and 28 nm, respectively. Highly dispersed Pd nanoparticles with sizes of 2.5 ± 0.5 nm were observed on the BiVO4 surface. Two Pd valence states, Pd(II) and Pd(0), were identified in a 2:1 ratio. Pd–BiVO4 exhibited excellent activity for paracetamol (PCT) degradation, with 100% removal achieved in 1 h under visible light irradiation. During degradation, the mineralization ratio reached up to 40% total organic carbon removal. Two highly active species, namely, hydroxyl and superoxide radicals, were determined by electron spin resonance (ESR). Furthermore, the potential degradation of PCT in this system was proposed based on intermediate information obtained using HPLC-MS and Gauss analysis. The high dispersion and small size of Pd nanoparticles might favor the removal of emerging contaminants using the Pd–BiVO4 photocatalytic system. © 2019 Elsevier Ltd.

Yin, H., Sun, J., Yan, X.*, et al.* (2020) Effects of Co(II) ion exchange, Ni(II)- and V(V)-doping on the transformation behaviors of Cr(III) on hexagonal turbostratic birnessite-water interfaces. *Environmental Pollution,* 256.
Keywords: Coprecipitation; Cr(III) oxidation; Mn oxide; Transition metals; XAFS; Agglomeration; Cobalt compounds; Ion exchange; Minerals; Nickel compounds; Oxidation; Particle size analysis; Linear relationships; Mn oxides; Particle aggregation; Removal efficiencies; Specific capacitance; Transformation behavior; Transitional metals; Chromium compounds; birnessite; chromium derivative; cobalt complex; metal oxide; nickel complex; vanadium derivative; water; chromium; cobalt; mineral; nickel; oxide; vanadium; manganese; precipitation (chemistry); adsorption; biotransformation; controlled study; cyclic potentiometry; dispersity; electric capacitance; Fourier transform spectroscopy; morphology; oxidation kinetics; particle size; surface property; X ray absorption fine structure spectroscopy; X ray absorption near edge structure spectroscopy; X ray absorption spectroscopy; X ray photoemission spectroscopy; zeta potential; chemistry; kinetics; oxidation reduction reaction; Kobus; Oxidation-Reduction; Oxides

Abstract:
Natural birnessite-like minerals are commonly enriched in various transitional metals (TMs), which greatly modify the mineral structure and properties. However few studies are yet conducted systematically on the effects of TM doping on birnessite reactivity towards Cr(III) oxidation. In the present study, the transformation behaviors of Cr(III) on Co-, Ni-, V-

containing birnessites were investigated. Co and Ni doping generally decrease the mineral crystalline sizes and hydrodynamic sizes (DH) while V-doping greatly decreases the crystalline sizes but not the DH, owing to particle aggregation. Co and Ni firstly decrease and then increase the mineral zeta potentials (ζ) at pH4 while V decreases ζ. Electrochemical specific capacitances for Co-containing birnessites are gradually reduced, while those for Ni-doped birnessites are slightly reduced and for V-doped birnessites increased, which have a positively linear relationship with the amounts of Cr(III) oxidized by these samples. Cr(III) removal efficiencies from solution by these Co-, Ni- and V-containing birnessites are 26–51%, ∼62–72% and ∼96–100%, respectively, compared to ∼92% by pure birnessite. Cr(III) oxidation kinetics analysis demonstrates the gradual decrease of Mn(IV) and concurrent increase of Mn(III) and the adsorption of mainly Cr(III) on mineral surfaces. A negatively linear relationship exists between birnessite lateral sizes and the proportions of Mn(IV/III) consumed to oxidize Cr(III). Apparent initial Cr(III) oxidation rate (kobs) for Co-containing birnessites are greatly reduced, while those for Ni-doped samples moderately decreased and for V-doped samples first increased and then decreased. A positively or negatively linear relationship exists between kobs or the amount of Mn(II) released and the mineral Mn(IV) content respectively. Cr(III) oxidation probably initiates from layer edge sites of Ni-doped birnessites but the vacancies of Co- and V-containing birnessites. These results provide insights into the reaction mechanisms of Cr(III) with natural birnessite-like minerals.

Yuan, H., Shen, P., Pan, H.*, et al.* (2020) Mineralogy and mineral geochemistry of the Tuwu porphyry Cu deposit, Eastern Tianshan, NW China: implication for the ore-forming condition and Cu mineralization. *Arabian Journal of Geosciences,* 13(2).
Keywords: Mineral geochemistry; Mineralization; Mineralogy; Physicochemical condition; Tuwu porphyry Cu deposit; copper; geochemistry; hydrothermal alteration; ore deposit; physicochemical property; porphyry; Tien Shan

Abstract:
The Tuwu deposit is one of the largest porphyry copper deposits in Eastern Tianshan, NW China. The widespread hydrothermal alteration is associated with porphyries and their wall-rocks in the porphyry deposit can be divided into potassic, chlorite–sericite, phyllic, and propylitic zones. In this study, we conducted a detailed study on the mineralogy of hydrothermal magnetite, mica, and epidote. Magnetite is closely related to the potassic alteration, and evolves from earlier disseminated magnetite (Mt-I) to the later magnetite–quartz ± biotite ± pyrite ± bornite ± chalcopyrite veins (Mt-II). The significant decrease in the Cr2O3 and V2O3 contents of magnetite from early to late period indicates the gradual increase of oxygen fugacity. The crystallization of magnetite supplies enough reduced sulfur that promotes the sulfide precipitation. The dominance of muscovite (Mc-I) in the early phyllic stage and the increasing of phengite muscovite (Mc-II) in the late phyllic stage suggest the evolution of hydrothermal fluid from a high-temperature and acidic environment to a low-temperature and less acidic environment. This process also results in the decrease of sulfide mineral deposition in the late phyllic stage. Epidote from propylitic zones at Tuwu has similar characteristic with the overprinting epidote in the Yandong porphyry Cu systems. Propylitic Ep-I have higher FeO content than Ep-II. The interaction of Fe-rich propylitic epidote with hydrothermal fluid enhanced both Ca2+ activity and pH value, and favored the precipitation of sulfides (e.g., chalcopyrite). In addition, the Fe-rich and less acidic fluids, which derived from the propylitic zones and flow though the sericitic rocks in the phyllic zones, also promote the deposition of Cu mineralization. Our results, combined with previous research on fluid inclusion, isotopes, and mass transfer, suggest that the

changes in temperature, oxygen fugacity, and pH caused by the fluid–rock interaction played a critical role for the Cu mineralization at Tuwu. © 2020, Saudi Society for Geosciences.

Zhang, D., Ma, Z., Wang, B.*, et al.* (2020) VxMn(4-x)Mo3Ce3/Ti catalysts for selective catalytic reduction of NO by NH3. *Journal of Environmental Sciences,* 88: 145-154.
Keywords: Selective catalytic reduction; Vanadium; Molybdenum; Manganese; Cerium; LOW-TEMPERATURE SCR; SO2 TOLERANCE; NITRIC-OXIDE; PHYSICOCHEMICAL; PROPERTIES; V2O5-WO3/TIO2 CATALYSTS; MN-CE/TIO2 CATALYST; V2O5/TIO2; CATALYSTS; NH3-SCR ACTIVITY; CERIA; BISULFATE; Environmental Sciences & Ecology

Abstract:
A series of vanadium based catalysts (VxMn(4-x)Mo3Ce3/Ti) with different vanadium (x wt.%) and manganese ((4-x) wt.%) contents have been prepared by the wet impregnation method and investigated for selective catalytic reduction (SCR) of NOx by NH3 in the presence of 8 vol.% H2O and 500 ppmV SO2. The physicochemical characteristics of the catalysts were thoroughly characterized. The SCR of NOx by NH3 (NH3-SCR) activity, especially the low-temperature activity, significantly increased with increasing V2O5 content in the catalyst until the V2O5 content reached 1.5 wt.%, which corresponds well with the redox properties of the catalyst. All of the metal oxides were well dispersed and strongly interacted with each other on the catalyst surface. V mainly exists in the V5+ state in the catalysts. The strong synergistic effect between the vanadium and cerium species led to formation of more Ce3+ species, and that between the vanadium and manganese species contributed to formation of more manganese species with low valences. All of the catalysts exhibited strong acidity, while the redox properties determined the NH3-SCR activity, especially the low-temperature activity. H2O and SO2 had severe inhibiting effects on the activity of V1.5Mn2.5Mo3Ce3/Ti. However, good H2O and SO2 resistance and high NOx conversion by V1.5Mn2.5Mo3Ce3/Ti could be achieved in the presence of SO2 and almost no decline was observed in a long-term test at 275 degrees C for 168 hr in the presence of SO2 and H2O, which can be attributed to the sulfate species formed on the catalyst surface. (C) 2019 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Zhao, Z., Li, E., Qin, Y.*, et al.* (2020) Density functional theory (DFT) studies of vanadium-titanium based selective catalytic reduction (SCR) catalysts. *Journal of Environmental Sciences,* 90: 119-137.
Keywords: Selective catalytic reduction (SCR); Structure model; Vanadium-titanium based catalyst; Density functional theory (DFT); Adsorption; TIO2 ANATASE; NITRIC-OXIDE; PERIODIC DFT; IN-SITU; CHEMICAL; DEACTIVATION; MERCURY OXIDATION; REACTION PATHWAYS; LUBRICATION OILS; UREA SOLUTION; ACTIVE-SITES; Environmental Sciences & Ecology

Abstract:
Based on density functional theory (DFT) and basic structure models, the chemical reactions on the surface of vanadium-titanium based selective catalytic reduction (SCR) denitrification catalysts were summarized. Reasonable structural models (non-periodic and periodic structural models) are the basis of density functional calculations. A periodic structure model was more appropriate to represent the catalyst surface, and its theoretical calculation results were more comparable with the experimental results than a non-periodic model. It is generally believed that the SCR mechanism where NH3 and NO react to produce N-2 and H2O follows an Eley-Rideal type mechanism. NH2NO was found to be an important intermediate in the SCR reaction, with multiple production routes. Simultaneously, the

effects of H2O, SO2 and metal on SCR catalysts were also summarized. (C) 2019 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Velenturf, A.P.M., Archer, S.A., Gomes, H.I.*, et al.* (2019) Circular economy and the matter of integrated resources. *Science of the Total Environment,* 689: 963-969.
Keywords: Resource efficiency; Waste management; Whole system design; Resource recovery technology; Circular business models; Governance; STEEL SLAG; RECOVERY; METALS; LEACHATES; VANADIUM; WASTE; SUSTAINABILITY; EFFICIENCY; CATALYSTS; REMOVAL; Environmental Sciences & Ecology

Abstract:
A circular economy offers solutions for global sustainability challenges through the transition from the linear take-make-use-dispose economy to a better organisation of resources. However, realising a circular economy has ran into various biophysical constraints. Circular economy implementation is shaped by the Ellen MacArthur Foundation's butterfly diagram that depicts 'biological' and 'technical' flows as separate cycles, subsequently interpreted as organic materials circulating in open loop systems via the environment and inorganic materials circulating in closed loop systems within society. Conversely, in our view, resource flows often contain tightly bound combinations of organic and inorganic materials either due to their natural composition or due to their technical design. Building on this observation, a new diagram is proposed that broadens the scope of the circular economy to cover extractive sectors and the return of materials from anthropogenic use to natural reserves, thereby reshaping the conceptual space within which solutions such as effective zero-waste-residue technologies, business models, and policies can be developed for the optimal management of integrated resources from a whole-system perspective. The diagram offers a realistic outlook on the biophysical limitations of circularity and endeavours to inspire discussion that supports the transition towards a sustainable circular economy. (C) 2019 The Authors. Published by Elsevier B.V.