



## Vanadium Health Research Programme: Recent Published Literature

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# Introduction

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This report presents the bibliographic details of the 91 papers identified as being published during the period April 2019 to June 2019.

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

**Berlinger, B., Weinbruch, S., Ellingsen, D.G., et al. (2019) On the bio-accessibility of 14 elements in welding fumes. *Environmental Science: Processes and Impacts*, 21(3): 497-505.**

Keywords: cadmium; chromium; cobalt; copper; divalent cation; iron; lead; manganese; molybdenum; nickel; titanium; trace metal; tungsten; vanadium; zinc; air sampling; Article; chemical composition; corrosion; ecotoxicity; exposure; limit of detection; particulate matter; principal component analysis; priority journal; solubility; welding; welding fume; air pollutant; analysis; bioavailability; chemistry; gas; human; male; metallurgy; occupational exposure; Russian Federation; Air Pollutants, Occupational; Biological Availability; Gases; Humans; Russia

## **Abstract:**

The bio-accessibility of 14 elements in welding fume particulate matter was investigated in 325 personal air samples collected during welding in two shipyards and one factory producing heavy machinery. The apparent solubility in a synthetic lung lining fluid (Hatch's solution) was used as proxy for the bio-accessibility. The Hatch solubility of the different elements was highly variable with a median < 1% for Al, Fe, Pb, Ti, between 4 and 6% for Co, Cr, Ni, V, W, between 13 and 27% for Cd, Cu, Mn, Zn, and 41% for Mo. For many elements, the solubility varied over a wide range of several tens of percent. The welding techniques used influenced the solubility of Co, Cr, Cu, Mn and V significantly. The plants investigated (i.e., the welded materials and used electrodes) had a significant influence on the solubility of Co, Cr, Cu, Mn, Mo, V and W. According to principal component analysis (PCA), the variation in solubility can be described by four components, which explain 69% of the variance. The first principal component mostly comprises elements that can predominantly occur as divalent cations, the second principal component elements often forming oxyanions. The principal components are independent of the absolute value of the Hatch solubility. The results of PCA indicate that the co-variation of Hatch solubility is mainly controlled by the most soluble compounds in contrast to the absolute value of apparent solubility, which is strongly influenced by the distribution of the elements between compounds with different equilibrium solubilities. The observed large variability and the significant differences between welding techniques and plants clearly show that the bio-accessibility cannot be obtained from the literature but has to be studied experimentally at each location of interest. © 2019 The Royal Society of Chemistry.

**Camargo, J., Pumarega, J.A., Alguacil, J., et al. (2019) Toenail concentrations of trace elements and occupational history in pancreatic cancer. *Environment International*, 127: 216-225.**

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018327077/pdf?md5=0ab4d2d389662c56fa2f4f70b0ba8563&pid=1-s2.0-S0160412018327077-main.pdf>

Keywords: Arsenic; Cadmium; Manganese; Occupation; Pancreatic cancer; Trace elements; Diseases; Employment; Formaldehyde; Mass spectrometry; Mineral oils; Pesticides; Polycyclic aromatic hydrocarbons; Risk assessment; Solvents; Sulfur compounds; Vanadium; Chlorinated hydrocarbon solvents; Confidence interval; International standards; Occupational exposure; Pancreatic cancers; Polycyclic aromatic hydrocarbons (PAHS); Volatile sulphur compounds; Occupational risks; aromatic hydrocarbon; iron; lead; pesticide; polycyclic aromatic hydrocarbon; trace element; bioaccumulation; cancer; concentration (composition); health risk; lifestyle; PAH; adult; aged; Article; cancer patient; cancer risk; concentration (parameter); controlled study; female; human; inductively coupled plasma mass spectrometry; industrial

hygienist; major clinical study; male; medical history; middle aged; named groups by occupation; occupational disease; pancreas cancer; priority journal; toe nail; Finland

**Abstract:**

Background: Some occupations potentially entailing exposure to cadmium, arsenic, lead, selenium, nickel, and chromium have been associated with an increased risk of exocrine pancreatic cancer (EPC), but no studies have assessed whether body concentrations of such compounds differed among subjects occupationally exposed and unexposed. No studies which found that exposure to such metals increased the risk of EPC assessed whether past occupations were the source of exposure. Objective: The aim was to analyse the relationship between toenail concentrations of trace elements and occupational history in EPC patients. Methods: The study included 114 EPC cases personally interviewed on occupational history and lifestyle factors. Occupations were coded according to the International Standard Classification of Occupations 1988. Selected occupational exposures were assessed by two industrial hygienists and with the Finnish job-exposure matrix (Finjem). Concentrations of 12 trace elements were determined in toenail samples by inductively coupled plasma mass spectrometry. Adjusted geometric means (aGMs) and 95% confidence intervals (95% CI) were calculated. Results: Patients occupationally exposed to aromatic hydrocarbon solvents (AHs) had higher concentrations of cadmium, manganese, lead, iron and vanadium. The aGM of cadmium concentrations for cases exposed to any pesticide was 0.056 µg/g [95% CI: 0.029–0.108], and, for unexposed cases, 0.023 µg/g [0.017–0.031]. Patients occupationally exposed to pesticides had higher concentrations of cadmium and manganese. Higher concentrations of vanadium, lead and arsenic were related to exposure to formaldehyde. Vanadium and lead were also associated with exposure to chlorinated hydrocarbon solvents, and arsenic was related to exposure to polycyclic aromatic hydrocarbons (PAHs). Conclusions: Patients occupationally exposed to AHs, pesticides, chlorinated hydrocarbon solvents, formaldehyde, volatile sulphur compounds and PAHs had higher concentrations of several metals. These elements may account for some of the occupational risks previously reported for pancreatic cancer. © 2019 The Authors.

**Chen, G., Wang, X., Wang, R., et al. (2019) Health risk assessment of potentially harmful elements in subsidence water bodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. *Ecotoxicology and Environmental Safety*, 171: 737-745.**

Keywords: Coal mining area; Health risk assessment; Monte Carlo simulation; Potentially harmful elements; Subsidence water bodies; arsenic; cadmium; chromium; cobalt; copper; environmental, industrial and domestic chemicals; iron; lead; manganese; nickel; potentially harmful element; surface water; unclassified drug; vanadium; zinc; heavy metal; atomic absorption spectroscopy; carcinogen; coal mining; concentration (composition); health risk; Monte Carlo analysis; risk assessment; Article; atomic absorption spectrometry; atomic fluorescence spectrometry; cancer risk; China; concentration (parameter); contact dermatitis; controlled study; environmental exposure; health hazard; ingestion; Monte Carlo method; water analysis; water pollution; water quality; analysis; environmental monitoring; human; water pollutant; Anhui; Huainan; Humans; Metals, Heavy; Spectrophotometry, Atomic; Water Pollutants, Chemical

**Abstract:**

Enrichment of potentially harmful elements in surface water results in ecological risk to the surrounding environment. Assessing the environmental risk of these elements is of great importance. In this study, surface water samples from 6 different subsidence water bodies in the Huainan coal mining area were collected. The concentrations of Cu, Ni, Pb, Cd, Co, Cr, V, Fe, Mn and Zn were measured by atomic absorption spectrophotometry, and those of As and

Hg were analyzed by atomic fluorescence spectrometry. Then, human health risks through the ingestion and dermal contact pathways were assessed and analyzed on the basis of a Monte Carlo simulation. The mean and 95th percentile risks were reported. The results showed that the total carcinogenic risk values in every subsidence water body summed for Cr, Ni and As via two exposure pathways were greater than the maximum acceptable level ( $1 \times 10^{-4}$ ), and Xinji'er water body had the highest carcinogenic risk. Among three elements, Ni was the highest contributor to carcinogenic risk. All non-carcinogenic health risk (hazard quotients) values except for one water area of Co (Xinji'er) were less than 1; however, the total non-carcinogenic health risks of two water bodies (Xinji'er, Xinjiyi) summed for all the elements based on mean concentrations were higher than 1. Xinji'er had the highest hazard index. The extent of the impacts of the total hazard quotients followed the order of  $Co > As > Cd > Hg > Pb > V > Fe > Ni > Mn > Zn > Cr$ . Furthermore, the total hazard quotients of Co and As via ingestion pathway summed for the six subsidence water areas were greater than 1, which should be a concern. © 2019 Elsevier Inc.

**Dai, X., Deng, Q., Guo, D., et al. (2019) Association of urinary metal profiles with serum uric acid: a cross-sectional study of traffic policemen in Wuhan, China. *BMJ Open*, 9(5): e022542.**

Available at: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6530447/pdf/bmjopen-2018-022542.pdf>

Keywords: serum uric acid; traffic policemen; urinary metal profiles

**Abstract:**

**OBJECTIVES:** Serum uric acid (SUA) is both a strong antioxidant and one of the key risk factors of cardiovascular diseases (CVDs). We aimed to investigate the associations of urinary metal profile with SUA in traffic policemen in Wuhan, China. **DESIGN:** A cross-sectional study was carried out in traffic policemen. **SETTING:** A seriously polluted Chinese city. **PARTICIPANTS:** A total of 186 traffic policemen were recruited in this study. About 56 of them worked in the logistics department and the other 130 maintained traffic order or dealt with traffic accidents on the roads. All these subjects had worked as a policeman for at least 1 year. **MAIN OUTCOME MEASURES:** SUA. **RESULTS:** The significantly negative association of lead with SUA was consistent between single-metal and multiple-metal models ( $p=0.004$  and  $p=0.020$ , respectively). Vanadium, chromium and tin were reversely associated with SUA levels in the single-metal models after false discovery rate (FDR) adjustment (all  $P_{FDR} < 0.05$ ). One IQR increase in vanadium, chromium, tin and lead was associated with 26.9 micromol/L (95% CI -44.6 to -9.2;  $p=0.003$ ), 27.4 micromol/L (95% CI -46.1 to -8.8;  $p=0.004$ ), 11.2 micromol/L (95% CI -18.9 to -3.4;  $p=0.005$ ) and 16.4 micromol/L (95% CI -27.6 to -5.2;  $p=0.004$ ) decrease in SUA, respectively. Significant interaction between smoking and vanadium on decreased SUV was found ( $p$  for interaction = 0.007 and  $p_{FDR} = 0.028$ ). **CONCLUSIONS:** Urinary vanadium, chromium, tin and lead were negatively associated with SUA. Vanadium and cigarette smoking jointly affected SUA levels. Further studies are needed to replicate these findings and to investigate the potential mechanisms.

**Garza-Galindo, R., Morton-Bermea, O., Hernández-Álvarez, E., et al. (2019) Spatial and temporal distribution of metals in PM 2.5 during 2013: assessment of wind patterns to the impacts of geogenic and anthropogenic sources. *Environmental Monitoring and Assessment*, 191(3): 165.**

Keywords: Geogenic and anthropogenic sources; Metals; Mexico City; PM 2.5; Wind plots; Chemical analysis; Inductively coupled plasma mass spectrometry; Anthropogenic sources; Controlling mechanism; Inductively coupled plasma mass spectrometries (ICPMS); Metal concentrations; Mexico City metropolitan areas; PM2.5; Spatial and temporal distribution; Principal component analysis; antimony; cadmium; cerium; chromium; cobalt; copper;

europium; lanthanum; lead; manganese; metal; molybdenum; nickel; samarium; silver; titanium; vanadium; anthropogenic source; concentration (composition); geogenic source; heavy metal; particulate matter; spatial distribution; temporal distribution; wind velocity; air pollution; Article; mass spectrometry; Mexico; seasonal variation; spatial analysis; wind; air pollutant; analysis; city; environmental monitoring; season; Federal District [Mexico]; Mexico [North America]; Air Pollutants; Cities; Seasons

**Abstract:**

The Mexico City Metropolitan Area (MCMA) was the object of a chemical elemental characterization (Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Ag, Cd, Sb, Pb, La, Sm, Ce, and Eu) of PM 2.5 collected during 2013 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Sampling campaigns were carried out at five locations simultaneously—northwest, northeast, center, southwest, and southeast—during dry-warm season (April), rainy season (August), and dry-cold season (November). By means of enrichment factor (EF) and principal component analysis (PCA), it was possible to attribute the analyzed elements to geogenic and anthropogenic sources, as well as to identify a group of elements with mixed provenance sources. The highest concentrations for most metals were found in northwest and northeast, and during dry-warm (DW), confirming the trend observed in PM 2.5 samples collected in 2011. Despite similarities between 2011 and 2013, an increase of 17% in PM 2.5 mass concentration was observed, mainly attributable to geogenic sources, whereby the importance of wind intensity to the impact of emission sources is highlighted. The effect of wind intensity was revealed, by means of polar plots, as the controlling mechanism for this increase. This allowed us to conclude that high-speed episodes ( $5 \text{ m s}^{-1}$ ) were responsible for raising geogenic metal concentrations rather than wind direction. © 2019, Springer Nature Switzerland AG.

**Guo, H-B., Li, M., Lyu, Y., et al. (2019) Size-resolved particle oxidative potential in the office, laboratory, and home: Evidence for the importance of water-soluble transition metals. *Environmental Pollution*, 246: 704-709.**

Keywords: Indoor air quality; Lung deposition model; Particle size distribution; Water-soluble oxidative potential; Water-soluble transition metals; Air quality; Biological organs; Deposition; Indoor air pollution; Particle size; Particle size analysis; Size distribution; Deposition efficiencies; Dominant contributions; Lung depositions; Occupant activities; Oxidative potential; Size-resolved particles; Watersoluble; Transition metals; cobalt; copper; dithiothreitol; iron; lead; manganese; nickel; transition element; unclassified drug; vanadium; water; water soluble transition metal; heavy metal; indoor air; adult; air conditioning; ambient air; Article; catalyst; China; concentration (parameter); controlled study; home; human; laboratory; male; occupation; oxidation reduction potential; particulate matter; air pollutant; analysis; biological model; drug effect; environmental monitoring; housing; lung; metabolism; oxidative stress; procedures; workplace; Air Pollutants; Air Pollution, Indoor; Laboratories; Metals, Heavy; Models, Biological; Transition Elements

**Abstract:**

Particulate matter (PM) oxidative potential (OP) is an emerging health metric, but studies examining the OP of indoor PM are rare. This paper focuses on the relationships between respiratory exposure to OP and PM water-soluble composition in indoor environments. Size-resolved PM samples were collected between November 2015 and June 2016 from an office, home (including bedroom, living room, and storeroom), and laboratory using a MOUDI sampler. Particles from each source were segregated into eleven size bins, and the water-soluble metal content and dithiothreitol (DTT) loss rate were measured in each PM extract. The water-soluble OP ( $OP_{ws}$ ) of indoor PM was highest in the office and lowest in the home,

varying by factors of up to 1.2; these variations were attributed to differences in occupation density, occupant activity, and ventilation. In addition, the particulate Cu, Mn, and Fe concentrations were closely correlated with OP ws in indoor particles; the transition metals may have acted as catalysts during oxidation processes, inducing ·OH formation through the concomitant consumption of DTT. The OP ws particle size distributions featured single modes with peaks between 0.18 and 3.2 μm across all indoor sites, reflecting the dominant contribution of PM 3.2 to total PM levels and the enhanced oxidative activity of the PM 3.2 compared to PM >3.2. Lung-deposition model calculations indicated that PM 3.2 dominated the pulmonary deposition of the OP ws (>75%) due to both the high levels of metals content and the high deposition efficiency in the alveolar region. Therefore, because OP ws has been directly linked to various health effects, special attention should be given to PM 3.2. © 2019 Elsevier Ltd.

**Kocylowski, R., Grzesiak, M., Gaj, Z., et al. (2019) Evaluation of Essential and Toxic Elements in Amniotic Fluid and Maternal Serum at Birth. *Biological Trace Element Research*, 189(1): 45-54.**

Keywords: Amniotic fluid; Delivery; Essential and toxic elements; Maternal serum; Reference values; aluminum; antimony; arsenic; barium; cadmium; calcium; chromium; cobalt; copper; iron; lead; magnesium; manganese; selenium; strontium; uranium; vanadium; zinc; adult; amnion fluid; amnion fluid analysis; Article; blood analysis; blood sampling; body mass; Caucasian; concentration (parameter); female; human; inductively coupled plasma mass spectrometry; maternal age; normal human; obstetric delivery; Polish citizen; prediction; pregnancy; reference value; regression analysis; young adult

**Abstract:**

The objective of this study was to determine the concentration and the reference ranges of essential and toxic elements in amniotic fluid (AF) and maternal serum (MS) at birth. This study was conducted among 175 healthy pregnant Caucasian European women aged 18–42. AF and maternal blood samples were collected during delivery. An inductively coupled plasma mass spectrometry (ICP-MS) technique was used to determine the levels of Mg, Co, Cu, Zn, Sr, Cd, Ba, Pb, U, Ca, Cr, Al, Mn, V, Fe, As, Se and Sb in AF and MS. The range of reference values was calculated for all analyzed elements in the serum and AF. The mean concentrations of elements, except Pb, were generally higher in MS than in AF. Multiple regression analysis showed that the maternal/newborn body mass (MBM/NBM) ratio was a strong negative predictor (among maternal age and gravidity) of Mg concentration in amniotic fluid. In the serum, MBM/NBM ratio was a strong positive predictor of Cu concentration. Moreover, regression analysis showed that maternal age was an independent positive predictor of the Se level in maternal serum. The reference value ranges of 18 essential and toxic elements were established in AF and MS among a population of healthy pregnant Polish women at delivery. The level of Mg, Co, Cu, Ca and Se in AF and MS can be determined by maternal age and MBM/NBM ratio. These results can be useful in counseling individuals with pregnancies affected by exposure to one of the parameters under investigation. © 2018, The Author(s).

**Kulikova, T., Hiller, E., Jurkovic, L., et al. (2019) Total mercury, chromium, nickel and other trace chemical element contents in soils at an old cinnabar mine site (Mernik, Slovakia): anthropogenic versus natural sources of soil contamination. *Environmental Monitoring and Assessment*, 191(5): 263.**

Keywords: Chromium/analysis; Environmental Monitoring; Human Activities; Humans; Mercury/analysis; Mercury Compounds; Mining; Nickel/analysis; Slovakia; Soil/chemistry; Soil Pollutants/analysis; Trace Elements/analysis; Compositional data analysis; Contamination; Mercury; Mine soil; Nickel

**Abstract:**

The aims of this study were to investigate the occurrence and distribution of total mercury (Hg) and other trace elements of environmental concern, such as arsenic (As), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn) and vanadium (V), in soils from the abandoned Mernik cinnabar mine in eastern Slovakia. For this purpose, thirty soil samples from two depth intervals within the mine area (n = 60 soil samples) and additional sixteen soil samples from adjacent areas (n = 25 soil samples) were collected. Total Hg was measured by atomic absorption spectrometry, while As and other metals were analyzed using inductively coupled plasma atomic emission spectrometry. High mercury concentrations (> 100 mg/kg with a maximum of 951 mg/kg) were observed only in surface soils close to mine waste heaps and adits. Otherwise, Hg concentrations in the majority of surface soils were lower (0.14-19.7 mg/kg), however, higher than Hg in soils collected from sites outside the mine area (0.19-6.92 mg/kg) and even considerably higher than Hg in soils at sites not influenced by the Mernik mine. Elevated Cr and Ni concentrations in soils regardless of their sampling sites (mean of 276 mg/kg and median of 132 mg/kg for Cr and 168 mg/kg and 81 mg/kg for Ni, respectively) were attributed to the lithology of the area; the soils are underlain by the sediments of the Central Carpathian Palaeogene, containing a detritus of ultrabasic rocks. As our geochemical data are compositional in nature, they were further treated by compositional data analysis (CoDA). Robust principal component analysis (RPCA) applied on centred (clr) log-ratio-transformed data and correlation analysis of compositional parts based on symmetric balances distinguished very well different sources of origin for the chemical elements. The following three element associations were identified: Hg association with the main source in mining/roasting, Cr-Ni association derived from bedrock and As-Cu-Mn-Pb-Zn-V association (natural background and minor sulphides/sulfosalts in mineralized rocks). The values of geoaccumulation index and enrichment factor suggested that concentrations of Hg in the soils were influenced by human industrial activities.

**Li, A., Zhuang, T., Shi, J., et al. (2019) Heavy metals in maternal and cord blood in Beijing and their efficiency of placental transfer. *Journal of Environmental Sciences (China)*, 80: 99-106.**

Available at:

[http://www.jesc.ac.cn/jesc/En/ch/reader/create\\_pdf.aspx?file\\_no=S1001074218328687](http://www.jesc.ac.cn/jesc/En/ch/reader/create_pdf.aspx?file_no=S1001074218328687)

Keywords: Cord blood; Heavy metal; Maternal blood; Newborn; Placental transfer efficiency; Blood; Disease control; Efficiency; Mass spectrometry; Vanadium compounds; Center for disease controls; High detection rate; Maternal bloods; Placental transfer; Prenatal exposure; Threshold limits; Heavy metals; bioaccumulation; child health; health risk; maternal health; pollutant source; pollution exposure; pregnancy; Beijing [Beijing (ADS)]; Beijing [China]; China; adult; child; environmental monitoring; female; fetus blood; human; maternal exposure; metabolism; placenta; pollutant; Beijing; Environmental Pollutants; Fetal Blood; Humans; Infant, Newborn; Metals, Heavy

**Abstract:**

This study aimed to determine the effect of exposure to heavy metals in pregnant women in Beijing, China. We also evaluated the association of these heavy metals with birth weight and length of newborns. We measured the levels of 10 heavy metals, including lead (Pb), titanium (Ti), manganese (Mn), nickel (Ni), cadmium (Cd), chromium (Cr), antimony (Sb), stannum (Sn), vanadium (V), and arsenic (As), in 156 maternal and cord blood pairs. An inductively coupled plasma mass spectrometry method was used for measurement. Pb, As, Ti, Mn, and Sb showed high detection rates (> 50%) in both maternal and cord blood. Fourteen (9%) mothers had blood Pb levels greater than the United States Center for Disease Control allowable threshold limit for children (50 µg/L). In prenatal exposure to these heavy metals, there was no

significant association between any heavy metal and birth weight/length. Moreover, we estimated the placental transfer efficiency of each heavy metal, and the median placental transfer efficiency ranged from 49.6% (Ni) to 194% (Mn) (except for Cd and Sn). The level and detection rate of Cd in maternal blood were much higher than that in cord blood, which suggested that Cd had difficulty in passing the placental barrier. Prospective research should focus on the source and risk of heavy metals in non-occupationally exposed pregnant women in Beijing. © 2018.

**Longley, I., Tunno, B., Somervell, E., et al. (2019) Assessment of Spatial Variability across Multiple Pollutants in Auckland, New Zealand. *International Journal of Environmental Research and Public Health*, 16(9): 1567.**

Available at: <https://www.mdpi.com/1660-4601/16/9/1567/pdf>

Keywords: particle composition; spatial saturation; source identification; shipping emissions; POLYCYCLIC AROMATIC-HYDROCARBONS; FINE PARTICULATE MATTER; LAND-USE; REGRESSION; AIR-POLLUTION; NEW-YORK; SOURCE APPORTIONMENT; ORGANIC-COMPOUNDS; NITROGEN-DIOXIDE; PM2.5; AMBIENT; Environmental Sciences & Ecology; Public, Environmental & Occupational Health

**Abstract:**

Spatial saturation studies using source-specific chemical tracers are commonly used to examine intra-urban variation in exposures and source impacts, for epidemiology and policy purposes. Most such studies, however, has been performed in North America and Europe, with substantial regional combustion-source contributions. In contrast, Auckland, New Zealand, a large western city, is relatively isolated in the south Pacific, with minimal impact from long-range combustion sources. However, fluctuating wind patterns, complex terrain, and an adjacent major port complicate pollution patterns within the central business district (CBD). We monitored multiple pollutants (fine particulate matter (PM2.5), black carbon (BC), elemental composition, organic diesel tracers (polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes), and nitrogen dioxide (NO2)) at 12 sites across the similar to 5 km(2) CBD during autumn 2014, to capture spatial variation in traffic, diesel, and proximity to the port. PM2.5 concentrations varied 2.5-fold and NO2 concentrations 2.9-fold across the CBD, though constituents varied more dramatically. The highest-concentration constituent was sodium (Na), a distinct non-combustion-related tracer for sea salt ( $\mu = 197.8 \text{ ng/m}^3$ ) (SD = 163.1 ng/m(3)). BC, often used as a diesel-emissions tracer, varied more than five-fold across sites. Vanadium (V), higher near the ports, varied more than 40-fold across sites. Concentrations of most combustion-related constituents were higher near heavy traffic, truck, or bus activity, and near the port. Wind speed modified absolute concentrations, and wind direction modified spatial patterns in concentrations (i.e., ports impacts were more notable with winds from the northeast).

**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: 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. © 2018 The Author(s).

**Rinklebe, J., Antoniadis, V., Shaheen, S.M., et al. (2019) Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International*, 126: 76-88.**

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018324954/pdf?md5=5cfea4ef254356ae57dbf4b647181f6b&pid=1-s2.0-S0160412018324954-main.pdf>

Keywords: Heavy metals; Risk assessment; Riverine ecosystems; Trace elements; Wetland soil; Arsenic; Chromium; Contamination; Copper compounds; Health; Health risks; Hydrogeology; River pollution; Soil conservation; Soil surveys; Soils; Tin; X ray spectrometers; Contaminated areas; Contaminated sites; Contamination factors; Pollution load indices; Potentially toxic elements; Wetland soils; X-ray fluorescence spectrometer; barium; copper; lead; nickel; rubidium; strontium; vanadium; zinc; zirconium; freshwater ecosystem; health risk; heavy metal; soil pollution; soil profile; trace element; wetland; adult; Article; chemical composition; child; Contaminated Sites Ordinance; Contamination factor; controlled study; environmental parameters; environmental policy; female; German Federal Soil Protection; Germany; health hazard; high risk population; human; male; mathematical analysis; median children hazard index; Pollution Load Index; Precautionary Value; priority journal; river; sandy soil; sex difference; soil analysis; soil property; topsoil; toxicity testing; X ray fluorescence spectrometry; Elbe River

#### **Abstract:**

Floodplain soils across Central Elbe River (CER), Germany, vary considerably in potentially toxic element (PTE) content. However, there has never been a comprehensive study that links PTE levels with human health risk for children and adults. Our objective was to determine the contamination of 13 PTEs in 94 soil profiles along CER and assess the associated health risk via diverse indices for adults and children. Of 94 soil profiles, we measured soil properties and total content of arsenic, barium, chromium, copper, nickel, lead, rubidium, tin, strontium, vanadium, zinc, and zirconium using x-ray fluorescence spectrometer (XRF). We calculated the Contamination Factor and the Pollution Load Index (PLI), and assessed the health risk for male and female adults as well as for children. Topsoil median contents of Cr (84 mg kg<sup>-1</sup>), Cu (42), Ni (33), and Zn (195) exceeded the Precautionary Values for sandy soils according to the German Federal Soil Protection and Contaminated Sites Ordinance, while As, Pb, and V were 32, 73, and 77 mg kg<sup>-1</sup>, respectively. Median topsoil PLI was 1.73, indicating elevated multi-element contamination, with 90th percentile and maximum values being 3.20 and 4.31, respectively. All PTE concentrations were higher in top- compared to subsoils. Also at the 50th percentile the most enriched elements were Sn and As, followed by Zr and Rb, while in the 90th percentile Sn and As were followed by Zn, Pb and Cu. Median children's hazard index (HI) was higher than unity (HI = 2.27) and the 90th percentile was 5.53, indicating elevated health risk. Adult median HIs were 0.18 for male and 0.21 for female persons. Arsenic was found to

be the primary contributor to total risk, accounting of 57.4% of HI in all three-person groupings, with Cr (17.3%) being the second, and V (10.2%) the third. Children's health is at dramatically higher risk than that of adults; also As, Cr, Pb, and V have a predominant role in contamination-related health risks. The presence of V, a less-expected element, among those of major risk contribution, reveals the necessity of monitoring areas at large scale. Our results demonstrate that our study may serve as a model for similar works studying multi-element-contaminated areas in future. © 2019 The Authors.

**Soltani, N., Moore, F., Keshavarzi, B., et al. (2019) Potentially toxic elements (PTEs) and polycyclic aromatic hydrocarbons (PAHs) in fish and prawn in the Persian Gulf, Iran. *Ecotoxicology and Environmental Safety*, 173: 251-265.**

Keywords: Fish; Human health risk assessment; Persian Gulf; Polycyclic aromatic hydrocarbon; Potentially toxic element; Prawn; arsenic; cadmium; chromium; cobalt; copper; fluorene; lead; manganese; mercury; naphthalene; nickel; phenanthrene; selenium; potentially toxic element; toxic substance; unclassified drug; vanadium; zinc; heavy metal; concentration (composition); crustacean; food intake; hazard assessment; health risk; PAH; risk assessment; animal tissue; Article; bioaccumulation; controlled study; *Coptodon zillii*; food contamination; health hazard; Iran; *Leuciscus vorax*; *Liza abu*; maximum permissible dose; *Metapenaeus affinis*; muscle tissue; nonhuman; *Penaeus semisulcatus*; sea food; shrimp; adult; analysis; animal; child; Decapoda (Crustacea); environmental monitoring; estuary; human; Indian Ocean; river; water pollutant; Arabian Sea; Khuzestan; Musa Estuary; Shatt al Arab; *Leuciscus*; *Musa*; Animals; Estuaries; Fishes; Humans; Metals, Heavy; Polycyclic Aromatic Hydrocarbons; Rivers; Seafood; Water Pollutants, Chemical

**Abstract:**

This study aimed to speciate and quantify potentially toxic elements (PTEs) and polycyclic aromatic hydrocarbons (PAHs), in addition to estimate potential human health risk of PTEs (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn) through the consumption of three edible fish species (*Leuciscus vorax*, *Liza abu*, and *Coptodon zillii*) and two prawn species (*Metapenaeus affinis* and *Penaeus semisulcatus*) collected from Arvand River and Musa Estuary in the Persian Gulf. The concentration of As in prawn species exceeded permissible limit set by international organizations. PAHs were dominated by low molecular weight species such as naphthalene, phenanthrene, and fluorene but generally exhibited low mean concentrations in fish and prawn samples. The human health hazard posed by PTEs was assessed using methods that consider estimated daily intake (EDI), estimated weekly intake (EWI), target hazard quotients (THQ), and combined THQ. The results suggested that elevated As concentrations in almost all prawn samples may pose a probable health hazard to local inhabitants. © 2019 Elsevier Inc.

**Stachiw, S., Bicalho, B., Grant-Weaver, I., et al. (2019) Trace elements in berries collected near upgraders and open pit mines in the Athabasca Bituminous Sands Region (ABSR): Distinguishing atmospheric dust deposition from plant uptake. *Science of the Total Environment*, 670: 849-864.**

Keywords: Atmospheric aerosols; Bituminous sands; Micronutrients; Mineral dust; Native berries; Trace elements; Antennas; Atmospheric chemistry; Deposition rates; Dust; Fruits; Health risks; Oil sands; Open pit mining; Elevated concentrations; Environmental emissions; Indigenous community; Lithophile elements; Positive correlations; aluminum; antimony; barium; beryllium; cadmium; chromium; copper; iron; lead; lithium; manganese; molybdenum; nickel; rhenium; rubidium; scandium; selenium; silver; strontium; thallium; thorium; trace element; uranium; vanadium; zinc; asphalt; hydrocarbon; metal; silicon dioxide; aerosol; atmospheric deposition; biological uptake; concentration (composition);

fruit; mineral; open pit mine; plant; sand; Article; blueberry; concentration (parameter); controlled study; cranberry; food washing; health hazard; inductively coupled plasma mass spectrometry; limit of detection; lingonberry; measurement accuracy; mining; nonhuman; physical chemistry; phytotoxicity; plant root; priority journal; soil pollution; Sphagnum; surface area; tar sand; air pollutant; Alberta; analysis; atmosphere; chemistry; environmental monitoring; soil; Sphagnopsida; wetland; Athabasca Oil Sands; Canada; Bryophyta; Vaccinium; Air Pollutants; Hydrocarbons; Metals; Wetlands

**Abstract:**

There are ongoing concerns regarding environmental emissions of trace elements (TEs) from bitumen mining and upgrading in the Athabasca Bituminous Sands Region (ABSR). Depending on their physical and chemical forms, elevated concentrations of potentially toxic TEs in berries could pose a health risk to local indigenous communities because native fruits are an important part of their traditional diet. The objective of this study was to distinguish between aerial deposition of TEs versus plant uptake, in cranberries, lingonberries, and blueberries growing in the ABSR. The concentrations of TEs were determined using ICP-MS in the metal-free, ultraclean SWAMP lab at the University of Alberta. The spatial variation in abundance of conservative, lithophile elements such as Y in berries resembles the published map of dust deposition rates obtained using Sphagnum moss. The presence of dust particles on the surface of the berries near open pit mines and upgraders was confirmed using SEM. Elements which show strong, positive correlation with Y include Al, Cr, Pb, U, and V; these are supplied mainly by dust. Elements which are largely independent of Y concentrations include Ba, Cd, Cu, Mn, Mo, Ni, Rb, Sr, and Zn; these are obtained primarily by plant uptake from soil. The concentrations of elements associated with dust were considerably reduced after washing with water, but the elements independent of dust inputs were unaffected. Elements which are supplied almost exclusively by dust (e.g. Y) are more abundant in berries from the ABS region (2 to 24 times), compared to berries from remote locations. © 2019 Elsevier B.V.

**Vänskä, M., Diab, S.Y., Perko, K., et al. (2019) Toxic Environment of war: Maternal prenatal heavy metal load predicts infant emotional development. *Infant Behavior and Development*, 55: 1-9.**

Keywords: Child development; Emotional development; Heavy metals; PTSD; War trauma; chromium; heavy metal; mercury; strontium; uranium; vanadium; adult; Article; birth weight; childbirth; clinical feature; disease association; emotion; emotionality; female; first trimester pregnancy; gestational age; hair level; Harvard Trauma Questionnaire; human; inductively coupled plasma mass spectrometry; infant; Infant Behavior Questionnaire; male; mood disorder; Palestinian; posttraumatic stress disorder; prediction; pregnant woman; prenatal exposure; priority journal; questionnaire; risk factor; war exposure

**Abstract:**

Background: People in war zones are exposed to heavy metal contamination deriving from new-generation weapons, in addition to exposure to psychologically traumatizing war events. Pregnant women and their children-to-be are particularly vulnerable to both biological and psychological war effects. Objective: The aim of the current study was to analyse the impact of maternal prenatal heavy metal contamination on infant emotional development and to examine the potential moderating role of maternal symptoms of post-traumatic stress disorder (PTSD) in the association between heavy metal load and infant emotional development. Methods: The participants were 502 Palestinian mothers, pregnant in their first trimester during the 2014 War on Gaza. The mothers were recruited at their delivery (T1) and followed at the infants' age of 6–7 months (T2; N = 392). The load of five weapon-related heavy metals (chromium, mercury, vanadium, strontium, and uranium) was analysed by

Inductively Coupled Plasma Mass Spectrometry (ICP/MS) from mothers' hair samples at childbirth (T1). Assessment of maternal PTSD symptoms was based on the Harvard Trauma Questionnaire (HTQ) and infant emotional development on the Infant Behavior Questionnaire (IBQ), both reported by mothers (T2). Results: Two of the analysed metals, chromium and uranium, adversely predicted children's early emotional development, indicated by decreased positive affectivity, increased negative emotionality, and problems in early orientation and regulation. Mother's PTSD did not moderate the impact of heavy metal contamination on children's emotional development. Conclusions: Adverse impact of war is not limited to those who experience it directly, but is passed on to future generations through multiple mechanisms. International organizations are obliged to protect parents and infants from the modern weaponry in wars. © 2019.

**Wang, X., Shen, Y., Lin, Y., et al. (2019) Atmospheric pollution from ships and its impact on local air quality at a port site in Shanghai. *Atmospheric Chemistry & Physics*, 19(9): 6315-6320.**

Available at: <https://www.atmos-chem-phys.net/19/6315/2019/acp-19-6315-2019.pdf>  
Keywords: Air quality; Airports; Particulate matter; Particle size distribution; Mass spectrometry; Trace metals

**Abstract:**

Growing shipping activities in port areas have generated negative impacts on climate, air quality and human health. To better evaluate the environmental impact of ship emissions, an experimental characterization of air pollution from ships was conducted in Shanghai Port in the summer of 2016. The ambient concentrations of gaseous NO, NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub> in addition to fine particulate matter concentrations (PM<sub>2.5</sub>), particle size distributions and the chemical composition of individual particles from ship emission were continuously monitored for 3 months. Ship emission plumes were visible at the port site in terms of clear peaks in the gaseous species and particulate matter concentrations. The SO<sub>2</sub> and vanadium particle numbers were found to correlate best with ship emissions in Shanghai Port. Single-particle data showed that ship emission particles at the port site mainly concentrated in a smaller size range (<0.4 μm), where their number contributions were more important than their mass contributions to ambient particulate matter. The composition of ship emission particles at the port site suggested that they were mostly freshly emitted particles: their mass spectra were dominated by peaks of sulfate, elemental carbon (EC), and trace metals such as V, Ni, Fe and Ca, in addition to displaying very low nitrate signals. The gaseous NO<sub>x</sub> composition in some cases of plumes showed evidence of atmospheric transformation by ambient O<sub>3</sub>, which subsequently resulted in O<sub>3</sub> depletion in the area. Quantitative estimations in this study showed that ship emissions contributed 36.4 % to SO<sub>2</sub>, 0.7 % to NO, 5.1 % to NO<sub>2</sub>, -0.9 % to O<sub>3</sub>, 5.9 % to PM<sub>2.5</sub> and 49.5 % to vanadium particles in the port region if land-based emissions were included, and 57.2 % to SO<sub>2</sub>, 71.9 % to NO, 30.4 % to NO<sub>2</sub>, -16.6 % to O<sub>3</sub>, 27.6 % to PM<sub>2.5</sub> and 77.0 % to vanadium particles if land-based emissions were excluded.

**Wang, X., Mukherjee, B., Batterman, S., et al. (2019) Urinary metals and metal mixtures in midlife women: The Study of Women's Health Across the Nation (SWAN). *International Journal of Hygiene and Environmental Health*, 222(5): 778-789.**

Keywords: Clustering analysis; Metals; Mid-life; Mixtures; Women

**Abstract:**

Background: Little is known about the extent of exposure to metals and metal mixtures among midlife women. Objectives: We assessed exposure to multiple metals in the Study of Women's Health Across the Nation (SWAN), a multi-site, multi-racial/ethnic cohort of women at midlife.

Methods: We measured urinary concentrations of 21 metals (arsenic, barium, beryllium, cadmium, cobalt, chromium, cesium, copper, mercury, manganese, molybdenum, nickel, lead, platinum, antimony, tin, thallium, uranium, vanadium, tungsten and zinc) using high-resolution inductively coupled plasma-mass spectrometry among 1335 white, black, Chinese and Japanese women aged 45–56 years at the third SWAN annual visit (1999–2000). Least squared geometric mean concentrations were compared across race/ethnicity, education, financial hardship, smoking, secondhand smoking, seafood intake and rice intake groups. Overall exposure patterns of multiple metals were derived using k-means clustering method. Results: The percentage of women with detectable concentrations of metals ranged from 100% for arsenic, cesium, molybdenum and zinc, to less than 5% for platinum; 15 metals had detection rates of 70% or more. Asian women, both Chinese and Japanese, had higher urinary concentrations of arsenic, cadmium, copper, mercury, molybdenum, lead and thallium, compared with other race/ethnic groups, independent of sociodemographic, lifestyle, dietary, and geographic characteristics. Seafood and rice intake were important determinants of urinary arsenic, cesium, mercury, molybdenum and lead levels. Two distinct overall exposure patterns- “high” vs. “low” — were identified. Women in the “high” overall exposure pattern were more likely to be Asians, current smokers, and to report high consumption of seafood and rice. Black women were less likely to have the high exposure pattern. Conclusions: Metal exposure of midlife women differs by racial/ethnic, sociodemographic, lifestyle, dietary, and geographic characteristics. Asian women may be experiencing the highest exposures to multiple metals compared with other racial/ethnic groups in the United States. © 2019 Elsevier GmbH.

**Yang, Y., Ruan, Z., Wang, X., et al. (2019) Short-term and long-term exposures to fine particulate matter constituents and health: A systematic review and meta-analysis. *Environmental Pollution (Barking, Essex : 1987)*, 247: 874-882.**

Keywords: Air Pollutants/analysis/toxicity; Air Pollution/adverse effects/statistics & numerical data; Environmental Exposure/adverse effects/statistics & numerical data; Humans; Nitrates; Particulate Matter/toxicity; Seasons; Soot; Sulfates; Vanadium; Air pollution; Constituents of fine particulate matter; Morbidity; Mortality; PM(2.5)

**Abstract:**

BACKGROUND: Fine particulate matter (Particulate matter with diameter  $\leq 2.5\mu\text{m}$ ) is associated with multiple health outcomes, with varying effects across seasons and locations. It remains largely unknown that which components of PM<sub>2.5</sub> are most harmful to human health. METHODS: We systematically searched all the relevant studies published before August 1, 2018, on the associations of fine particulate matter constituents with mortality and morbidity, using Web of Science, MEDLINE, PubMed and EMBASE. Studies were included if they explored the associations between short term or long term exposure of fine particulate matter constituents and natural, cardiovascular or respiratory health endpoints. The criteria for the risk of bias was adapted from OHAT and New Castle Ottawa. We applied a random-effects model to derive the risk estimates for each constituent. We performed main analyses restricted to studies which adjusted the PM<sub>2.5</sub> mass in their models. RESULTS: Significant associations were observed between several PM<sub>2.5</sub> constituents and different health endpoints. Among them, black carbon and organic carbon were most robustly and consistently associated with all natural, cardiovascular mortality and morbidity. Other potential toxic constituents including nitrate, sulfate, Zinc, silicon, iron, nickel, vanadium, and potassium were associated with adverse cardiovascular health, while nitrate, sulfate and vanadium were relevant for adverse respiratory health outcomes. CONCLUSIONS: Our analysis suggests that black carbon and organic carbon are important detrimental

components of PM2.5, while other constituents are probably hazardous to human health. However, more studies are needed to further confirm our results.

## 2. HEALTH EFFECTS

**Bai, Y., Wang, G., Fu, W., et al. (2019) Circulating essential metals and lung cancer: Risk assessment and potential molecular effects. *Environment International*, 127: 685-693.**

Available at: <https://www.sciencedirect.com/science/article/pii/S0160412019302272>

Keywords: Cohort study; Essential metals; Gene expression; Lung cancer; Telomere attrition; Zinc; Biological organs; Gene expression regulation; Histology; Metals; Risk assessment; Tumors; Carcinogenic process; Cohort studies; Plasma concentration; Potential mechanism; Telomeres; Transcriptional regulation; Diseases; cobalt; copper; heavy metal; iron; manganese; molybdenum; rubidium; selenium; strontium; tin; vanadium; cancer; chromosome; cohort analysis; metal; aged; APE gene; Article; blood level; cancer incidence; cancer prevention; cancer risk; case control study; controlled study; female; gene expression profiling; gene overexpression; human; human tissue; HUWE1 gene; LPTM4B gene; major clinical study; male; occupational health; priority journal; risk factor; SOD1 gene; telomere length; TP53BP1 gene; transcription regulation; TRIT1 gene; tumor gene; WDR33 gene; ZNF813 gene

### **Abstract:**

Objective: Essential metals play important roles in the carcinogenic process. However, seldom longitudinal investigations have evaluated their roles in lung cancer development. We aimed to investigate the associations between multiple essential metals and lung cancer incidence and to explore the potential mechanisms. Methods: A nested case-control study of 440 incident lung cancer cases and 1:3 frequency matched 1320 healthy controls from the Dongfeng-Tongji Cohort was conducted. The baseline plasma concentrations of 11 essential metals (cobalt, copper, iron, manganese, molybdenum, rubidium, selenium, strontium, stannum, vanadium, and zinc) were measured, and their associations with lung cancer incidence were estimated. Effect of positive metal (zinc) on 4-year telomere attrition was then evaluated among an occupational cohort of 724 workers. We also assessed the transcriptional regulation effects of plasma zinc on mRNA expression profiles, and the expressions of zinc-related genes were further compared in pair-wised lung tumor and normal tissues. Results: Elevated plasma level of zinc was associated with lower incident risk of lung cancer [OR (95% CI) = 0.89 (0.79, 0.99)] and decreased 4-year telomere attrition [ $\beta$  (95% CI) = -0.73 (-1.27, -0.19)]. These effects were pronounced among males. In particular, zinc could regulate the expressions of 8 cancer-related genes, including SOD1, APE, TP53BP1, WDR33, LPTM4B, TRIT1, HUWE1, and ZNF813, which were over-expressed in lung tumor tissues. Conclusions: We propose that high plasma zinc could prevent incident lung cancer, probably by slowing down telomere attrition and regulating the expressions of cancer-related genes. These results provided a new insight into lung cancer prevention. © 2019.

**Camargo, J., Pumarega, J.A., Alguacil, J., et al. (2019) Toenail concentrations of trace elements and occupational history in pancreatic cancer. *Environment International*, 127: 216-225.**

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018327077/pdf?md5=0ab4d2d389662c56fa2f4f70b0ba8563&pid=1-s2.0-S0160412018327077-main.pdf>

Keywords: Arsenic; Cadmium; Manganese; Occupation; Pancreatic cancer; Trace elements; Diseases; Employment; Formaldehyde; Mass spectrometry; Mineral oils; Pesticides; Polycyclic aromatic hydrocarbons; Risk assessment; Solvents; Sulfur compounds; Vanadium; Chlorinated hydrocarbon solvents; Confidence interval; International standards; Occupational exposure;

Pancreatic cancers; Polycyclic aromatic hydrocarbons (PAHS); Volatile sulphur compounds; Occupational risks; aromatic hydrocarbon; iron; lead; pesticide; polycyclic aromatic hydrocarbon; trace element; bioaccumulation; cancer; concentration (composition); health risk; lifestyle; PAH; adult; aged; Article; cancer patient; cancer risk; concentration (parameter); controlled study; female; human; inductively coupled plasma mass spectrometry; industrial hygienist; major clinical study; male; medical history; middle aged; named groups by occupation; occupational disease; pancreas cancer; priority journal; toe nail; Finland

**Abstract:**

Background: Some occupations potentially entailing exposure to cadmium, arsenic, lead, selenium, nickel, and chromium have been associated with an increased risk of exocrine pancreatic cancer (EPC), but no studies have assessed whether body concentrations of such compounds differed among subjects occupationally exposed and unexposed. No studies which found that exposure to such metals increased the risk of EPC assessed whether past occupations were the source of exposure. Objective: The aim was to analyse the relationship between toenail concentrations of trace elements and occupational history in EPC patients. Methods: The study included 114 EPC cases personally interviewed on occupational history and lifestyle factors. Occupations were coded according to the International Standard Classification of Occupations 1988. Selected occupational exposures were assessed by two industrial hygienists and with the Finnish job-exposure matrix (Finjem). Concentrations of 12 trace elements were determined in toenail samples by inductively coupled plasma mass spectrometry. Adjusted geometric means (aGMs) and 95% confidence intervals (95% CI) were calculated. Results: Patients occupationally exposed to aromatic hydrocarbon solvents (AHs) had higher concentrations of cadmium, manganese, lead, iron and vanadium. The aGM of cadmium concentrations for cases exposed to any pesticide was 0.056 µg/g [95% CI: 0.029–0.108], and, for unexposed cases, 0.023 µg/g [0.017–0.031]. Patients occupationally exposed to pesticides had higher concentrations of cadmium and manganese. Higher concentrations of vanadium, lead and arsenic were related to exposure to formaldehyde. Vanadium and lead were also associated with exposure to chlorinated hydrocarbon solvents, and arsenic was related to exposure to polycyclic aromatic hydrocarbons (PAHs). Conclusions: Patients occupationally exposed to AHs, pesticides, chlorinated hydrocarbon solvents, formaldehyde, volatile sulphur compounds and PAHs had higher concentrations of several metals. These elements may account for some of the occupational risks previously reported for pancreatic cancer. © 2019 The Authors.

**Chen, G., Wang, X., Wang, R., et al. (2019) Health risk assessment of potentially harmful elements in subsidence water bodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. *Ecotoxicology and Environmental Safety*, 171: 737-745.**

Keywords: Coal mining area; Health risk assessment; Monte Carlo simulation; Potentially harmful elements; Subsidence water bodies; arsenic; cadmium; chromium; cobalt; copper; environmental, industrial and domestic chemicals; iron; lead; manganese; nickel; potentially harmful element; surface water; unclassified drug; vanadium; zinc; heavy metal; atomic absorption spectroscopy; carcinogen; coal mining; concentration (composition); health risk; Monte Carlo analysis; risk assessment; Article; atomic absorption spectrometry; atomic fluorescence spectrometry; cancer risk; China; concentration (parameter); contact dermatitis; controlled study; environmental exposure; health hazard; ingestion; Monte Carlo method; water analysis; water pollution; water quality; analysis; environmental monitoring; human; water pollutant; Anhui; Huainan; Humans; Metals, Heavy; Spectrophotometry, Atomic; Water Pollutants, Chemical

**Abstract:**

Enrichment of potentially harmful elements in surface water results in ecological risk to the surrounding environment. Assessing the environmental risk of these elements is of great importance. In this study, surface water samples from 6 different subsidence water bodies in the Huainan coal mining area were collected. The concentrations of Cu, Ni, Pb, Cd, Co, Cr, V, Fe, Mn and Zn were measured by atomic absorption spectrophotometry, and those of As and Hg were analyzed by atomic fluorescence spectrometry. Then, human health risks through the ingestion and dermal contact pathways were assessed and analyzed on the basis of a Monte Carlo simulation. The mean and 95th percentile risks were reported. The results showed that the total carcinogenic risk values in every subsidence water body summed for Cr, Ni and As via two exposure pathways were greater than the maximum acceptable level ( $1 \times 10^{-4}$ ), and Xinji'er water body had the highest carcinogenic risk. Among three elements, Ni was the highest contributor to carcinogenic risk. All non-carcinogenic health risk (hazard quotients) values except for one water area of Co (Xinji'er) were less than 1; however, the total non-carcinogenic health risks of two water bodies (Xinji'er, Xinjiyi) summed for all the elements based on mean concentrations were higher than 1. Xinji'er had the highest hazard index. The extent of the impacts of the total hazard quotients followed the order of  $Co > As > Cd > Hg > Pb > V > Fe > Ni > Mn > Zn > Cr$ . Furthermore, the total hazard quotients of Co and As via ingestion pathway summed for the six subsidence water areas were greater than 1, which should be a concern. © 2019 Elsevier Inc.

**Gaus, C., Villa, C.A., Dogruer, G., et al. (2019) Evaluating internal exposure of sea turtles as model species for identifying regional chemical threats in nearshore habitats of the Great Barrier Reef. *Science of the Total Environment*, 658: 732-743.**

Keywords: Bioanalytical screening; Blood; Contaminants; Multi-element screening; Non-target screening; Alkalinity; Animals; Biomarkers; Chemical analysis; Chemical hazards; Cobalt; Health; Health hazards; Impurities; Indicators (chemical); Offshore oil well production; Phosphatases; Population statistics; ALkaline phosphatase; Bioanalytical; Development and applications; Elevated concentrations; Epidemiological studies; Multi-element; Non-target screenings; Trace-element exposures; Trace elements; aluminum; antimony; arsenic; barium; bilirubin; cadmium; calcium; chromium; copper; indolepropionic acid; iron; lead; magnesium; manganese; molybdenum; nickel; potassium; selenium; silver; sodium; thallium; thorium; tin; titanium; uranium; vanadium; zinc; biomarker; chemical pollutant; epidemiology; foraging behavior; habitat structure; nearshore environment; pollution exposure; population dynamics; trace element; turtle; adult; Article; concentration (parameters); controlled study; coral reef; foraging; limit of detection; limit of quantitation; lipid peroxidation; measurement accuracy; nonhuman; oxidative stress; priority journal; sea turtle; species habitat; steady state; wildlife; analysis; animal; environmental exposure; environmental monitoring; metabolism; procedures; Queensland; water pollutant; Australia; Coral Sea; Great Barrier Reef; Chelonia (genus); Cheloniidae; Reptilia; Testudines; Vertebrata; Coral Reefs; Turtles; Water Pollutants, Chemical

**Abstract:**

Marine megafauna that forage in proximity to land can be exposed to a diverse mixture of chemicals that - individually or combined - have the potential to affect their health. Characterizing such complex exposure and examining associations with health still poses considerable challenges. The present study summarizes the development and application of novel approaches to identifying chemical hazards and their potential impacts on the health of coastal wildlife, using green sea turtles as model species. We used an epidemiological study approach to collect blood and keratinized scute samples from free-ranging turtles foraging in nearshore areas and an offshore control site. These were analyzed using a combination of non-targeted, effect-based and multi-chemical analytical screening approaches to assess

internal exposure to a wide range of chemicals. The screening phase identified a suite of elements (essential and non-essential) as priority for further investigation. Many of these elements are not commonly analyzed in marine wildlife, illustrating that comprehensive screening is important where exposure is unknown or uncertain. In particular, cobalt was present at highly elevated concentrations, in the order of those known to elicit acute effects across other vertebrate species. Several trace elements, including cobalt, were correlated with clinical indicators of impaired turtle health. In addition, biomarkers of oxidative stress (e.g. 3-indolepropionic acid and lipid peroxidation products) identified in the blood of turtles showed significant correlations with clinical health markers (particularly alkaline phosphatase and total bilirubin), as well as with cobalt. To assist interpretation of trace element blood data in the absence of sufficient information on reptile toxicity, we established exposure reference intervals using a healthy control population. In addition, trace element exposure history was investigated by establishing temporal exposure indices using steady-state relationships between blood and scute. Overall, the data provide a strong argument for the notion that trace element exposure is having an impact on the health of coastal sea turtle populations. © 2018.

**Li, A., Zhuang, T., Shi, J., et al. (2019) Heavy metals in maternal and cord blood in Beijing and their efficiency of placental transfer. *Journal of Environmental Sciences (China)*, 80: 99-106.**

Available at:

[http://www.jesc.ac.cn/jesc\\_En/ch/reader/create\\_pdf.aspx?file\\_no=S1001074218328687](http://www.jesc.ac.cn/jesc_En/ch/reader/create_pdf.aspx?file_no=S1001074218328687)

Keywords: Cord blood; Heavy metal; Maternal blood; Newborn; Placental transfer efficiency; Blood; Disease control; Efficiency; Mass spectrometry; Vanadium compounds; Center for disease controls; High detection rate; Maternal bloods; Placental transfer; Prenatal exposure; Threshold limits; Heavy metals; bioaccumulation; child health; health risk; maternal health; pollutant source; pollution exposure; pregnancy; Beijing [Beijing (ADS)]; Beijing [China]; China; adult; child; environmental monitoring; female; fetus blood; human; maternal exposure; metabolism; placenta; pollutant; Beijing; Environmental Pollutants; Fetal Blood; Humans; Infant, Newborn; Metals, Heavy

**Abstract:**

This study aimed to determine the effect of exposure to heavy metals in pregnant women in Beijing, China. We also evaluated the association of these heavy metals with birth weight and length of newborns. We measured the levels of 10 heavy metals, including lead (Pb), titanium (Ti), manganese (Mn), nickel (Ni), cadmium (Cd), chromium (Cr), antimony (Sb), stannum (Sn), vanadium (V), and arsenic (As), in 156 maternal and cord blood pairs. An inductively coupled plasma mass spectrometry method was used for measurement. Pb, As, Ti, Mn, and Sb showed high detection rates (> 50%) in both maternal and cord blood. Fourteen (9%) mothers had blood Pb levels greater than the United States Center for Disease Control allowable threshold limit for children (50 µg/L). In prenatal exposure to these heavy metals, there was no significant association between any heavy metal and birth weight/length. Moreover, we estimated the placental transfer efficiency of each heavy metal, and the median placental transfer efficiency ranged from 49.6% (Ni) to 194% (Mn) (except for Cd and Sn). The level and detection rate of Cd in maternal blood were much higher than that in cord blood, which suggested that Cd had difficulty in passing the placental barrier. Prospective research should focus on the source and risk of heavy metals in non-occupationally exposed pregnant women in Beijing. © 2018.

**Mustapha, O.A., Olude, M.A., Bello, S.T., et al. (2019) Peripheral axonopathy in sciatic nerve of adult Wistar rats following exposure to vanadium. *Journal of the Peripheral Nervous System*, 24(1): 94-99.**

Keywords: axon; degeneration; myelin; peripheral nervous system; sciatic nerve; vanadium

**Abstract:**

Depletion of myelin and neurobehavioural deficits are indications that vanadium crosses the blood-brain barrier and such neurotoxic effects of vanadium on the brain of Wistar rats have been elucidated. The effect however on the peripheral nerves, is yet to be reported. Thus, this work was designed to evaluate the axonal and myelin integrity of sciatic nerves in Wistar rats following exposure to vanadium. Ten male Wistar rats were exposed to 3 mg/kg body weight of sodium metavanadate for 7 days, subjected to rearing and forelimb grip behavioural tests, and sciatic nerves processed for histology (haematoxylin and eosin, cresyl violet, and luxol fast blue). Dystrophic axons with vesiculated myelin, thinned myelin sheath, and demyelinated axons were observed in the vanadium exposed rats, suggestive of axonopathy, classified as fourth-degree nerve injury. Lower behavioural scores were recorded for vanadium-dosed rats; thus, corroborating histological pictures observed of the sciatic nerves. Authors posit that vanadium crossed the "blood-nerve" barrier and caused the observed axonal pathologies and myelin depletion in the sciatic nerves of these rodents with resultant motor deficits. The present paper discusses possible motor deficits and the likely public health importance in regions with crude oil pollution and gas flaring rich in vanadium products.

**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: 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. © 2018 The Author(s).

**Rinklebe, J., Antoniadis, V., Shaheen, S.M., et al. (2019) Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International*, 126: 76-88.**

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018324954/pdf?md5=5cfea4ef254356ae57dbf4b647181f6b&pid=1-s2.0-S0160412018324954-main.pdf>

Keywords: Heavy metals; Risk assessment; Riverine ecosystems; Trace elements; Wetland soil; Arsenic; Chromium; Contamination; Copper compounds; Health; Health risks; Hydrogeology; River pollution; Soil conservation; Soil surveys; Soils; Tin; X ray spectrometers; Contaminated

areas; Contaminated sites; Contamination factors; Pollution load indices; Potentially toxic elements; Wetland soils; X-ray fluorescence spectrometer; barium; copper; lead; nickel; rubidium; strontium; vanadium; zinc; zirconium; freshwater ecosystem; health risk; heavy metal; soil pollution; soil profile; trace element; wetland; adult; Article; chemical composition; child; Contaminated Sites Ordinance; Contamination factor; controlled study; environmental parameters; environmental policy; female; German Federal Soil Protection; Germany; health hazard; high risk population; human; male; mathematical analysis; median children hazard index; Pollution Load Index; Precautionary Value; priority journal; river; sandy soil; sex difference; soil analysis; soil property; topsoil; toxicity testing; X ray fluorescence spectrometry; Elbe River

**Abstract:**

Floodplain soils across Central Elbe River (CER), Germany, vary considerably in potentially toxic element (PTE) content. However, there has never been a comprehensive study that links PTE levels with human health risk for children and adults. Our objective was to determine the contamination of 13 PTEs in 94 soil profiles along CER and assess the associated health risk via diverse indices for adults and children. Of 94 soil profiles, we measured soil properties and total content of arsenic, barium, chromium, copper, nickel, lead, rubidium, tin, strontium, vanadium, zinc, and zirconium using x-ray fluorescence spectrometer (XRF). We calculated the Contamination Factor and the Pollution Load Index (PLI), and assessed the health risk for male and female adults as well as for children. Topsoil median contents of Cr (84 mg kg<sup>-1</sup>), Cu (42), Ni (33), and Zn (195) exceeded the Precautionary Values for sandy soils according to the German Federal Soil Protection and Contaminated Sites Ordinance, while As, Pb, and V were 32, 73, and 77 mg kg<sup>-1</sup>, respectively. Median topsoil PLI was 1.73, indicating elevated multi-element contamination, with 90th percentile and maximum values being 3.20 and 4.31, respectively. All PTE concentrations were higher in top- compared to subsoils. Also at the 50th percentile the most enriched elements were Sn and As, followed by Zr and Rb, while in the 90th percentile Sn and As were followed by Zn, Pb and Cu. Median children's hazard index (HI) was higher than unity (HI = 2.27) and the 90th percentile was 5.53, indicating elevated health risk. Adult median HIs were 0.18 for male and 0.21 for female persons. Arsenic was found to be the primary contributor to total risk, accounting of 57.4% of HI in all three-person groupings, with Cr (17.3%) being the second, and V (10.2%) the third. Children's health is at dramatically higher risk than that of adults; also As, Cr, Pb, and V have a predominant role in contamination-related health risks. The presence of V, a less-expected element, among those of major risk contribution, reveals the necessity of monitoring areas at large scale. Our results demonstrate that our study may serve as a model for similar works studying multi-element-contaminated areas in future. © 2019 The Authors.

**Roberts, G., Elsass, K., Fallacara, D., et al. (2019) 3-Month Toxicity Studies of Tetravalent and Pentavalent Vanadium Compounds in Hsd:Sprague-Dawley SD Rats and B6C3F1/N Rice via Drinking Water Exposure *The Toxicologist: Supplement to Toxicological Sciences*, 168(1): 237 (no. 2374).**

Poster Abstract presented at the Convention Center, Baltimore, Maryland, March 10–14, 2019. Available at: <https://www.toxicology.org/pubs/docs/Tox/2019Tox.pdf>

**Abstract:**

The National Toxicology Program performed 3-month toxicity studies of tetravalent (vanadyl sulfate; VS) and pentavalent (sodium metavanadate; SM) vanadium compounds in drinking water, due to potential human exposure and lack of robust toxicity data. Time-mated Hsd:Sprague Dawley SD rats were exposed via dosed drinking water during gestation (beginning GD6) and lactation. Pups were exposed in utero, during lactation, and continued

exposure for 3 months post-weaning. Adult B6C3F1/N mice were exposed for 3 months. Animals were exposed to VS at 0, 21, 41.9, 83.8, 167.5 or 335 mg/L, or to SM at 0, 31.3, 62.5, 125, 250 or 500 mg/L. There was higher morbidity in the 500 mg/L SM dams and pups throughout the postnatal period. There were lower percent live pups at birth (-25%), lower number of viable pups at PND4 (-45%; pre-standardization) and throughout lactation after litter standardization (-28%; PND4-28) compared to controls. There were no effects on littering or pup survival in VS exposed dams or pups. For both compounds, in rats and mice, water consumption (g/day) was lower in correlation with increasing exposure concentration. At study termination, there were lower body weights observed at the highest concentration for rats (-14 to -20%) and mice (-12 to -27%) exposed to SM and mice exposed to VS (-9 to -12%). In male and female mice exposed to SM, there were consistent increases in erythrocytes and reticulocytes and decreases in hematocrit and hemoglobin; changes in rats and in VS exposed animals were sporadic. In general, organ weight effects were attributed to body weight changes, except for treatment-related decreases in thymus weights for SM mice. Histopathological findings were limited for both sex/species, exposed to either compound. Based on plasma and urine total vanadium levels, and estimated vanadium consumption from water consumption data, the exposure to vanadium from SM appears to be higher than from VS. For both SM and VS, internal exposure increased proportionally with increasing estimated vanadium consumption. In general, effects were more frequently observed in SM exposed animals which may be attributable to higher systemic exposure to vanadium at similar compound concentrations.

**Vänskä, M., Diab, S.Y., Perko, K., et al. (2019) Toxic Environment of war: Maternal prenatal heavy metal load predicts infant emotional development. *Infant Behavior and Development*, 55: 1-9.**

Keywords: Child development; Emotional development; Heavy metals; PTSD; War trauma; chromium; heavy metal; mercury; strontium; uranium; vanadium; adult; Article; birth weight; childbirth; clinical feature; disease association; emotion; emotionality; female; first trimester pregnancy; gestational age; hair level; Harvard Trauma Questionnaire; human; inductively coupled plasma mass spectrometry; infant; Infant Behavior Questionnaire; male; mood disorder; Palestinian; posttraumatic stress disorder; prediction; pregnant woman; prenatal exposure; priority journal; questionnaire; risk factor; war exposure

**Abstract:**

Background: People in war zones are exposed to heavy metal contamination deriving from new-generation weapons, in addition to exposure to psychologically traumatizing war events. Pregnant women and their children-to-be are particularly vulnerable to both biological and psychological war effects. Objective: The aim of the current study was to analyse the impact of maternal prenatal heavy metal contamination on infant emotional development and to examine the potential moderating role of maternal symptoms of post-traumatic stress disorder (PTSD) in the association between heavy metal load and infant emotional development. Methods: The participants were 502 Palestinian mothers, pregnant in their first trimester during the 2014 War on Gaza. The mothers were recruited at their delivery (T1) and followed at the infants' age of 6–7 months (T2; N = 392). The load of five weapon-related heavy metals (chromium, mercury, vanadium, strontium, and uranium) was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) from mothers' hair samples at childbirth (T1). Assessment of maternal PTSD symptoms was based on the Harvard Trauma Questionnaire (HTQ) and infant emotional development on the Infant Behavior Questionnaire (IBQ), both reported by mothers (T2). Results: Two of the analysed metals, chromium and uranium, adversely predicted children's early emotional development, indicated by decreased positive affectivity, increased negative emotionality, and problems in early orientation and

regulation. Mother's PTSD did not moderate the impact of heavy metal contamination on children's emotional development. Conclusions: Adverse impact of war is not limited to those who experience it directly, but is passed on to future generations through multiple mechanisms. International organizations are obliged to protect parents and infants from the modern weaponry in wars. © 2019.

**Yang, Y., Ruan, Z., Wang, X., et al. (2019) Short-term and long-term exposures to fine particulate matter constituents and health: A systematic review and meta-analysis. *Environmental Pollution (Barking, Essex : 1987)*, 247: 874-882.**

Keywords: Air Pollutants/analysis/toxicity; Air Pollution/adverse effects/statistics & numerical data; Environmental Exposure/adverse effects/statistics & numerical data; Humans; Nitrates; Particulate Matter/toxicity; Seasons; Soot; Sulfates; Vanadium; Air pollution; Constituents of fine particulate matter; Morbidity; Mortality; PM(2.5)

#### **Abstract:**

**BACKGROUND:** Fine particulate matter (Particulate matter with diameter  $\leq 2.5\mu\text{m}$ ) is associated with multiple health outcomes, with varying effects across seasons and locations. It remains largely unknown that which components of PM<sub>2.5</sub> are most harmful to human health. **METHODS:** We systematically searched all the relevant studies published before August 1, 2018, on the associations of fine particulate matter constituents with mortality and morbidity, using Web of Science, MEDLINE, PubMed and EMBASE. Studies were included if they explored the associations between short term or long term exposure of fine particulate matter constituents and natural, cardiovascular or respiratory health endpoints. The criteria for the risk of bias was adapted from OHAT and New Castle Ottawa. We applied a random-effects model to derive the risk estimates for each constituent. We performed main analyses restricted to studies which adjusted the PM<sub>2.5</sub> mass in their models. **RESULTS:** Significant associations were observed between several PM<sub>2.5</sub> constituents and different health endpoints. Among them, black carbon and organic carbon were most robustly and consistently associated with all natural, cardiovascular mortality and morbidity. Other potential toxic constituents including nitrate, sulfate, Zinc, silicon, iron, nickel, vanadium, and potassium were associated with adverse cardiovascular health, while nitrate, sulfate and vanadium were relevant for adverse respiratory health outcomes. **CONCLUSIONS:** Our analysis suggests that black carbon and organic carbon are important detrimental components of PM<sub>2.5</sub>, while other constituents are probably hazardous to human health. However, more studies are needed to further confirm our results.

### **3. BIOLOGICAL MECHANISMS**

**Bai, Y., Wang, G., Fu, W., et al. (2019) Circulating essential metals and lung cancer: Risk assessment and potential molecular effects. *Environment International*, 127: 685-693.**

Available at: <https://www.sciencedirect.com/science/article/pii/S0160412019302272>

Keywords: Cohort study; Essential metals; Gene expression; Lung cancer; Telomere attrition; Zinc; Biological organs; Gene expression regulation; Histology; Metals; Risk assessment; Tumors; Carcinogenic process; Cohort studies; Plasma concentration; Potential mechanism; Telomeres; Transcriptional regulation; Diseases; cobalt; copper; heavy metal; iron; manganese; molybdenum; rubidium; selenium; strontium; tin; vanadium; cancer; chromosome; cohort analysis; metal; aged; APE gene; Article; blood level; cancer incidence; cancer prevention; cancer risk; case control study; controlled study; female; gene expression profiling; gene overexpression; human; human tissue; HUWE1 gene; LAPTM4B gene; major clinical study; male; occupational health; priority journal; risk factor; SOD1 gene; telomere length; TP53BP1 gene; transcription regulation; TRIT1 gene; tumor gene; WDR33 gene; ZNF813 gene

**Abstract:**

Objective: Essential metals play important roles in the carcinogenic process. However, seldom longitudinal investigations have evaluated their roles in lung cancer development. We aimed to investigate the associations between multiple essential metals and lung cancer incidence and to explore the potential mechanisms. Methods: A nested case-control study of 440 incident lung cancer cases and 1:3 frequency matched 1320 healthy controls from the Dongfeng-Tongji Cohort was conducted. The baseline plasma concentrations of 11 essential metals (cobalt, copper, iron, manganese, molybdenum, rubidium, selenium, strontium, stannum, vanadium, and zinc) were measured, and their associations with lung cancer incidence were estimated. Effect of positive metal (zinc) on 4-year telomere attrition was then evaluated among an occupational cohort of 724 workers. We also assessed the transcriptional regulation effects of plasma zinc on mRNA expression profiles, and the expressions of zinc-related genes were further compared in pair-wised lung tumor and normal tissues. Results: Elevated plasma level of zinc was associated with lower incident risk of lung cancer [OR (95% CI) = 0.89 (0.79, 0.99)] and decreased 4-year telomere attrition [ $\beta$  (95% CI) = -0.73 (-1.27, -0.19)]. These effects were pronounced among males. In particular, zinc could regulate the expressions of 8 cancer-related genes, including SOD1, APE, TP53BP1, WDR33, LAPT4B, TRIT1, HUWE1, and ZNF813, which were over-expressed in lung tumor tissues. Conclusions: We propose that high plasma zinc could prevent incident lung cancer, probably by slowing down telomere attrition and regulating the expressions of cancer-related genes. These results provided a new insight into lung cancer prevention. © 2019.

**Dankhoff, K., Ahmad, A., Weber, B., et al. (2019) Anticancer properties of a new non-oxido vanadium(IV) complex with a catechol-modified 3,3'-diindolylmethane ligand. *Journal of Inorganic Biochemistry*, 194: 1-6.**

Keywords: Anticancer drugs; Diindolylmethane; DNA binding; Reactive oxygen species; Vanadium; antineoplastic agent; bis (triethylammonium) tri[1,1 bis (indol 3 yl) 1 (3,4 catecholate) methane] vanadate 3; reactive oxygen metabolite; unclassified drug; antiproliferative activity; apoptosis; Article; cell cycle progression; cell damage; cell growth; cell viability; controlled study; flow cytometry; fluorescence; G2 phase cell cycle checkpoint; growth inhibition; human; human cell; IC50; mitochondrial membrane potential; MTT assay

**Abstract:**

In order to identify new active drug candidates against cancer diseases we investigated the tumor cell growth inhibition, formation of reactive oxygen species, mitochondrial membrane damage, cell cycle arrest and DNA binding activity of a new bis(triethylammonium) tris[1,1-bis(indol-3-yl)-1-(3,4-catecholate)methane]vanadate(IV) complex. It exhibited significant antiproliferative activity against various cancer cell lines, showed a stronger DNA binding than cisplatin and led to mitochondrial damage, a formation of reactive oxygen species, and a cell cycle arrest in the G2/M phase of cancer cells. © 2019 Elsevier Inc.

**Huang, Y., Liu, F., Zhang, F., et al. (2018) Vanadium(IV)-chlorodipicolinate alleviates hepatic lipid accumulation by inducing autophagy via the LKB1/AMPK signaling pathway in vitro and in vivo. *Journal of Inorganic Biochemistry*, 183: 66-76.**

Keywords: AMP-Activated Protein Kinases/metabolism; Animals; Autophagy/drug effects/genetics/physiology; Cells, Cultured; Diet, High-Fat/adverse effects; Hep G2 Cells; Hepatocytes/drug effects/metabolism; Humans; Hypolipidemic Agents/chemistry/pharmacology; Lipid Metabolism/drug effects/physiology; Liver/drug effects/metabolism; Mice; Mice, Inbred C57BL; Phosphorylation/drug effects; Protein-Serine-Threonine Kinases/metabolism; Rats; Signal Transduction/drug effects/genetics/physiology;

Vanadium/chemistry/pharmacology; AMPK; Autophagy; Hepatic lipid metabolism; LKB1; VOdipic-Cl

**Abstract:**

Numerous studies have demonstrated that vanadium compounds are able to improve lipemia and triglyceridemia in both humans and animals. However, the molecular mechanism remains elusive. The present study was conducted to investigate the anti-hyperlipidemic effect of vanadium(IV) complex with 4-chlorodipicolinic acid (VOdipic-Cl)-induced autophagy on hepatic lipid accumulation. To explore the possible underlying mechanisms, primary rat hepatocytes, human hepatoma cell line HepG2, and liver tissue from C57BL/6 mice fed a high-fat diet (HFD) were used. In vitro, cultured primary rat hepatocytes were treated with palmitate (0.25, 0.5 and 0.75mM) prior to VOdipic-Cl (50, 100, and 200µM) for 24h, respectively. In vivo, C57BL/6 mice were fed with high-fat diet for 16weeks. VOdipic-Cl (10mgV/kg body weight) was given by daily gavage for 4weeks. In vitro results showed that VOdipic-Cl significantly inhibited lipid droplet formation by increasing the level of conversion and punctuation of microtubule-associated proteins light chain 3 (LC3) in a dose-dependent manner, and activated liver kinase B-1 (LKB1) and adenosine monophosphate-activated protein kinase (AMPK) phosphorylation. Confocal microscopy images also showed that VOdipic-Cl induced sequestration of lipid droplets (LDs) by autophagy. In vivo, VOdipic-Cl attenuated the increase in serum and liver triglyceride levels in the mice fed with high-fat diet, while significantly increased autophagy induction and activated LKB1 and AMPK phosphorylation in the liver. Taken together, these results suggest that VOdipic-Cl reduces hepatic lipid accumulation by inducing autophagy via the activation of LKB1/AMPK-dependent signaling pathway.

**Mustapha, O.A., Olude, M.A., Bello, S.T., et al. (2019) Peripheral axonopathy in sciatic nerve of adult Wistar rats following exposure to vanadium. *Journal of the Peripheral Nervous System*, 24(1): 94-99.**

Keywords: axon; degeneration; myelin; peripheral nervous system; sciatic nerve; vanadium

**Abstract:**

Depletion of myelin and neurobehavioural deficits are indications that vanadium crosses the blood-brain barrier and such neurotoxic effects of vanadium on the brain of Wistar rats have been elucidated. The effect however on the peripheral nerves, is yet to be reported. Thus, this work was designed to evaluate the axonal and myelin integrity of sciatic nerves in Wistar rats following exposure to vanadium. Ten male Wistar rats were exposed to 3 mg/kg body weight of sodium metavanadate for 7 days, subjected to rearing and forelimb grip behavioural tests, and sciatic nerves processed for histology (haematoxylin and eosin, cresyl violet, and luxol fast blue). Dystrophic axons with vesiculated myelin, thinned myelin sheath, and demyelinated axons were observed in the vanadium exposed rats, suggestive of axonopathy, classified as fourth-degree nerve injury. Lower behavioural scores were recorded for vanadium-dosed rats; thus, corroborating histological pictures observed of the sciatic nerves. Authors posit that vanadium crossed the "blood-nerve" barrier and caused the observed axonal pathologies and myelin depletion in the sciatic nerves of these rodents with resultant motor deficits. The present paper discusses possible motor deficits and the likely public health importance in regions with crude oil pollution and gas flaring rich in vanadium products.

**Nisak, K. & Khotib, J. (2019) Effectiveness and Mechanism of Action of Vanadyl Sulfate in Increasing Pancreatic  $\beta$  Cell Proliferation of DM Mice Due to Streptozotocin Induction. *Indian Journal of Public Health Research & Development*, 10(4): 1195-1199.**

Keywords: Diabetes Mellitus; Langerhans Islet; Streptozotocin; Vanadyl Sulfate.

**Abstract:**

Diabetes mellitus (DM) is a metabolic disorder characterized by hyperglycemia as a result of damage to insulin secretion, insulin action, or both. Vanadyl sulfate is one of the form of vanadium which has begun to be used to treat diabetes in humans. In this study, investigation on the effectiveness of vanadyl sulfate in increasing pancreatic  $\beta$  cell proliferation of diabetes mice due to streptozotocin induction. There were 30 healthy mice were subjected to this experimental study. Findings from this experiment proved that administration of vanadyl sulfate at various doses can significantly increase the amount of pancreatic  $\beta$  cell proliferation and eventually reduced blood glucose levels in a meaningless manner. However, those mice that administrated of vanadyl sulfate at a dose of 30 mg/kgBW had a higher amount of Langerhans Islet than those in the vanadyl sulfate group at a dose of 5 mg/kgBW and 100 mg/kgBW. Similar observations were obtained for the Ki-67 expression. The highest Ki-67 expression was obtained at a dose of 30 mg/kgBW but it decreased with a dose of 100 mg/kgBW of vanadyl sulfate.

**Terada, Y., Higashi, N., Hidaka, Y., et al. (2019) Protein Tyrosine Phosphatase Inhibitor, Orthovanadate, Induces Contraction via Rho Kinase Activation in Mouse Thoracic Aortas. *Biological & Pharmaceutical Bulletin*, 42(6): 877-885.**

Available at: [https://www.jstage.jst.go.jp/article/bpb/42/6/42\\_b18-00708/pdf](https://www.jstage.jst.go.jp/article/bpb/42/6/42_b18-00708/pdf)

Keywords: myosin light chain phosphatase; orthovanadate; thoracic aorta; mouse; Epidermal-Growth-Factor; Vanadate-Induced Contraction; Smooth-Muscle; Factor Receptor; Ca<sup>2+</sup> Sensitivity; Phosphorylation; Cytoskeleton; Mechanism; Cofilin; Vasoconstriction; Pharmacology & Pharmacy

**Abstract:**

Orthovanadate (OVA), a protein tyrosine phosphatase inhibitor, induces contraction in endothelium denuded mouse thoracic aortas. OVA-induced contraction was significantly (vs. control rings) suppressed by Rho kinase (Y-27632, 10  $\mu$  M), extracellular signal-regulated kinase 1 and 2 (Erk1/2, FR180204, 10  $\mu$  M), Erk1/2 kinase (MEK, PD98059, 10  $\mu$  M), epidermal growth factor receptor (EGFR, AG1478, 10  $\mu$  M), and Src inhibitors, and was partially suppressed by c-Jun N-terminal kinase (JNK, AS601245, 10  $\mu$  M) and p38 (SB203580, 10  $\mu$  M) inhibitors. However, a myosin light chain kinase inhibitor (ML-7, 10  $\mu$  M) and a metalloproteinase inhibitor (TAPI-0, 10  $\mu$  M) had no effect on OVA-induced contraction in mouse thoracic aortas. Phosphorylation of myosin phosphatase target subunit 1 (MYPTI) was abolished by inhibitors of Src, EGFR, MEK, Erk1/2, and Rho kinase, but not by inhibitors of JNK and p38. Erk1/2 phosphorylation by OVA was blocked by inhibitors of EGFR, Src, MEK, and Erk1/2, but not by Rho kinase inhibition. Src phosphorylation at Tyr-416 was abrogated by only Src inhibitor. EGFR phosphorylation at Tyr-1173 was suppressed by a Src inhibitor. These findings suggest that OVA induces contraction via activation of Src, EGFR, MEK, Erk1/2, and Rho kinase, leading to inactivation of myosin light chain phosphatase via MYPTI phosphorylation.

**Tian, X., Jiang, S., Zhang, X., et al. (2019) Potassium bisperoxo (1,10-phenanthroline) oxovanadate suppresses proliferation of hippocampal neuronal cell lines by increasing DNA methyltransferases. *Neural Regeneration Research*, 14(5): 826-833.**

Keywords: nerve regeneration; hippocampal neurons; potassium bisperoxo (1,10-phenanthroline) oxovanadate; DNA methyltransferase; p21; HT22 cell; cell cycle; immunoblotting; DNA methylation; neural regeneration; Tyrosine-Phosphatase Inhibition; Methylation Patterns; Colorectal-Cancer; Up-Regulation; Cycle Arrest; Peroxovanadium;

Compounds; Expression; Vanadium; Induction; Complex; Cell Biology; Neurosciences & Neurology

**Abstract:**

Bisperoxo (1,10-phenanthroline) oxovanadate (BpV) can reportedly block the cell cycle. The present study examined whether BpV alters gene expression by affecting DNA methyltransferases (DNMTs), which would impact the cell cycle. Immortalized mouse hippocampal neuronal precursor cells (HT22) were treated with 0.3 or 3  $\mu$  M BpV. Proliferation, morphology, and viability of HT22 cells were detected with an IncuCyte real-time video imaging system or inverted microscope and 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, respectively. mRNA and protein expression of DNMTs and p21 in HT22 cells was detected by real-time polymerase chain reaction and immunoblotting, respectively. In addition, DNMT activity was measured with an enzyme-linked immunosorbent assay. Effects of BpV on the cell cycle were analyzed using flow cytometry. Results demonstrated that treatment with 0.3  $\mu$  M BpV did not affect cell proliferation, morphology, or viability; however, treatment with 3  $\mu$  M BpV decreased cell viability, increased expression of both DNMT3B mRNA and protein, and inhibited the proliferation of HT22 cells; and 3  $\mu$  M BpV also blocked the cell cycle and increased expression of the regulatory factor p21 by increasing DNMT expression in mouse hippocampal neurons.

**Treviño, S., Díaz, A., Sánchez-Lara, E., et al. (2019) Vanadium in Biological Action: Chemical, Pharmacological Aspects, and Metabolic Implications in Diabetes Mellitus. *Biological Trace Element Research*, 188(1): 68-98.**

Keywords: Biological action; Diabetes mellitus; Metabolic aspects; Metabolic implications; Metallopharmaceuticals; Vanadium; albumin; ammonium vanadate; bis(2 ethyl 3 hydroxy 4 pyronato)oxovanadium; decavanadate; hemoglobin; phosphate; phosphotransferase; unclassified drug; vanadate sodium; vanadium derivative; abdominal discomfort; antidiabetic activity; Article; atmospheric transport; biochemistry; cell interaction; diarrhea; drug absorption; drug activity; drug design; drug metabolism; drug transport; drug uptake; environmental release; glucose homeostasis; human; in vivo study; inflammation; insulin dependent diabetes mellitus; insulin signaling; lipid homeostasis; lowest-observed-adverse-effect level; nausea and vomiting; no-observed-adverse-effect level; non insulin dependent diabetes mellitus; nonhuman; oxidation reduction reaction; protein interaction; signal transduction; tissue distribution; toxic inhalation; toxicology

**Abstract:**

Vanadium compounds have been primarily investigated as potential therapeutic agents for the treatment of various major health issues, including cancer, atherosclerosis, and diabetes. The translation of vanadium-based compounds into clinical trials and ultimately into disease treatments remains hampered by the absence of a basic pharmacological and metabolic comprehension of such compounds. In this review, we examine the development of vanadium-containing compounds in biological systems regarding the role of the physiological environment, dosage, intracellular interactions, metabolic transformations, modulation of signaling pathways, toxicology, and transport and tissue distribution as well as therapeutic implications. From our point of view, the toxicological and pharmacological aspects in animal models and humans are not understood completely, and thus, we introduced them in a physiological environment and dosage context. Different transport proteins in blood plasma and mechanistic transport determinants are discussed. Furthermore, an overview of different vanadium species and the role of physiological factors (i.e., pH, redox conditions, concentration, and so on) are considered. Mechanistic specifications about different signaling

pathways are discussed, particularly the phosphatases and kinases that are modulated dynamically by vanadium compounds because until now, the focus only has been on protein tyrosine phosphatase 1B as a vanadium target. Particular emphasis is laid on the therapeutic ability of vanadium-based compounds and their role for the treatment of diabetes mellitus, specifically on that of vanadate- and polioxovanadate-containing compounds. We aim at shedding light on the prevailing gaps between primary scientific data and information from animal models and human studies. © 2018, The Author(s).

**Vuong, M.C., Hasegawa, L.S. & Eastmond, D.A. (2019) An Evaluation of the Cytotoxicity and Chromosome-Altering Effects of Vanadium Pentoxide and Sodium Metavanadate In Vitro *The Toxicologist: Supplement to Toxicological Sciences*, 68(1): 14 (no. 1064).**

Abstract presented at 58th Annual Meeting of the Society of Toxicology, held at the Baltimore Convention Center, Baltimore, Maryland, March 10–14, 2019. Available at: <https://www.toxicology.org/pubs/docs/Tox/2019Tox.pdf>

**Abstract:**

Vanadium compounds are found in mineral ores and have become increasingly important in industrial manufacturing. Vanadium exists in several oxidation states with vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) and sodium metavanadate (NaVO<sub>3</sub>) being among the more common. Previous studies by the National Toxicology Program have shown that vanadium pentoxide is carcinogenic in rodents inducing alveolar/bronchiolar neoplasms. However, the mechanisms by which vanadium pentoxide causes its genotoxic and carcinogenic effects are unknown. The objective of this study was to more fully characterize the cytotoxic and genotoxic effects of vanadium pentoxide and compare them with those of sodium metavanadate in human TK6 lymphoblastoid cells using microscopic and flow cytometric approaches. Significant dose-related increases in hypodiploidy, hyperdiploidy and polyploidy were seen for both compounds with vanadium pentoxide being more potent than sodium metavanadate. Similarly, dose-related increases in micronuclei were seen with vanadium pentoxide, which were shown by CREST staining to have originated primarily from chromosome loss. Both vanadium pentoxide and sodium metavanadate were cytotoxic affecting cell division and proliferation, again with vanadium pentoxide being more cytotoxic than sodium metavanadate. For sodium metavanadate, the aneugenic effects were seen primarily at concentrations at which extensive cytotoxicity occurred. With vanadium pentoxide, significant increases in aneuploidy were seen across a broader range of concentrations including lower ones exhibiting less cytotoxicity. Our microscopy and flow cytometry results indicate that numerical chromosome alterations are the primary type of chromosomal change induced by vanadium pentoxide and sodium metavanadate in vitro in human cells.

**Yu, Q., Jiang, W., Li, D., et al. (2019) Sodium orthovanadate inhibits growth and triggers apoptosis of human anaplastic thyroid carcinoma cells in vitro and in vivo. *Oncology Letters*, 17(5): 4255-4262.**

**Abstract:**

Vanadium and its compounds exhibit concentration- and time-dependent anticancer effects on various types of tumor; however, the effects of sodium orthovanadate (SOV) on anaplastic thyroid carcinoma (ATC) have not yet been reported. In the present study, the anticancer effects of SOV on ATC were evaluated. In vitro experiments, including cell viability assays, plate colony formation assays, cell cycle analysis and apoptosis analysis were used to study the role of SOV in ATC. Using in vivo experiments, the effects of SOV on the growth and apoptosis of an ATC-xenograft tumor were studied by comparing the SOV-treatment with the control group. The results revealed that treatment of the human ATC cell line 8505C with SOV

inhibited cell viability, induced G2/M phase cell cycle arrest, stimulated apoptosis and reduced mitochondrial membrane potential in a concentration-dependent manner. These findings were confirmed in vivo in a nude mouse ATC xenograft model. In conclusion, the present study demonstrated that SOV inhibited human ATC by regulating proliferation, cell cycle progression and apoptosis, thus suggesting that SOV may be considered a novel option for the treatment of ATC.

**Zendeboodi, S., Esmaili, A., Movahed, A., et al. (2019) The attenuative effects of oral resveratrol on renal changes induced by vanadium injection in rats. *Journal of Renal Injury Prevention*, 8(2): 127-132.**

Available at: <http://www.journalrip.com/Files/Inpress/jrip-567.pdf>

Keywords: Ammonium metavanadate; Resveratrol; Tubular necrosis; Transforming growth factor beta 1; Superoxide dismutase; CHRONIC KIDNEY-DISEASE; TOXICITY; FIBROSIS; VANADATE; Urology & Nephrology

**Abstract:**

Introduction: Resveratrol (trans-3,5,4'-trihydroxystilbene) as a polyphenol with potential antioxidant and anti-inflammatory properties is known as an effective herbal medicine in different disorders in rats. Objectives: The present study was carried out to investigate the protective effects of oral consumption of resveratrol on vanadium induced renal injury in male Wistar rats. Materials and Methods: Animals received either ammonium metavanadate (AMV, 5 mg/kg/d, intraperitoneally; 14 consecutive days) or resveratrol solution (10 mg/kg and 50 mg/kg, gastric gavage) along with AMV treatment. The last group received resveratrol alone (50 mg/kg, gastric gavage) for 4 weeks. Results: AMV injection caused progressive tubular damages resembling acute tubular necrosis. Microscopic views revealed tubular attenuation and blebbing. In addition, progressive peritubular congestion of the capillaries observed while no evidence of renal fibrosis was present in trichrome staining. Further, levels of the renal transforming growth factor beta 1 (TGF-beta 1) as an index of fibrosis had no difference in treated animals as compared with the control (13.4 +/- 1.2 versus 11.24 +/- 0.93 pg/mg protein) at the P < 0.05. However, in AMV-treated animals receiving the higher dose of resveratrol (50 mg/kg), the renal superoxide dismutase (SOD) activity, showed no difference as compared with the saline-treated rats (42 +/- 1.3 versus 51 +/- 1.4). Conclusions It is evident that AMV injection had no ability to induce renal fibrosis in rats while it evokes renal destructive lesions based on pathological results and enzyme levels. Moreover, our preliminary results suggest that resveratrol in high dose (50 mg/kg) could confer a minor role against AMV induced renal tubular necrosis in rats due to pathological results.

## 4. USES OF VANADIUM

**Crans DC, Henry L, Cardiff G and Posner BI (2019) Developing Vanadium as an Antidiabetic or Anticancer Drug: A Clinical and Historical Perspective. In: Carver PL (ed) *Essential Metals in Medicine: Therapeutic use and Toxicity of Metal Ions in the Clinic*: Walter de Gruyter GmbH & Co KG, 203-230.**

**Abstract:**

Vanadium has been known for centuries to have beneficial effects on health and has the potential to be used as an alternative to other diabetic and anticancer medicines. The beneficial effects of vanadium salts or organic compounds have been explored in vitro, ex vivo, and in vivo in animal and human studies. A consensus among researchers is that increased bioavailability of these compounds could markedly increase the efficacy of this class of compounds. In addition, because many commercially available vanadium derivatives are being used by body builders to enhance performance, more understanding of their mode of

action is desirable. Future studies of various vanadium compounds need to evaluate their biodistribution, biotransformation, and the effects of food and formulation on the bioavailability of the compounds. To date, most studies in humans have employed vanadium salts, mainly vanadyl sulfate, and dose-limiting side effects were reported at therapeutic doses. One organic vanadium compound, bis(ethylmaltolato)oxovanadium(IV), had improved efficacy compared to the vanadyl sulfate and was selected for Phase 1 and 2 clinical trials. Future studies should be conducted as randomized, placebo controlled trials lasting several months, with monitoring of both fasting blood glucose and hemoglobin A1c. Now, the most promising potential uses of vanadium compounds are as nutritional supplements to control glucose levels and perhaps, as an anticancer agent potentiated by immunotherapy.

**Crans DC, Barkley NE, Montezinho L and Castro MM (2019) CHAPTER 7 Vanadium Compounds as Enzyme Inhibitors with a Focus on Anticancer Effects. In: Anonymous *Metal-Based Anticancer Agents: The Royal Society of Chemistry*, 169-195.**

**Abstract:**

Vanadium salts and coordination compounds have desirable cellular anticancer effects, and although they have been investigated in detail as a potential treatment for diabetes, less attention has been given to the anticancer effects. The inhibition of some signal transduction enzymes is known, and studies of the metabolism and activation pathways both in vitro and in vivo are important for future investigations and development of vanadium's role as a new potential drug. In addition, a new approach has demonstrated that the enhancement of oncolytic viruses using vanadium salts and coordination complexes for immunotherapy is very promising. Some differences exist between this approach and current antidiabetic and anticancer studies because vanadium(IV) complexes have been found to be most potent in the latter approach, but the few compounds investigated with oncolytic viruses show that vanadium(V) systems are more effective. We conclude that recent studies demonstrate effects on signal transduction enzymes and anticancer pathways, thus suggesting potential applications of vanadium as anticancer agents in the future both as standalone treatments as well as combination therapies.

**Dankhoff, K., Ahmad, A., Weber, B., et al. (2019) Anticancer properties of a new non-oxido vanadium(IV) complex with a catechol-modified 3,3'-diindolylmethane ligand. *Journal of Inorganic Biochemistry*, 194: 1-6.**

Keywords: Anticancer drugs; Diindolylmethane; DNA binding; Reactive oxygen species; Vanadium; antineoplastic agent; bis (triethylammonium) tri[1,1 bis (indol 3 yl) 1 (3,4 catecholate) methane] vanadate 3; reactive oxygen metabolite; unclassified drug; antiproliferative activity; apoptosis; Article; cell cycle progression; cell damage; cell growth; cell viability; controlled study; flow cytometry; fluorescence; G2 phase cell cycle checkpoint; growth inhibition; human; human cell; IC50; mitochondrial membrane potential; MTT assay

**Abstract:**

In order to identify new active drug candidates against cancer diseases we investigated the tumor cell growth inhibition, formation of reactive oxygen species, mitochondrial membrane damage, cell cycle arrest and DNA binding activity of a new bis(triethylammonium) tris[1,1-bis(indol-3-yl)-1-(3,4-catecholate)methane]vanadate(IV) complex. It exhibited significant antiproliferative activity against various cancer cell lines, showed a stronger DNA binding than cisplatin and led to mitochondrial damage, a formation of reactive oxygen species, and a cell cycle arrest in the G2/M phase of cancer cells. © 2019 Elsevier Inc.

**Kondaparthi, V., Shaik, A., Reddy, K.B., et al. (2019) Studies on interaction of vanadium metal complexes with bovine serum albumin - Fluoremetric and UV-visible spectrophotometric studies. *Chemical Data Collections*, 20: 100203.**

Keywords: Drug – protein interactions; BSA; Fluoremetry; UV-visible spectroscopy; Quenching

**Abstract:**

Vanadium metal complexes are known to have anti diabetic activity in type-II diabetic mellitus patients. Few vanadium metal complexes are under clinical trials. We have prepared few vanadium metal complexes using substituted acetylacetone viz, 4,4,4-trifloro-(2-naphthyl)-1,3-butadione, 1,3-di(2-pyridyl)-1,3-propanedione, hexafluoro acetylacetone, 3-chloro-2,4-pentadione and 2,4-pentadione. These complexes have been characterized using different spectras. In this paper we are reporting the interaction of vanadium metal complexes with Bovine Serum Albumin (BSA), since BSA is known as a carrier of a drug in in vitro studies. The binding parameters of BSA- vanadium metal complexes are evaluated and compared with the parameters obtained from molecular modeling studies. "

**Lu, L.P., Suo, F.Z., Feng, Y.L., et al. (2019) Synthesis and biological evaluation of vanadium complexes as novel anti-tumor agents. *European Journal of Medicinal Chemistry*, 176: 1-10.**

Keywords: Antiproliferative effects; Apoptosis; Migration; Vanadium complex

**Abstract:**

A class of vanadium complexes were prepared and investigated for their antiproliferative effects by MTT assay. The structure-activity relationship was extensively studied through the ligand variation. The results showed that the synthetic vanadium complexes demonstrated moderate to good antiproliferative activities against the four cancer cell lines including MGC803, EC109, MCF7 and HepG2, respectively. Of note was that most of the complexes showed preferential growth inhibitory activity to some degree toward gastric cancer line MGC803. Among them, complex 19 exhibited the most and broad-spectrum proliferative inhibition against the tested cell lines. In addition, mechanism studies illustrated that complex 19 could prevent the colony formation, migration and EMT process, as well as induce apoptosis of MGC803 cells. Furthermore, Western blot experiments revealed that the expression of apoptosis-related proteins changed, including up-regulation of Bax, PARP and caspase-3/9, as well as down-regulation of Bcl-2.

**Melounková, L., Machálková, A., Havelek, R., et al. (2019) Vanadocene complexes bearing N,N'-chelating ligands: Synthesis, structures and in vitro cytotoxic studies on the A549 lung adenocarcinoma cell line. *Journal of Inorganic Biochemistry*, 195: 182-193.**

Keywords: A549 lung adenocarcinoma cells; Apoptosis; Cytotoxicity; Vanadium(IV); caspase 3; caspase 7; caspase 8; checkpoint kinase 1; checkpoint kinase 2; cytotoxic agent; lactate dehydrogenase; mitogen activated protein kinase 1; mitogen activated protein kinase 3; phosphatidylserine; protein bcl 2; protein p21; protein p53; vanadium derivative; A-549 cell line; A2780 cell line; antiproliferative activity; Article; cell cycle; cell cycle G2 phase; cell cycle regulation; cell cycle S phase; cell death; cell survival; cell viability; controlled study; crystal structure; cytotoxicity assay; DNA damage response; drug cytotoxicity; drug structure; drug synthesis; electron spin resonance; electrophoresis; elemental analysis; female; human; human cell; IC50; immunoblotting; in vitro study; infrared spectroscopy; mass spectrometry; MCF-7 cell line; PANC-1 cell line; signal transduction; staining; upregulation; Western blotting; WST-1 assay; X ray diffraction

**Abstract:**

Ten new vanadocene complexes bearing N,N'-chelating ligands were prepared, characterized, and their cytotoxicity toward a panel of cancer cells was measured. Structures of four vanadocene compounds were determined by single crystal X-ray diffraction analysis. Complexes containing 1,2-bis(phenylimino)acenaphthene (bian) and 1,2-bis(4-methoxyphenylimino)acenaphthene (4-MeO-bian) exhibit higher cytotoxicity than those with dipyrido[3,2-a:2',3'-c]phenazine (dppz) and (E)-N-((pyridin-2-yl)methylene)benzenamine (pyma). In light of the finding, cytotoxic mechanisms of two highly effective complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{V}(\text{bian})][\text{OTf}]_2$  (3b) and  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{V}(4\text{-MeO-bian})][\text{OTf}]_2$  (4b) against human A549 lung adenocarcinoma cells were investigated by following membrane leakage of intracellular lactate dehydrogenase, Trypan Blue staining and activation of tumor protein p53 (p53). Evaluated complexes have a potent dose-dependent antiproliferative activity, causing cell cycle redistribution by the increased accumulation of cells in the G2 and S phase. In accord with the observed cell cycle deceleration, cyclin-dependent kinase inhibitor-interacting protein 1 (p21 WAF1/Cip1), extracellular signal-regulated kinases 1 and 2 (ERK1/2), Checkpoint kinase 1 (Chk1), Checkpoint kinase 2 (Chk2) and their phosphorylated forms Chk1 at serine 345 and Chk2 at threonine 68 increased. In the cells exposed to complexes, dose- and time-dependent apoptotic process is initiated by the activation of the initiator caspase 8, followed by activation of effector caspase 3/7 and phosphatidylserine externalization. Moreover, because of treatment, A549 cells activate prosurvival mitogen-activated protein kinases (MAPK) signaling and up-regulate antiapoptotic protein B-cell lymphoma (Bcl-2), thereby promoting evasion of cell death. Both complexes exhibited considerably higher cytotoxic effect than the reference anticancer drug cis-platin and the cytotoxicity was more pronounced at higher treatment time. © 2019 Elsevier Inc.

**Naglah, A.M., Refat, M.S., Al-Omar, M.A., et al. (2019) Synthesis of a vanadyl (IV) folate complex for the treatment of diabetes: spectroscopic, structural, and biological characterization. *Drug Design, Development and Therapy*, 13: 1409-1420.**

Available at: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6498434/pdf/dddt-13-1409.pdf>

Keywords: diabetes; folic acid; spectroscopic; streptozotocin; vanadyl; vitamin B9

#### **Abstract:**

**Background:** This study aimed to design a compound with folic acid (FAH2) and vanadyl (IV) for use in the treatment of diabetes. **Materials and methods:** A novel vanadyl (IV) FAH2 complex was synthesized and characterized  $[(\text{FA}(2-))(\text{VO}(2+))]\text{3H}_2\text{O}$ . The speculated structure of this folate complex was determined using physicochemical techniques including microanalytical analysis, conductivity studies, spectroscopic examination, magnetic measurements, thermogravimetric analyses, and morphological X-ray powder diffraction, and scanning and transmission electron microscopies. The anti-diabetic therapeutic potential of the complexes was tested in a 30-day streptozotocin-induced diabetes rat model. **Results:** The conductivity test of the complex implied electrolyte behavior. The spectroscopic assessments of the isolated dark yellow solid complex revealed that FAH2 acts as a bidentate ligand. The coordination process with two vanadyl (IV) ions occurred through the deprotonation of both carboxyl groups of FAH2 in a regular square pyramid arrangement at a 2(FA)(2-): 2(VO)(2+) molar ratio. XRD, SEM, and TEM analyses revealed the complex crystalline nature of the complex. Treating diabetic rats with vanadyl (IV) FAH2 complex significantly improved many biological parameters relevant to diabetes pathology with minimal toxicity. **Conclusion:** The data generated in this study indicate that the synthesized vanadyl (IV) folate complex acts as a model of anti-diabetic agent.

**Nisak, K. & Khotib, J. (2019) Effectiveness and Mechanism of Action of Vanadyl Sulfate in Increasing Pancreatic  $\beta$  Cell Proliferation of DM Mice Due to Streptozotocin Induction. *Indian Journal of Public Health Research & Development*, 10(4): 1195-1199.**

Keywords: Diabetes Mellitus; Langerhans Islet; Streptozotocin; Vanadyl Sulfate.

**Abstract:**

Diabetes mellitus (DM) is a metabolic disorder characterized by hyperglycemia as a result of damage to insulin secretion, insulin action, or both. Vanadyl sulfate is one of the form of vanadium which has begun to be used to treat diabetes in humans. In this study, investigation on the effectiveness of vanadyl sulfate in increasing pancreatic  $\beta$  cell proliferation of diabetes mice due to streptozotocin induction. There were 30 healthy mice were subjected to this experimental study. Findings from this experiment proved that administration of vanadyl sulfate at various doses can significantly increase the amount of pancreatic  $\beta$  cell proliferation and eventually reduced blood glucose levels in a meaningless manner. However, those mice that administrated of vanadyl sulfate at a dose of 30 mg/kgBW had a higher amount of Langerhans Islet than those in the vanadyl sulfate group at a dose of 5 mg/kgBW and 100 mg/kgBW. Similar observations were obtained for the Ki-67 expression. The highest Ki-67 expression was obtained at a dose of 30 mg/kgBW but it decreased with a dose of 100 mg/kgBW of vanadyl sulfate.

**Padua, M.M.C-D., Noieto, G.R., de Oliveira Petkowicz, C.L., et al. (2019) Hypoxia protects against the cell death triggered by oxovanadium–galactomannan complexes in HepG2 cells. *Cellular and Molecular Biology Letters*, 24(1): 18.**

Available at: <https://cdbl.biomedcentral.com/track/pdf/10.1186/s11658-019-0135-3>

Keywords: Hepatocellular carcinoma; Hypoxia; MSAGM:VO; Polysaccharides; galactomannan; oxovanadium; protein Bax; protein bcl 2; protein bcl xl; protein mcl 1; unclassified drug; vanadium; mannan; oxovanadium IV; vanadic acid; antineoplastic activity; Article; autophagy; cell death; cell proliferation; cell protection; cell viability; combination drug therapy; controlled study; cytotoxicity; Hep-G2 cell line; human; human cell; protein expression; solid malignant neoplasm; cell hypoxia; drug effect; Cytoprotection; Hep G2 Cells; Humans; Mannans; Vanadates

**Abstract:**

Background: Polysaccharides from various sources have been used in traditional medicine for centuries. The beneficial pharmacological effects of plant-derived polysaccharides include anti-tumor activity. Methods: Here, we evaluated the anti-cancer effect of the MSAGM:VO complex under hypoxic conditions (1% oxygen). MSAGM:VO is a complex of the hydrolysate of galactomannan (MSAGM) from *Schizolobium amazonicum* with oxovanadium (IV/V). The hepatocellular carcinoma (HCC) cell line HepG2 was selected as HCC are one of the most hypoxic solid tumors. Results: Our results showed that the strong apoptotic activity of MSAGM:VO observed in HepG2 cells under normoxic conditions was completely lost under hypoxic conditions. We found a dynamic balance between the pro- and anti-apoptotic members of the Bcl-2 protein family. The expressions of anti-apoptotic Mcl-1 and Bcl-X L increased in hypoxia, whereas the expression of pro-apoptotic Bax decreased. MSAGM:VO strongly induced autophagy, which was previously characterized as a pro-survival mechanism in hypoxia. These results demonstrate total elimination of the anti-cancer activity of MSAGM:VO with activation of autophagy under conditions of hypoxia. Conclusion: Although this study is a proof-of-concept of the impact of hypoxia on the potential of polysaccharides, further study is encouraged. The anti-tumor activity of polysaccharides could be achieved in normoxia or through raising the activity of the immune system. In addition, combination strategies for therapy with anti-autophagic drugs could be proposed. © 2019, The Author(s).

**Treviño, S., Díaz, A., Sánchez-Lara, E., et al. (2019) Vanadium in Biological Action: Chemical, Pharmacological Aspects, and Metabolic Implications in Diabetes Mellitus. *Biological Trace Element Research*, 188(1): 68-98.**

Keywords: Biological action; Diabetes mellitus; Metabolic aspects; Metabolic implications; Metallopharmaceuticals; Vanadium; albumin; ammonium vanadate; bis(2 ethyl 3 hydroxy 4 pyronato)oxovanadium; decavanadate; hemoglobin; phosphate; phosphotransferase; unclassified drug; vanadate sodium; vanadium derivative; abdominal discomfort; antidiabetic activity; Article; atmospheric transport; biochemistry; cell interaction; diarrhea; drug absorption; drug activity; drug design; drug metabolism; drug transport; drug uptake; environmental release; glucose homeostasis; human; in vivo study; inflammation; insulin dependent diabetes mellitus; insulin signaling; lipid homeostasis; lowest-observed-adverse-effect level; nausea and vomiting; no-observed-adverse-effect level; non insulin dependent diabetes mellitus; nonhuman; oxidation reduction reaction; protein interaction; signal transduction; tissue distribution; toxic inhalation; toxicology

**Abstract:**

Vanadium compounds have been primarily investigated as potential therapeutic agents for the treatment of various major health issues, including cancer, atherosclerosis, and diabetes. The translation of vanadium-based compounds into clinical trials and ultimately into disease treatments remains hampered by the absence of a basic pharmacological and metabolic comprehension of such compounds. In this review, we examine the development of vanadium-containing compounds in biological systems regarding the role of the physiological environment, dosage, intracellular interactions, metabolic transformations, modulation of signaling pathways, toxicology, and transport and tissue distribution as well as therapeutic implications. From our point of view, the toxicological and pharmacological aspects in animal models and humans are not understood completely, and thus, we introduced them in a physiological environment and dosage context. Different transport proteins in blood plasma and mechanistic transport determinants are discussed. Furthermore, an overview of different vanadium species and the role of physiological factors (i.e., pH, redox conditions, concentration, and so on) are considered. Mechanistic specifications about different signaling pathways are discussed, particularly the phosphatases and kinases that are modulated dynamically by vanadium compounds because until now, the focus only has been on protein tyrosine phosphatase 1B as a vanadium target. Particular emphasis is laid on the therapeutic ability of vanadium-based compounds and their role for the treatment of diabetes mellitus, specifically on that of vanadate- and polioxovanadate-containing compounds. We aim at shedding light on the prevailing gaps between primary scientific data and information from animal models and human studies. © 2018, The Author(s).

**Xu, J., Zhang, B., Gong, G., et al. (2019) Inhibitory effects of oxidovanadium complexes on the aggregation of human islet amyloid polypeptide and its fragments. *Journal of Inorganic Biochemistry*, 197: 110721.**

Keywords: hIAPP/hAPP19-37/hAPP20-29 Aggregation Oxidovanadium complexes Inhibition

**Abstract:**

Human islet amyloid polypeptide (hIAPP) is synthesized by pancreatic  $\beta$ -cells and co-secreted with insulin. Misfolding and amyloidosis of hIAPP induce  $\beta$ -cell dysfunction in type II diabetes mellitus. Numerous small organic molecules and metal complexes act as inhibitors against amyloid-related diseases, justifying the need to explore the inhibitory mechanism of these compounds. In this work, three oxidovanadium complexes, namely,  $(\text{NH}_4)[\text{VO}(\text{O}_2)_2(\text{bipy})]\cdot 4\text{H}_2\text{O}$  (**1**) (bipy = 2,2' bipyridine), bis(ethyl-maltolato, *O,O*)oxido-

vanadium(IV) (**2**), and  $(\text{bipyH}_2)_2\text{H}_2[\text{O}\{\text{VO}(\text{O}_2)(\text{bipy})\}_2]\cdot 5\text{H}_2\text{O}$  (**3**), were synthesized and used to inhibit the aggregation of hIAPP and its fragments, namely, hIAPP19–37 and hIAPP20–29. Results revealed that shortening the peptide sequence decreased the aggregation capability of hIAPP fragments, and the oxidovanadium complexes inhibited the fibrillization of hIAPP better than its fragments. Interestingly, the binding of oxidovanadium complexes to hIAPP and its fragments presented a distinct thermodynamic behavior. Oxidovanadium complexes featured the disaggregation capability against hIAPP, better than against its fragments. These complexes also decreased the cytotoxicity caused by hIAPP and its fragments by reducing the production of oligomers. **3** may be a good hIAPP inhibitor based on its inhibition, disaggregation capability, and regulatory effect on peptide-induced cytotoxicity. Oxidovanadium complexes exhibit potential as metallodrugs against amyloidosis-related diseases.

**Yu, Q., Jiang, W., Li, D., et al. (2019) Sodium orthovanadate inhibits growth and triggers apoptosis of human anaplastic thyroid carcinoma cells in vitro and in vivo. *Oncology Letters*, 17(5): 4255-4262.**

**Abstract:**

Vanadium and its compounds exhibit concentration- and time-dependent anticancer effects on various types of tumor; however, the effects of sodium orthovanadate (SOV) on anaplastic thyroid carcinoma (ATC) have not yet been reported. In the present study, the anticancer effects of SOV on ATC were evaluated. In vitro experiments, including cell viability assays, plate colony formation assays, cell cycle analysis and apoptosis analysis were used to study the role of SOV in ATC. Using in vivo experiments, the effects of SOV on the growth and apoptosis of an ATC-xenograft tumor were studied by comparing the SOV-treatment with the control group. The results revealed that treatment of the human ATC cell line 8505C with SOV inhibited cell viability, induced G2/M phase cell cycle arrest, stimulated apoptosis and reduced mitochondrial membrane potential in a concentration-dependent manner. These findings were confirmed in vivo in a nude mouse ATC xenograft model. In conclusion, the present study demonstrated that SOV inhibited human ATC by regulating proliferation, cell cycle progression and apoptosis, thus suggesting that SOV may be considered a novel option for the treatment of ATC.

## **5. ENVIRONMENTAL EFFECTS in PLANTS and SOIL**

**Adimalla, N., Qian, H. & Wang, H. (2019) Assessment of heavy metal (HM) contamination in agricultural soil lands in northern Telangana, India: an approach of spatial distribution and multivariate statistical analysis. *Environmental Monitoring and Assessment*, 191: 246.**

Keywords: Ecological risk assessment; Geo-accumulation index; Heavy metal contamination; Spatial distribution; Statistical analysis; Agriculture; Contamination; Copper; Copper compounds; Eigenvalues and eigenfunctions; Heavy metals; Metal analysis; Multivariate analysis; Principal component analysis; Risk assessment; Soil surveys; Soils; Statistical methods; Agricultural sites; Anthropogenic activity; Multivariate statistical analysis; Pollution load indices; Spatial distribution map; Soil pollution; arsenic; barium; chromium; cobalt; heavy metal; lead; nickel; vanadium; zinc; agricultural soil; ecological impact; geoaccumulation index; geostatistics; soil quality; agricultural land; Article; concentration (parameter); multivariate analysis; spatial analysis; Telangana; analysis; chemistry; environmental monitoring; India; pollution; procedures; soil; soil pollutant; Environmental Pollution; Metals, Heavy; Soil Pollutants

**Abstract:**

The contamination of heavy metals (HMs) in agricultural soil lands has attracted the

environmental world due to their abundance, persistence, and toxicity. A study has been conducted to evaluate the degree of HM contamination in the agricultural soils of northern Telangana, using geo-accumulation index ( $I_{geo}$ ), pollution index (PI), pollution load index (PLI), enrichment factor (EF), statistical analysis, and also spatial distribution. In this study, a total of 15 surface agricultural soil samples were collected and analyzed for the concentration of HMs including Cr, Cu, Co, Ba, V, As, Ni, Pb, and Zn. Their average values vary from 3.5 to 778, which show the increasing order of their abundance:  $As < Ni < Pb < Co < Cu < Zn < Cr < V < Ba$ . The concentrations of Ba, V, Zn, and Cu are significantly higher than their guideline values, while Co, Ni, Pb, Zn, and As are within prescribed limits proposed by Canadian soil quality guidelines. The highest  $I_{geo}$  (1.04) indicated the extreme degree of contamination due to Cu. The estimated PI and PLI specified the low to moderate soil pollution, whereas EF showed the moderate soil pollution due to Cr, Co, V, Zn, and As. According to principal component analysis with eigenvalue, more than one account for 53.020% of the total variance, indicating the major source of anthropogenic activity. Spatial distribution maps of HMs displayed four highly polluted zones found in the agricultural sites such as Oni, Yamcha, Bederelli, and Mudhol, in northern Telangana. © 2019, Springer Nature Switzerland AG.

**Almahasheer, H. (2019) High levels of heavy metals in Western Arabian Gulf mangrove soils. *Molecular Biology Reports*, 46(2): 1585-1592.**

Keywords: *Avicennia marina*; Bio-concentration factor; Biogeochemical processes; Contaminants; Stabilization; aluminum; arsenic acid; cadmium; chromium; copper; heavy metal; iron; lead; manganese; molybdenum; nickel; silver; vanadium; air temperature; Article; concentration (parameter); controlled study; environmental monitoring; mangrove; nonhuman; Persian Gulf; plant leaf; soil acidity; soil pollution; soil quality; summer

**Abstract:**

Major development along the Western Arabian Gulf coast has disturbed the marine environment, and led to increased concentrations of heavy metals in the coastal soils. The amount of 13 of these metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn) in *Avicennia marina* branches and leaves as well as in rhizosphere soil samples from two Bays 70 km apart (Tarut Bay; Saudi Arabia and Tubli Bay; Bahrain) was quantified. Heavy metal concentration in the two bays were similar and higher than those reported in other regions suggesting a generalized heavy metal pollution in the area. These concentrations are much higher than the international permissible limits of soil contaminations except for Iron and Manganese which were within the limits. The results indicate that marine environments in the area need recovery plans and monitoring. © 2019, Springer Nature B.V.

**Ameh, E.G., Omatola, O.D. & Akinde, S.B. (2019) Phytoremediation of toxic metal polluted soil: screening for new indigenous accumulator and translocator plant species, northern Anambra Basin, Nigeria. *Environmental Earth Sciences*, 78(12): 345.**

Keywords: Anyigba; Toxic metals; Phytoremediation; Indigenous plants; Accumulator; Translocator; Heavy-Metals; Hyperaccumulator; Cadmium; Environmental Sciences & Ecology; Geology; Water Resources

**Abstract:**

Ten plant species were identified and sampled from seven sites in the study. Eighty-one soil samples were collected. Both plant and soil samples were digested in acid mixtures, extracted and were analysed for V, Mn, Ni, Cu, Zn, Pb and Mo. The amount of metals accumulated and translocated in plant tissues was calculated to determine native plants that are suitable as hyperaccumulators, phytoextractors and phytostabilizers of the metals under study. The bioconcentration factor (BCF), translocation factor (TF) and bioaccumulation coefficient (BAC)

were calculated for all plant species to enable categorization of the species. From this study, phytoextractors of vanadium (V) are *Zea mays*, *Sida acuta* and *Amaranthus hybridus* and a few other species as stabilizers. Based on the BCF, TF and BAC, *Amaranthus viridis*, *Laportea aestuans* possess phytoextraction potential while *Amaranthus hybridus*, *Corchorus aestuans*, *Sida acuta* and *Zea mays* are phytostabilizers of Mn. There are no hyperaccumulators and phytoextractors of Ni in the study area but *Amaranthus hybridus*, *Corchorus aestuans*, *Physalis angulata* and *Zea mays* are potential stabilizers. Suitable phytoextractors of Cu include *Amaranthus hybridus*, *Amaranthus viridis*, *Sida acuta* and *Zea mays*. On the other hand, *Abelmoschus esculentus*, *Cucurbita maxima*, *Corchorus aestuans*, *Laportea aestuans*, *Physalis angulata* and *Sida acuta* are all potential candidates for phytostabilization of Cu. Plant species such as *Sida acuta*, *Laportea*, *Cucurbita maxima* and *Abelmoschus esculentus* have potential for phytoextraction of Zn while *Amaranthus hybridus*, *Amaranthus viridis*, *Colocasia asculenta*, *Corchorus aestuans* and *Physalis angulata* are suitable stabilizers of Zn. Only *Physalis angulata* have phytoextraction potential for Pb while *Abelmoschus esculentus*, *Colocasia asculenta* and *Laportea aestuans* are suitable as stabilizers. Phytoextractors of Mo include *Amaranthus hybridus*, *Amaranthus viridis*, *Abelmoschus esculentus*, *Cucurbita maxima* and *Sida acuta* while *Colocasia asculenta*, *Corchorus aestuans*, *Sida acuta* and *Zea mays* are stabilizers of Mo. There were no hyperaccumulator(s) of any of the metals and no suitable phytoextractor of nickel from the area.

**Bernardino, C.A.R., Mahler, C.F., Santelli, R.E., et al. (2019) Metal accumulation in roadside soils of Rio de Janeiro, Brazil: impact of traffic volume, road age, and urbanization level. *Environmental Monitoring and Assessment*, 191(3): 156.**

Keywords: Highways; Metal emissions; Metal pollution; Soil pollution; Traffic; cadmium; chromium; cobalt; copper; iron; lead; manganese; metal; nickel; strontium; vanadium; zinc; heavy metal; Article; Brazil; environmental parameters; exhaust gas; geoaccumulation index; highway; principal component analysis; soil depth; urbanization; analysis; chemistry; environmental monitoring; pollution; procedures; soil; soil pollutant; statistics and numerical data; traffic and transport; Environmental Pollution; Metals, Heavy; Soil Pollutants; Transportation; Vehicle Emissions

**Abstract:**

Traffic-related metal emissions have become a global concern due to their deposition in roadside soils and potential hazardous effects. This study evaluates metal levels in soils adjoining four highways of Rio de Janeiro (Linha Vermelha, Via Dutra, BR-465, and Avenida Brasil), chosen for their diverse traffic volumes, age, and urban/rural settings. In addition to soil physicochemical properties, 11 elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn) were assessed on samples collected at different distances from the road (1, 3, 5, 10, 15 m) and soil depths (0–15 and 15–30 cm). Moreover, the geoaccumulation index was also computed to infer the soil contamination extent. The results indicate that soil metal levels at each highway are highly dependent on factors like traffic volume, distance to road, other anthropogenic sources of pollution, and their rural or urban location. The highways with greater traffic volume, Linha Vermelha and Avenida Brasil (154,000 and 126,000 vehicles day<sup>-1</sup>, respectively), clearly presented the highest soil metal concentrations. Still, as stressed by the principal component analysis, traffic volume alone fails to explain the distribution of metals in soils neighboring these highways. Thus, factors like their urban setting and larger exposure to anthropogenic activities may play a pivotal role. On the other hand, soils from Via Dutra and BR-465, both on a rural backdrop, were mostly influenced by traffic as their metal levels decreased with increasing distances from the road. Comparison with reference and preventive values for Brazilian soils and the assessment of the geoaccumulation index have

shown that concentrations of Pb and V have reached concerning thresholds at Linha Vermelha and Avenida Brasil. © 2019, Springer Nature Switzerland AG.

**Cowden, P. & Aherne, J. (2019) Interspecies comparison of three moss species (*Hylocomium splendens*, *Pleurozium schreberi*, and *Isoetecium stoloniferum*) as biomonitors of trace element deposition. *Environmental Monitoring and Assessment*, 191(4): 220.**

Keywords: British Columbia; Bryophytes; Interspecies calibration; Kitimat; Large-point source emissions; Atmospheric chemistry; Calibration; Deposition; Metals; Meteorological problems; Surveys; Trace elements; Atmospheric depositions; Metal concentrations; Point source emissions; Spatial and temporal trends; Spearman correlation; Pollution; aluminum; arsenic; cadmium; chromium; cobalt; copper; iron; lead; manganese; nickel; selenium; vanadium; zinc; heavy metal; trace element; biomonitoring; bryophyte; concentration (composition); correlation; endemic species; moss; point source; Article; atmospheric deposition; bioaccumulation; biological monitoring; Canada; concentration (parameter); controlled study; correlation coefficient; *Hylocomium splendens*; *Isoetecium stoloniferum*; nonhuman; *Pleurozium schreberi*; species comparison; Wilcoxon signed ranks test; air pollutant; analysis; Bryopsida; chemistry; environmental monitoring; Europe; procedures; North America; Bryophyta; *Isoetecium myosuroides*; Air Pollutants; Metals, Heavy

**Abstract:**

Biomonitoring with mosses is a common method widely used to assess the spatial and temporal trends of atmospheric deposition in Europe since its introduction in the 1970s. Based on previous investigations, certain moss species provide the most accurate reflection of atmospheric deposition. However, sampling of just one species across large areas can pose a challenge, therefore the ability to use multiple moss species interchangeably is integral to an effective moss biomonitoring survey. In this study, biomonitoring abilities of two common species (*Hylocomium splendens* [Hs] and *Pleurozium schreberi* [Ps]) were compared to a potential new biomonitoring species endemic to North America (*Isoetecium stoloniferum* [Is]). Thirteen metal concentrations were analyzed (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, and Pb) in moss tissue from 20 sites with co-located species (Ps/Hs, Is/Hs). Five metals (Al, V, Fe, Ni, and Pb) showed significant and strong correlations (Spearman correlation,  $r \geq 0.7$   $\alpha = 0.05$ ) for all three species, reflecting the established deposition gradient in the region. Furthermore, there was no significant difference in observations (and moderate correlation) for Cr, which suggests that all species exhibited similar uptake abilities for these six metals (Al, V, Cr, Fe, Ni, and Pb). Four metals (Co, As, Se, and Cd) exhibited concentrations below detection at a number of sites, which may have influenced the assessment of interspecies relationships. It is recommended that interspecies calibration be carried out under all surveys that employ multiple moss species. © 2019, Springer Nature Switzerland AG.

**Das Sharma, S. (2019) Risk Assessment and Mitigation Measures on the Heavy Metal Polluted Water and Sediment of the Kolleru Lake in Andhra Pradesh, India. *Pollution*, 5(1): 161-178.**

Keywords: Kolleru Lake; Ramsar wetland; toxic element; pollution indices; ecosystem; X-Ray-Fluorescence; Geochemical Distribution; Trace-Elements; Contamination; Wetland; Plant; Phytoextraction; Bioavailability; Soils; Index; Environmental Sciences & Ecology

**Abstract:**

The Kolleru Lake is a famous Ramsar wetland of international significance. In this study heavy metal contents in water and sediment samples are reported. It is found that certain potentially toxic metal ions like chromium (4.5-80  $\mu\text{g/L}$ ), copper (1-20  $\mu\text{g/L}$ ), manganese (1-313  $\mu\text{g/L}$ ) and zinc (1.2-57  $\mu\text{g/L}$ ) are present in variable quantities in the lake water. When

normalized with respect to concentration of each element in clean surface waters, the normalized ratio is found to be highly heterogeneous (chromium=4.5-80, copper=0.3-3.3, manganese=0.07-20.8, zinc=negligible to 2.8). At several places, the normalized ratio is greater than 1, indicating anthropogenic input. The concentration of iron (4-20  $\mu\text{g/L}$ ) in water, however, is less compared to the clean surface waters. Chemical analyses and quality assessment of Kolleru Lake sediments have been carried out through estimation of four pollution indices, which include enrichment factor (EF), geoaccumulation index (I-geo), contamination factor (CF) and pollution load index (PLI). Evaluation of these contamination indices with respect to average sediment composition of Taylor & McLennan (2001) confirmed that the Kolleru Lake sediment is polluted with a number of heavy metals that include cobalt (EF=2, I-geo=0.64, CF=2.4), chromium (EF=1.5, I-geo=0.18, CF=1.7), copper (EF=1.6, I-geo=0.29, CF=1.9), manganese (EF=1.3, I-geo=0, CF=1.4), vanadium (EF=1.5, I-geo=0.19, CF=1.7) and zinc (EF=1.5, I-geo=0, CF=1.5). The level of contamination, however, is minor to moderate and is in good agreement with the heavy metal chemistry of the lake water. Based on these results some measures for environmental rehabilitation of the lake and its surroundings have been proposed.

**Gautam, M.K., Lee, K.-., Berg, B., et al. (2019) Trends of major, minor and rare earth elements in decomposing litter in a cool temperate ecosystem, South Korea. *Chemosphere*, 222: 214-226.**

Keywords: Cool temperate; Litter decomposition; Minor elements; Rare earth elements; South Korea; Carbon; Ecosystems; Fruits; Principal component analysis; Rare earths; Vanadium compounds; Decomposition dynamic; Element concentrations; Major and minor elements; Nutrient dynamics; Pinus densiflora; Decomposition; aluminum; antimony; arsenic; barium ion; cadmium; cesium ion; chromium; cuprous ion; gadolinium; iron; lanthanide; lanthanum; lead; lithium ion; manganese; molybdenum; nickel; scandium; sodium ion; strontium; sulfur; terbium; thorium; titanium; uranium; vanadium; zinc ion; zirconium; concentration (composition); coniferous tree; dicotyledon; leaf litter; rare earth element; temperate environment; trend analysis; Article; atmospheric deposition; Castanea crenata; chestnut; cold; dry mass; ecosystem; immobilization; pine; wet deposition; angiosperm; chemistry; environment; plant leaf; soil; Pinus resinosa; Magnoliopsida; Metals, Rare Earth; Pinus; Plant Leaves; Republic of Korea

**Abstract:**

The decomposition dynamics of 34 different elements in four different litter types (foliar and woody litter) from Pinus densiflora (Korean red pine) and Castanea crenata (Korean chestnut) was investigated in a cool temperate ecosystem using the litterbag method. Two contrasting trends were observed in the dynamics of elements with accumulated mass loss of litter and carbon. Leaf litter of Korean chestnut, which was richer in elements, showed a general decrease in concentrations of elements with accumulated mass loss of litter and carbon on a dry mass basis during decomposition in the field. Other litter types, with initially lower concentrations of elements, exhibited an increase in concentration on a dry mass basis during field incubation. Highest relative increase in the concentration was noticed for the minor elements, and for the woody litters. Concentrations of major and minor elements increased by factors ranging from 1.07 for antimony (Sb) to 853.7 for vanadium (V). Rare earth elements (REE) concentrations increased by factors ranging from 1.04 for scandium (Sc) to 83.5 for thorium (Th). Our results suggest that litter type plays an important role for nutrient dynamics. Results from principal component analysis for major, minor, and rare earth elements showed grouping of elements and high correlation among them ( $P < 0.05$ ), which suggests a common source. At both sites, element concentrations were high in the soil, especially for REE. This

suggests that increase in element concentrations during field incubation probably was due to transfer of elements from soil to the overlying decomposing litter. © 2019 Elsevier Ltd.

**Kubes, J., Skalicky, M., Tumova, L., et al. (2019) Vanadium elicitation of *Trifolium pratense* L. cell culture and possible pathways of produced isoflavones transport across the plasma membrane. *Plant Cell Reports*, 38(5): 657-671.**

Keywords: Abiotic elicitation; Plasma-membrane transport; Red clover; Secondary metabolites

**Abstract:**

KEY MESSAGE: Vanadium compounds increased the content and release of distinct isoflavones in a *Trifolium pratense* suspension culture. Regarding transport-mechanism inhibitors, the process was mostly facilitated by ABC proteins and vesicular transport. The transport of isoflavones and other secondary metabolites is an important part of metabolism within plants and cultures in vitro regarding their role in defence against various abiotic and biotic stressors. This research focuses on the way how to increase production and exudation of isoflavones by application of chemical elicitor and the basic identification of their transport mechanisms across cell membranes. The release of five isoflavones (genistin, genistein, biochanin A, daidzein, and formononetin) into a nutrient medium was determined in a *Trifolium pratense* var. DO-8 suspension culture after two vanadium compound treatments and cultivation for 24 and 48 h. The  $\text{NH}_4\text{VO}_3$  solution caused a higher concentration of isoflavones in the medium after 24 h. This increased content of secondary metabolites was subsequently suppressed by distinct transport-mechanism inhibitors. The transport of isoflavones in *T. pratense* was mostly affected by ABC inhibitors from the multidrug-resistance-associated protein subfamily, but the genistein concentration in the medium was lower after treatment with multidrug-resistance protein subfamily inhibitors. Brefeldin A, which blocks vesicular transport, also decreased the concentration of some isoflavones in the nutrient medium.

**Kulikova, T., Hiller, E., Jurkovic, L., et al. (2019) Total mercury, chromium, nickel and other trace chemical element contents in soils at an old cinnabar mine site (Mernik, Slovakia): anthropogenic versus natural sources of soil contamination. *Environmental Monitoring and Assessment*, 191(5): 263.**

Keywords: Chromium/analysis; Environmental Monitoring; Human Activities; Humans; Mercury/analysis; Mercury Compounds; Mining; Nickel/analysis; Slovakia; Soil/chemistry; Soil Pollutants/analysis; Trace Elements/analysis; Compositional data analysis; Contamination; Mercury; Mine soil; Nickel

**Abstract:**

The aims of this study were to investigate the occurrence and distribution of total mercury (Hg) and other trace elements of environmental concern, such as arsenic (As), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn) and vanadium (V), in soils from the abandoned Mernik cinnabar mine in eastern Slovakia. For this purpose, thirty soil samples from two depth intervals within the mine area (n = 60 soil samples) and additional sixteen soil samples from adjacent areas (n = 25 soil samples) were collected. Total Hg was measured by atomic absorption spectrometry, while As and other metals were analyzed using inductively coupled plasma atomic emission spectrometry. High mercury concentrations (> 100 mg/kg with a maximum of 951 mg/kg) were observed only in surface soils close to mine waste heaps and adits. Otherwise, Hg concentrations in the majority of surface soils were lower (0.14-19.7 mg/kg), however, higher than Hg in soils collected from sites outside the mine area (0.19-6.92 mg/kg) and even considerably higher than Hg in soils at sites not

influenced by the Mernik mine. Elevated Cr and Ni concentrations in soils regardless of their sampling sites (mean of 276 mg/kg and median of 132 mg/kg for Cr and 168 mg/kg and 81 mg/kg for Ni, respectively) were attributed to the lithology of the area; the soils are underlain by the sediments of the Central Carpathian Palaeogene, containing a detritus of ultrabasic rocks. As our geochemical data are compositional in nature, they were further treated by compositional data analysis (CoDA). Robust principal component analysis (RPCA) applied on centred (clr) log-ratio-transformed data and correlation analysis of compositional parts based on symmetric balances distinguished very well different sources of origin for the chemical elements. The following three element associations were identified: Hg association with the main source in mining/roasting, Cr-Ni association derived from bedrock and As-Cu-Mn-Pb-Zn-V association (natural background and minor sulphides/sulfosalts in mineralized rocks). The values of geoaccumulation index and enrichment factor suggested that concentrations of Hg in the soils were influenced by human industrial activities.

**Rinklebe, J., Antoniadis, V., Shaheen, S.M., et al. (2019) Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International*, 126: 76-88.**

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018324954/pdf?md5=5cfea4ef254356ae57dbf4b647181f6b&pid=1-s2.0-S0160412018324954-main.pdf>

Keywords: Heavy metals; Risk assessment; Riverine ecosystems; Trace elements; Wetland soil; Arsenic; Chromium; Contamination; Copper compounds; Health; Health risks; Hydrogeology; River pollution; Soil conservation; Soil surveys; Soils; Tin; X ray spectrometers; Contaminated areas; Contaminated sites; Contamination factors; Pollution load indices; Potentially toxic elements; Wetland soils; X-ray fluorescence spectrometer; barium; copper; lead; nickel; rubidium; strontium; vanadium; zinc; zirconium; freshwater ecosystem; health risk; heavy metal; soil pollution; soil profile; trace element; wetland; adult; Article; chemical composition; child; Contaminated Sites Ordinance; Contamination factor; controlled study; environmental parameters; environmental policy; female; German Federal Soil Protection; Germany; health hazard; high risk population; human; male; mathematical analysis; median children hazard index; Pollution Load Index; Precautionary Value; priority journal; river; sandy soil; sex difference; soil analysis; soil property; topsoil; toxicity testing; X ray fluorescence spectrometry; Elbe River

**Abstract:**

Floodplain soils across Central Elbe River (CER), Germany, vary considerably in potentially toxic element (PTE) content. However, there has never been a comprehensive study that links PTE levels with human health risk for children and adults. Our objective was to determine the contamination of 13 PTEs in 94 soil profiles along CER and assess the associated health risk via diverse indices for adults and children. Of 94 soil profiles, we measured soil properties and total content of arsenic, barium, chromium, copper, nickel, lead, rubidium, tin, strontium, vanadium, zinc, and zirconium using x-ray fluorescence spectrometer (XRF). We calculated the Contamination Factor and the Pollution Load Index (PLI), and assessed the health risk for male and female adults as well as for children. Topsoil median contents of Cr (84 mg kg<sup>-1</sup>), Cu (42), Ni (33), and Zn (195) exceeded the Precautionary Values for sandy soils according to the German Federal Soil Protection and Contaminated Sites Ordinance, while As, Pb, and V were 32, 73, and 77 mg kg<sup>-1</sup>, respectively. Median topsoil PLI was 1.73, indicating elevated multi-element contamination, with 90th percentile and maximum values being 3.20 and 4.31, respectively. All PTE concentrations were higher in top- compared to subsoils. Also at the 50th percentile the most enriched elements were Sn and As, followed by Zr and Rb, while in the 90th percentile Sn and As were followed by Zn, Pb and Cu. Median children's hazard index (HI)

was higher than unity (HI = 2.27) and the 90th percentile was 5.53, indicating elevated health risk. Adult median HIs were 0.18 for male and 0.21 for female persons. Arsenic was found to be the primary contributor to total risk, accounting of 57.4% of HI in all three-person groupings, with Cr (17.3%) being the second, and V (10.2%) the third. Children's health is at dramatically higher risk than that of adults; also As, Cr, Pb, and V have a predominant role in contamination-related health risks. The presence of V, a less-expected element, among those of major risk contribution, reveals the necessity of monitoring areas at large scale. Our results demonstrate that our study may serve as a model for similar works studying multi-element-contaminated areas in future. © 2019 The Authors.

**Sun, W., Li, X., Padilla, J., et al. (2019) The influence of phosphate on the adsorption-desorption kinetics of vanadium in an acidic soil. *Journal of Environmental Quality*, 48(3): 686-693.**

Keywords: Adsorption; Binding energy; Desorption; Soils; Vanadium; Adsorption-desorption kinetics; Break through curve; Competitive retention; Dominant mechanism; Environmental risks; Multi-reaction model; Predictive modeling; Sorption capacities; Soil pollution

**Abstract:**

Quantitative understanding of the mechanisms controlling the competitive retention and transport of V and phosphate on soils is essential for accurately evaluating the environmental risks of contaminants in the environment. Batch and stir-flow chamber experiments were performed to quantify the extent of kinetics of V and phosphate competitive retention in an acidic soil (Sharkey clay). In this study, a stir-flow model was used to describe tracer and competitive reactive solute adsorption, and desorption processes in soils. Based on optimized and predictive modeling results, a fully reversible-irreversible multi-reaction model successfully described the time-dependent competitive V and phosphate retention and transport process in Sharkey soil. Adsorption for V and phosphate were highly nonlinear and time dependent, where V binding affinities were stronger than those for phosphate. Results from batch experiments indicated that that the rate and extent (amount) of V released increased significantly in the presence of phosphate. Breakthrough curves for V, from stir-flow experiments, were asymmetrical and exhibited slow release or tailing, indicating that nonequilibrium retention on the surface of soil was the dominant mechanism of the time-dependent adsorption of V. Results of stir-flow experiments indicated that increased mobility of V was observed in the presence of phosphate caused by direct competition for available retention sites. In conclusion, increased addition of phosphate causes decreasing sorption capacity and increasing mobility of V and needs to be considered in modeling the fate and transport of V in soil. © 2019 The Authors.

**Sun, W. & Selim, H.M. (2019) A general stirred-flow model for time-dependent adsorption and desorption of heavy metal in soils. *Geoderma*, 347: 25-31.**

Keywords: Vanadium; Molybdenum; Kinetic; Stirred-flow; Model; Sorption-Desorption; Zn Sorption; Kinetics; Retention; Molybdate; Arsenate; Transport; Agriculture

**Abstract:**

Quantitative understanding of kinetics and mechanisms heavy metal adsorption-desorption and transport processes, batch and stirred-flow experiments were carried out with vanadium (V) and molybdenum (Mo) on soils at different reaction conditions and time scale. Batch experiments indicated that adsorption of V and Mo on soils was highly nonlinear and time-dependent, where V and Mo retention showed typical biphasic reaction kinetics. The stirred-flow experiments showed that both V and Mo adsorption consisted of a fast initial reaction, as indicated by the fact that effluent solute concentration was close to zero for the first few

minutes. A stirred-flow multi-reaction model (MRM) which accounts for slow as well as fast reactions of the reversible and irreversible type was developed to describe V and Mo adsorption and desorption processes on soils. Based on model simulations and experimental tracer breakthrough curves (BTCs) results, we concluded that the proposed model is valid for stirred-flow conditions. The strong retardation and slow release behaviors of V and Mo from stirred-flow experiments were successfully described using the proposed stirred-flow MRM where retardation and irreversible reactions were necessary. Our work provides a general stirred-flow model which is capable of describing reactive and non-reactive solutes.

**Wang, J. (2019) Short-term geochemical investigation and assessment of dissolved elements from simulated ash reclaimed soil into groundwater. *Environmental Pollution*, 247: 302-311.**

Keywords: Ash reclaimed soil; Assessment; Groundwater; Leaching; Multivariate statistical analysis; Cluster analysis; Flow velocity; Fly ash; Geochemistry; Health risks; Multivariate analysis; Potable water; Quality control; Reclamation; Soils; Water quality; Dissolved element; Geochemical investigations; Geochemical partitioning; Leaching behavior; Reclaimed soil; Sampling stations; Land reclamation; aluminum; antimony; arsenic; cadmium; carbon monoxide; chromium; copper; ground water; iron; lead; magnesium; manganese; nickel; tin; vanadium; zinc; heavy metal; assessment method; multivariate analysis; soil remediation; Article; ash; concentration (parameter); environmental impact assessment; environmental monitoring; flow rate; geochemical analysis; simulation; water contamination; water pollutant; water sampling; analysis; chemistry; soil; soil pollutant; Coal Ash; Metals, Heavy; Soil Pollutants

**Abstract:**

A soil column migration trough was used to study the leaching behavior and geochemical partitioning of fifteen elements Al, As, Cr, Cu, Fe, Mg, Sn, Sb, Zn, V, Co, Mn, Pb, Ni and Cd in simulated ash reclaimed soil. According to the results of cluster analysis for the sampling stations, there were three clusters: Cluster 1 of 7 wells with relative good groundwater quality originated from the background control area, Cluster 2 of 9 wells with worst groundwater quality in the downstream parts of the simulated ash reclaimed soil, and Cluster 3 of 2 wells with representative of samples influenced by the combined effect of injection of leaching solution and the main current. Statistical analysis identified five factor types that accounted for 83.055% of the total variance, which declined in the order: ash-soil rate > leaching intensity > water depths > flow velocity > leaching time. As, Sb, Cd, Pb and Ni were the dominant contaminants. The water around ash reclaimed soil was unsuitable for drinking. As, Mn, Cd, Sb, Co and V were the largest contributors to health risks. Soils reclaimed with fly ash can consequently be a long-time source for the transfer of toxic elements into groundwater. © 2019 Elsevier Ltd.

**Zhang, B., Wang, S., Diao, M., et al. (2019) Microbial Community Responses to Vanadium Distributions in Mining Geological Environments and Bioremediation Assessment. *Journal of Geophysical Research: Biogeosciences*, 124(3): 601-615.**

Available at: <http://www.cugb.edu.cn/uploadCms/file/20600/20190430112825708780.pdf>

Keywords: vanadium; biogeochemical process; bioremediation; microbial community; geological environment

**Abstract:**

Vanadium mining activities can cause contamination of the surrounding geological environment. Vanadium may exist in multiple matrices due to its migration and transformation, forming interactive relationships; however, the connection between vanadium distributions in multiple matrices and microbial community responses remains

largely unknown. Vanadium is a redox-sensitive metal that can be microbiologically reduced and immobilized. To date, bioremediation of vanadium-contaminated environments by indigenous microorganisms has rarely been evaluated. This paper reports a systematic investigation into vanadium distributions and microbial communities in soils, water, and sediment from Panzhihua, China. Large vanadium contents of  $1130.1 \pm 9.8$  mg/kg and  $0.13 \pm 0.02$  mg/L were found in surface soil and groundwater. Vanadium in surface water tended to precipitate. Microbial communities isolated from similar environments were alike due to similarity in matrix chemistry whereas communities were distinct when compared to different matrices, with lower richness and diversity in groundwater. Proteobacteria was distributed widely and dominated microbial communities within groundwater. Redundancy analysis shows that vanadium and nutrients significantly affected metal-tolerant bacteria. Long-term cultivation (240 days) suggests the possibility of vanadium bioremediation by indigenous microorganisms, within acid-soluble fraction. This active fraction can potentially release mobile vanadium with shifted redox conditions. Vanadium (V) was bio-reduced to less toxic, mobile vanadium (IV) primarily by enriched *Bacillus* and *Thauera*. This study reveals the biogeochemical fate of vanadium in regional geological environments and suggests a bioremediation pathway via native vanadium-reducing microbes.

**Zou, Q., Li, D., Jiang, J., et al. (2019) Geochemical simulation of the stabilization process of vanadium-contaminated soil remediated with calcium oxide and ferrous sulfate. *Ecotoxicology and Environmental Safety*, 174: 498-505.**

Keywords: Adsorption; Calcium Compounds/chemistry; China; Computer Simulation; Environmental Restoration and Remediation/methods; Ferrous Compounds/chemistry; Models, Theoretical; Oxides/chemistry; Software; Soil/chemistry; Soil Pollutants/analysis; Vanadium/analysis; Geochemical modeling; Soil remediation; Stabilization mechanism; Vanadium; Visual MINTEQ

**Abstract:**

Vanadium (V)-contaminated soil poses health risks to plants, animals, and humans via both direct exposure and through the food chain. Stabilization treatment of metal-contaminated soil can chemically convert metal contaminants into less soluble, mobile, and toxic forms. However, the stabilization mechanisms of V-contaminated soil have not been thoroughly investigated. Therefore, we performed geochemical modeling of V-contaminated soil stabilized with the common binders calcium oxide (CaO) and ferrous sulfate (FeSO<sub>4</sub>), as well as their mixture, using Visual MINTEQ software. The results were validated and exhibited good agreement with experimental results. For CaO, the formation of Ca<sub>2</sub>V<sub>2</sub>O<sub>7</sub>(s) and Ca<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O(s) under mild and strong alkaline conditions (pH = 8.0-11.5 and 11.5-12.5), respectively, were predicted as the main immobilization routes. For FeSO<sub>4</sub>, there appeared to be three reaction routes, corresponding to approaches A, B, and C, during the stabilization process. In the simulation, approach C (adsorption of V(V) onto ferrihydrite) was undervalued, whereas approaches A (formation of Fe(VO<sub>3</sub>)<sub>2</sub>(s)) and B (reduction of V(V) into V(IV) to form V<sub>2</sub>O<sub>4</sub>(s) or adsorb onto soil organic matter) were overvalued. Among the three approaches, approach C had a dominant role and exhibited good agreement with the experimental results. Additionally, soil pH and the saturation index of precipitation had major roles in the stabilization process. The optimal pH ranges for the stabilization of V-contaminated soil using CaO and FeSO<sub>4</sub> were pH =9.5-12.5 and pH =4.0-5.0, respectively.

**Zou, Q., Gao, Y., Yi, S., et al. (2019) Multi-step column leaching using low-molecular-weight organic acids for remediating vanadium- and chromium-contaminated soil. *Environmental Science and Pollution Research*, 26(15): 15406-15413.**

Keywords: Soil flushing; Vanadium; Chromium; Organic acids; Potential mobile fractions; Multi-step leaching; Sequential Extraction Procedure; Heavy-Metals; Citric-Acid; Geochemical; Fractions; Mine Tailings; Paddy Soils; Edta; Removal; Mobilization; Profiles; Environmental Sciences & Ecology

**Abstract:**

In soil, vanadium (V) contamination is commonly concomitant with chromium (Cr) contamination, which poses potential risks to humans, animals, and plants due to the transfer of toxic metals and the increase in their concentrations via the food chain or through direct exposure. This study applied a multi-step column leaching process using low-molecular-weight organic acids (LMWOAs) to treat V-contaminated soil from a smelter site that contains 2015.1 mg V kg<sup>-1</sup> and 1060.3 mg Cr kg<sup>-1</sup>. After leaching three times with an equivalent solution/soil ratio of 0.3 mL/g using 1.0 M oxalic acid solution, the total removal rates reached 77.2% and 7.2% for V and Cr, respectively, while the removal rates of the extractable fractions reached 118.6% and 99.2% due to the reduction in residual fraction (F-4) of toxic metals. Simultaneously, the distribution and redistribution of geochemical fractions of V and Cr were determined with a sequential extraction technique, and the greater proportion of potential mobile fractions of V (65.1%) may increase its leaching from soil relative to Cr (7.1%). In addition, a lower pH of the leaching agent increased the efficiency of the leaching process to an extent. Compared with batch extraction with a typical solution to soil ratio of 10 mL/g, multi-step column leaching used less agent and hence produced less wastewater. This strategy could reduce the mobilization and bioavailability of toxic metals, and potentially enhance in situ soil flushing for the remediation of V- and Cr- contaminated soil.

## 6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

**Hu, X., Yue, Y. & Peng, X. (2019) Organic ligand induced release of vanadium from the dissolution of stone coal oxide ore. *Environmental Science and Pollution Research*, 26(18): 17891-17900.**

Keywords: Complexation; Dissolution; Dissolved organic matters; Kinetics; Stone coal; Vanadium

**Abstract:**

The effects of low-molecular-weight dissolved organic matters (LMWDOMs) on the release of vanadium (V) under environmental conditions are part of a broader study on the environmental geochemistry behavior of V. Eight typical naturally occurring LMWDOMs with carboxyl, hydroxyl, and amidogen groups were chosen: citric acid, oxalic acid, EDTA, salicylic acid, catechol, glycine, cysteine, and glucose. The results showed that the release of V was largely promoted by LMWDOMs with carboxyl functional groups under acidic conditions and with catechol under basic conditions. In the presence of citric acid, oxalic acid, or EDTA at pH 4.0, the initial release rates of V were approximately 25–39 times greater than the rates in the control experiments; the steady release rates were 164, 95, and 49 times than the rates in the control experiments, respectively. For catechol, the release rate at pH 8.0 was approximately 20 times the rate at pH 4.0. Amino acids and alcohols had a minimal effect on the release of V. Ligand-promoted release rates of V were found primarily due to the faster detachment of surface complexes, the protonated sites from the mineral surface and the reduction of dissolved V (V) in the presence of citric acid, oxalic acid, EDTA, and catechol. This study helps understand the pollution risk of V in some mine areas and the fate of V in the environment. © 2017, Springer-Verlag GmbH Germany.

**Hu, X., Peng, X., Kong, L., et al. (2019) The mechanism for promoted oxygenation of V(IV) by goethite: Positive effect of surface hydroxyl groups. *Journal of Hazardous Materials*, 369:**

## 254-260.

Keywords: Goethite; Oxidation; Surface hydroxyl groups; Vanadium; Dissolved oxygen; Iron compounds; Bulk solutions; Electron transfer; Environmental risks; Goethite suspensions; Similar elements; Surface groups; Vanadium compounds; ferric hydroxide; ferric ion; hydroxyl group; hydroxide; hydroxyl radical; oxygenation; adsorption; aqueous solution; Article; crystal structure; electron spin resonance; electron transport; pH; surface property; suspension; volume

### Abstract:

The most toxic and mobile form of vanadium (V) is V(V). Thus, the oxidation of V is a subject of considerable importance since the process may increase environmental risks of V. V(IV) is known to be stable when  $\text{pH} < 4.5$ . However, in this study, stable V(IV) was oxidized almost completely in goethite suspension within 60 min at  $\text{pH} 2.0$  and  $\text{pH} 4.0$ , correspondingly, only 25%–30% and 15%–20% of V(IV) were oxidized in equimolar  $\text{Fe}^{3+}$  solution and the blank solution, respectively. The promoted oxidation of V(IV) by FeOOH is attributed to the formation of the complex,  $\text{VO}(\text{OFe}^{2+})$  or  $\text{VO}(\text{OFe}^{2+})_2$ . On the one hand, the formation of the complex caused higher pH in the interface of solid FeOOH and corresponding lower conditional potential of V(V)/V(IV) than those in bulk solutions, which facilitates the oxidation of V(IV). On the other hand, the surface group  $\text{OFe}^{2+}$  may serve as a medium that facilitating the electron transfer from V(IV) ions to dissolved oxygen molecules, also favoring the oxidation of V(IV). This study not only deepens our understanding of the transfer, transformation, and risk of V in environments, but also provides a reference to speculate the fate of similar elements in environments. © 2019 Elsevier B.V.

**Stachiw, S., Bicalho, B., Grant-Weaver, I., et al. (2019) Trace elements in berries collected near upgraders and open pit mines in the Athabasca Bituminous Sands Region (ABSR): Distinguishing atmospheric dust deposition from plant uptake. *Science of the Total Environment*, 670: 849-864.**

Keywords: Atmospheric aerosols; Bituminous sands; Micronutrients; Mineral dust; Native berries; Trace elements; Antennas; Atmospheric chemistry; Deposition rates; Dust; Fruits; Health risks; Oil sands; Open pit mining; Elevated concentrations; Environmental emissions; Indigenous community; Lithophile elements; Positive correlations; aluminum; antimony; barium; beryllium; cadmium; chromium; copper; iron; lead; lithium; manganese; molybdenum; nickel; rhenium; rubidium; scandium; selenium; silver; strontium; thallium; thorium; trace element; uranium; vanadium; zinc; asphalt; hydrocarbon; metal; silicon dioxide; aerosol; atmospheric deposition; biological uptake; concentration (composition); fruit; mineral; open pit mine; plant; sand; Article; blueberry; concentration (parameter); controlled study; cranberry; food washing; health hazard; inductively coupled plasma mass spectrometry; limit of detection; lingonberry; measurement accuracy; mining; nonhuman; physical chemistry; phytotoxicity; plant root; priority journal; soil pollution; Sphagnum; surface area; tar sand; air pollutant; Alberta; analysis; atmosphere; chemistry; environmental monitoring; soil; Sphagnopsida; wetland; Athabasca Oil Sands; Canada; Bryophyta; Vaccinium; Air Pollutants; Hydrocarbons; Metals; Wetlands

### Abstract:

There are ongoing concerns regarding environmental emissions of trace elements (TEs) from bitumen mining and upgrading in the Athabasca Bituminous Sands Region (ABSR). Depending on their physical and chemical forms, elevated concentrations of potentially toxic TEs in berries could pose a health risk to local indigenous communities because native fruits are an important part of their traditional diet. The objective of this study was to distinguish between aerial deposition of TEs versus plant uptake, in cranberries, lingonberries, and blueberries

growing in the ABSR. The concentrations of TEs were determined using ICP-MS in the metal-free, ultraclean SWAMP lab at the University of Alberta. The spatial variation in abundance of conservative, lithophile elements such as Y in berries resembles the published map of dust deposition rates obtained using Sphagnum moss. The presence of dust particles on the surface of the berries near open pit mines and upgraders was confirmed using SEM. Elements which show strong, positive correlation with Y include Al, Cr, Pb, U, and V; these are supplied mainly by dust. Elements which are largely independent of Y concentrations include Ba, Cd, Cu, Mn, Mo, Ni, Rb, Sr, and Zn; these are obtained primarily by plant uptake from soil. The concentrations of elements associated with dust were considerably reduced after washing with water, but the elements independent of dust inputs were unaffected. Elements which are supplied almost exclusively by dust (e.g. Y) are more abundant in berries from the ABS region (2 to 24 times), compared to berries from remote locations. © 2019 Elsevier B.V.

**van Aswegen, J.D., Nel, L., Strydom, N.A., et al. (2019) Comparing the metallic elemental compositions of Kelp Gull *Larus dominicanus* eggs and eggshells from the Swartkops Estuary, Port Elizabeth, South Africa. *Chemosphere*, 221: 533-542.**

Keywords: Chromium; Cobalt; Copper; Indian ocean; Laridae; Mercury; Vanadium; Zinc; Atmospheric chemistry; Chemistry; Mercury (metal); Dry mass basis; Elemental compositions; Geological background; Mean concentrations; Metallic elements; Source identification; Biochemistry; selenium; strontium; uranium; metal; bioaccumulation; concentration (composition); dry matter; eggshell; seabird; trace element; trophic status; Article; Charadriiformes; dry mass; ecotoxicity; egg; egg shell; elemental analysis; estuary; *Larus dominicanus*; nonhuman; sediment; South Africa; animal; bird; embryology; environmental monitoring; ovum; Eastern Cape; Port Elizabeth; Swartkops Estuary; Animalia; Ardeidae; Lutrinae; Phalacrocoracidae; Animals; Birds; Estuaries; Metals

#### **Abstract:**

Metals attributed to pollution may increase their concentrations above the geological background and pose toxic challenges towards humans and biota. We analysed sixteen Kelp Gull eggs and eggshells for 30 metallic elements from the Swartkops Estuary (SE), an important recreational, industrial, and ecological asset for Port Elizabeth, the region, and South Africa. Mean concentrations for eggshell and egg content for Hg was 0.02 and 0.4 mg/kg dm, Cr was 4 and 18 mg/kg dm (the highest yet recorded for any gull or tern egg), for Zn 2.1 and 62 mg/kg dm, for Sr 880 and 12 mg/kg dm, for V 170 and 1.3 mg/kg dm, and for Co 1.7 and 0.002 mg/kg dm, respectively. Zinc, Se, and Hg, increased on a dry-mass basis from sediment via small fish to gull egg content, indicating bioaccumulation. No effect on eggshell thickness was seen. We also determined that eggshell concentrations cannot be used as a proxy for egg content concentrations. Mercury, Cr, V, Co, and Zn were elements we identified as potentially problematic that require source identification and mitigation. Further research into other high-trophic animals such as herons, egrets, cormorants, and otters in the SE system is proposed. © 2019 Elsevier Ltd.

## **7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS**

**Castillo, A., Valdes, J., Sifeddine, A., et al. (2019) Evaluation of redox-sensitive metals in marine surface sediments influenced by the oxygen minimum zone of the Humboldt Current System, Northern Chile. *International Journal of Sediment Research*, 34(2): 178-190.**

Keywords: Redox sensitive-metals; Atacama Desert; Enrichment factor; Mejillones del Sur Bay; Caldera Bay system; PCA; Continental-Margin Sediments; Ocean-Climatic Fluctuations; Del-Sur Bay; Organic-Matter; Mejillones Bay; Trace-Metals; Concepcion; Similar-To-36-Degrees-S; Upwelling Sediments; Rich Sediments; Geochemistry; Environmental Sciences & Ecology; Water Resources

**Abstract:**

Upwelling coastal systems can be used to understand how dissolved oxygen and biological productivity control the accumulation of redox-sensitive metals in marine sediments. The aluminium (Al), cadmium (Cd), iron (Fe), nickel (Ni), molybdenum (Mo), vanadium (V), total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) contents in surficial sediment collected from different water depths (30, 70, and 120 m) in three northern Chilean bays influenced by coastal upwelling and oxygen minimum zones (OMZs) were measured. Principal component analysis (PCA), cluster analysis, and Spearman's rank correlation were used to identify the mechanisms responsible for the redox-sensitive metal accumulation. The content of redox-sensitive metals and organic components in sediment increased with increasing water column depth, whereas lithogenic metals decreased. In the Mejillones del Sur and Caldera bays, the enrichment factors of the redox-sensitive metals showed enrichment for all metals with depth. The Cd and V enrichments are mainly the product of biogenic flow to the seabed, and the Mo and Ni enrichments are due to preservation under low subsurface oxygen conditions. Sulfate reduction is not an important mechanism in the accumulation of redox-sensitive metals in the sediment of the three bays. The PCA showed that the behaviors of the redox-sensitive metals and organic components reflect differences in the effects of the OMZ in sediment along the coast of northern Chile, with a more intense OMZ in Mejillones del Sur bay and weaker OMZs in Caldera and Inglesa bays. However, the high degree of enrichment in redox-sensitive metals in Caldera Bay can be attributed to the intense activity of the mining industry near the bay, a situation that produces geochemical behavior similar to that observed in Mejillones del Sur Bay. (C) 2018 International Research and Training Centre on Erosion and Sedimentation/the World Association for Sedimentation and Erosion Research. Published by Elsevier B.V. All rights reserved.

**Chen, G., Wang, X., Wang, R., et al. (2019) Health risk assessment of potentially harmful elements in subsidence water bodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. *Ecotoxicology and Environmental Safety*, 171: 737-745.**

Keywords: Coal mining area; Health risk assessment; Monte Carlo simulation; Potentially harmful elements; Subsidence water bodies; arsenic; cadmium; chromium; cobalt; copper; environmental, industrial and domestic chemicals; iron; lead; manganese; nickel; potentially harmful element; surface water; unclassified drug; vanadium; zinc; heavy metal; atomic absorption spectroscopy; carcinogen; coal mining; concentration (composition); health risk; Monte Carlo analysis; risk assessment; Article; atomic absorption spectrometry; atomic fluorescence spectrometry; cancer risk; China; concentration (parameter); contact dermatitis; controlled study; environmental exposure; health hazard; ingestion; Monte Carlo method; water analysis; water pollution; water quality; analysis; environmental monitoring; human; water pollutant; Anhui; Huainan; Humans; Metals, Heavy; Spectrophotometry, Atomic; Water Pollutants, Chemical

**Abstract:**

Enrichment of potentially harmful elements in surface water results in ecological risk to the surrounding environment. Assessing the environmental risk of these elements is of great importance. In this study, surface water samples from 6 different subsidence water bodies in the Huainan coal mining area were collected. The concentrations of Cu, Ni, Pb, Cd, Co, Cr, V, Fe, Mn and Zn were measured by atomic absorption spectrophotometry, and those of As and Hg were analyzed by atomic fluorescence spectrometry. Then, human health risks through the ingestion and dermal contact pathways were assessed and analyzed on the basis of a Monte Carlo simulation. The mean and 95th percentile risks were reported. The results showed that the total carcinogenic risk values in every subsidence water body summed for Cr,

Ni and As via two exposure pathways were greater than the maximum acceptable level ( $1 \times 10^{-4}$ ), and Xinji'er water body had the highest carcinogenic risk. Among three elements, Ni was the highest contributor to carcinogenic risk. All non-carcinogenic health risk (hazard quotients) values except for one water area of Co (Xinji'er) were less than 1; however, the total non-carcinogenic health risks of two water bodies (Xinji'er, Xinjiyi) summed for all the elements based on mean concentrations were higher than 1. Xinji'er had the highest hazard index. The extent of the impacts of the total hazard quotients followed the order of  $Co > As > Cd > Hg > Pb > V > Fe > Ni > Mn > Zn > Cr$ . Furthermore, the total hazard quotients of Co and As via ingestion pathway summed for the six subsidence water areas were greater than 1, which should be a concern. © 2019 Elsevier Inc.

**Gaus, C., Villa, C.A., Dogruer, G., et al. (2019) Evaluating internal exposure of sea turtles as model species for identifying regional chemical threats in nearshore habitats of the Great Barrier Reef. *Science of the Total Environment*, 658: 732-743.**

Keywords: Bioanalytical screening; Blood; Contaminants; Multi-element screening; Non-target screening; Alkalinity; Animals; Biomarkers; Chemical analysis; Chemical hazards; Cobalt; Health; Health hazards; Impurities; Indicators (chemical); Offshore oil well production; Phosphatases; Population statistics; ALkaline phosphatase; Bioanalytical; Development and applications; Elevated concentrations; Epidemiological studies; Multi-element; Non-target screenings; Trace-element exposures; Trace elements; aluminum; antimony; arsenic; barium; bilirubin; cadmium; calcium; chromium; copper; indolepropionic acid; iron; lead; magnesium; manganese; molybdenum; nickel; potassium; selenium; silver; sodium; thallium; thorium; tin; titanium; uranium; vanadium; zinc; biomarker; chemical pollutant; epidemiology; foraging behavior; habitat structure; nearshore environment; pollution exposure; population dynamics; trace element; turtle; adult; Article; concentration (parameters); controlled study; coral reef; foraging; limit of detection; limit of quantitation; lipid peroxidation; measurement accuracy; nonhuman; oxidative stress; priority journal; sea turtle; species habitat; steady state; wildlife; analysis; animal; environmental exposure; environmental monitoring; metabolism; procedures; Queensland; water pollutant; Australia; Coral Sea; Great Barrier Reef; Chelonia (genus); Cheloniidae; Reptilia; Testudines; Vertebrata; Coral Reefs; Turtles; Water Pollutants, Chemical

**Abstract:**

Marine megafauna that forage in proximity to land can be exposed to a diverse mixture of chemicals that - individually or combined - have the potential to affect their health. Characterizing such complex exposure and examining associations with health still poses considerable challenges. The present study summarizes the development and application of novel approaches to identifying chemical hazards and their potential impacts on the health of coastal wildlife, using green sea turtles as model species. We used an epidemiological study approach to collect blood and keratinized scute samples from free-ranging turtles foraging in nearshore areas and an offshore control site. These were analyzed using a combination of non-targeted, effect-based and multi-chemical analytical screening approaches to assess internal exposure to a wide range of chemicals. The screening phase identified a suite of elements (essential and non-essential) as priority for further investigation. Many of these elements are not commonly analyzed in marine wildlife, illustrating that comprehensive screening is important where exposure is unknown or uncertain. In particular, cobalt was present at highly elevated concentrations, in the order of those known to elicit acute effects across other vertebrate species. Several trace elements, including cobalt, were correlated with clinical indicators of impaired turtle health. In addition, biomarkers of oxidative stress (e.g. 3-indolepropionic acid and lipid peroxidation products) identified in the blood of turtles showed significant correlations with clinical health markers (particularly alkaline phosphatase

and total bilirubin), as well as with cobalt. To assist interpretation of trace element blood data in the absence of sufficient information on reptile toxicity, we established exposure reference intervals using a healthy control population. In addition, trace element exposure history was investigated by establishing temporal exposure indices using steady-state relationships between blood and scute. Overall, the data provide a strong argument for the notion that trace element exposure is having an impact on the health of coastal sea turtle populations. © 2018.

**Gillio Meina, E., Raes, K. & Liber, K. (2019) Models for the acute and chronic aqueous toxicity of vanadium to *Daphnia pulex* under a range of surface water chemistry conditions. *Ecotoxicology and Environmental Safety*, 179: 301-309.**

Keywords: Vanadium; Oil sands; OSPW; Water chemistry

**Abstract:**

Alberta's oil sands petroleum coke (PC) generation has in recent years surpassed 10 million tonnes. Petroleum coke has been proposed as an industrial-scale sorbent to reduce concentrations of organic chemicals in oil sands process-affected water (OSPW). However, PC contains up to 1000 mg of vanadium (V) per kg of PC, and during the treatment it leaches from coke reaching levels of up to 7 mg/L in "treated" OSPW. Little information is available on how common water quality variables affect the toxicity of V to aquatic organisms. Here descriptive relationships are presented to describe how site-specific surface water characteristics representative of the Alberta oil sands region influence the toxicity of V to *Daphnia pulex*. Results revealed that when *D. pulex* was exposed to an increase in pH, a threshold relationship was found where acute V toxicity increased from a lethal median concentration (LC50) of 1.7 to 1.2 mg V/L between pH 6 and 7 and then levelled off at around 1 mg V/L. When alkalinity (from 75 to 541 mg/L as CaCO<sub>3</sub>) and sulphate (from 54 to 394 mg/L) increased, the acute toxicity of V decreased slightly with LC50s changing from 0.6 to 1.6, and from 0.9 to 1.4, respectively. When the length of V exposure was extended (from 2 to 21 d), only an increase of sulphate from 135 to 480 mg/L caused a slight increase in V toxicity from a LC50 of 0.6 to 0.4 mg V/L, the opposite trend seen in the acute exposures. In addition, the influence of two OSPW representative mixtures of increasing sodium and sulphate, and increasing alkalinity and sulphate on V acute toxicity to *D. pulex* were evaluated; only the mixture of increasing sodium (from 18 to 536 mg/L) and sulphate (from 55 to 242 mg/L) caused a slight decrease in V acute toxicity (LC50 1.0–2.1 mg V/L). Evidence is presented that variations in surface water chemistry can affect V toxicity to daphnids, although only to a small degree (i.e. within a maximum factor of 2 in all cases evaluated here). These relationships should be considered when creating new water quality guidelines or local benchmarks for V. "

**Hudson-Edwards, K.A., Byrne, P., Bird, G., et al. (2019) Origin and Fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley Mine Tailings Spill in British Columbia, Canada. *Environmental Science and Technology*, 53(8): 4088-4098.**

Keywords: Aluminum hydroxide; Catchments; Clay minerals; Iron compounds; Magnetite; Manganese removal (water treatment); Runoff; Silicon compounds; Sols; Tailings; Water; X ray absorption; X ray absorption near edge structure spectroscopy; British Columbia, Canada; Conceptual model; Electron microprobes; Mine tailings dams; Mineral colloids; Pre-edge features; Secondary phasis; X-ray absorption near-edge structure; Manganese compounds

**Abstract:**

Results from the analysis of aqueous and solid-phase V speciation within samples collected from the Hazeltine Creek catchment affected by the August 2014 Mount Polley mine tailings

dam failure in British Columbia, Canada, are presented. Electron microprobe and X-ray absorption near-edge structure (XANES) analysis found that V is present as V<sup>3+</sup> substituted into magnetite and V<sup>3+</sup> and V<sup>4+</sup> substituted into titanite, both of which occur in the spilled Mount Polley tailings. Secondary Fe oxyhydroxides forming in inflow waters and on creek beds have V K-edge XANES spectra exhibiting E<sub>1/2</sub> positions and pre-edge features consistent with the presence of V<sup>5+</sup> species, suggesting sorption of this species on these secondary phases. PHREEQC modeling suggests that the stream waters mostly contain V<sup>5+</sup> and the inflow and pore waters contain a mixture of V<sup>3+</sup> and V<sup>5+</sup>. These data, and stream, inflow, and pore water chemical data, suggest that dissolution of V(III)-bearing magnetite, V(III)- and V(IV)-bearing titanite, V(V)-bearing Fe(-Al-Si-Mn) oxyhydroxides, and V-bearing Al(OH)<sub>3</sub> and/or clay minerals may have occurred. In the circumneutral pH environment of Hazeltine Creek, elevated V concentrations are likely naturally attenuated by formation of V(V)-bearing secondary Fe oxyhydroxide, Al(OH)<sub>3</sub>, or clay mineral colloids, suggesting that the V is not bioavailable. A conceptual model describing the origin and fate of V in Hazeltine Creek that is applicable to other river systems is presented. © Copyright 2019 American Chemical Society.

**Li, H-Y., Yang, Y., Zhang, M., et al. (2019) A novel anion exchange method based on in situ selectively reductive desorption of Cr(VI) for its separation from V(V): Toward the comprehensive use of hazardous wastewater. *Journal of Hazardous Materials*, 368: 670-679.**

Keywords: Anion exchange; Chromium (VI); Separation; Vanadium (V); Wastewater; Desorption; Ethanol; Extraction; Hazards; Negative ions; Physicochemical properties; Recovery; Transition metals; Vanadium pentoxide; Anion-exchange methods; Comprehensive method; Hazardous wastewaters; Organic reductants; Reductive desorption; Simultaneous separation; Vanadium extractions; Chromium compounds; alcohol; chromium; transition element; vanadium; in situ measurement; ion exchange; wastewater treatment; Article; heavy metal removal; metal recovery; physical chemistry; reduction (chemistry); separation technique; China

**Abstract:**

In China, the wastewater produced after vanadate precipitation (AVP wastewater) from industrial vanadium extraction contains toxic V(V) and carcinogenic Cr(VI). When considering environmental protection and wastewater use, V(V) and Cr(VI) must be extracted and separated from the hazardous AVP wastewater. However, separating V(V) and Cr(VI) is difficult because of their highly similar physicochemical properties. Herein, we propose a novel anion exchange method based on the in situ selectively reductive desorption of Cr(VI) to separate and extract V(V) and Cr(VI) using a weak organic reductant (ethanol) to selectively reduce Cr(VI) anions and transform them into Cr<sup>3+</sup> cations, while maintaining V(V) in a H<sub>2</sub>V<sub>10</sub>O<sub>28</sub><sup>4-</sup> anion form. We indicate that the efficient separation of Cr(VI) from V(V) can be attributed to selective Cr(VI) anion reduction via ethanol. We applied this anion exchange method to separate and recover Cr(VI) and V(V) in AVP wastewater with a Cr(VI) recovery of 95.59% and a V(V) recovery of 94.54%. The final Cr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> products had a purity of 98.03% and 96.82%, respectively. This study provides novel insights into the simultaneous separation and extraction of analog transition metals and a comprehensive method to use hazardous wastewater. © 2019 Elsevier B.V.

**Meina, E.G., Raes, K. & Liber, K. (2019) Models for the acute and chronic aqueous toxicity of vanadium to *Daphnia pulex* under a range of surface water chemistry conditions. *Ecotoxicology and Environmental Safety*, 179: 301-309.**

Keywords: Vanadium; Oil sands; OSPW; Water chemistry; Biotic Ligand Model; Oil Sands Coke; Fresh-Water; Ceriodaphnia-Dubia; Naphthenic Acids; Petroleum Coke; Life Stages; Major Ions; Salinity; Sulfate; Environmental Sciences & Ecology; Toxicology

**Abstract:**

Alberta's oil sands petroleum coke (PC) generation has in recent years surpassed 10 million tonnes. Petroleum coke has been proposed as an industrial-scale sorbent to reduce concentrations of organic chemicals in oil sands process-affected water (OSPW). However, PC contains up to 1000 mg of vanadium (V) per kg of PC, and during the treatment it leaches from coke reaching levels of up to 7 mg/L in "treated" OSPW. Little information is available on how common water quality variables affect the toxicity of V to aquatic organisms. Here descriptive relationships are presented to describe how site-specific surface water characteristics representative of the Alberta oil sands region influence the toxicity of V to *Daphnia pulex*. Results revealed that when *D. pulex* was exposed to an increase in pH, a threshold relationship was found where acute V toxicity increased from a lethal median concentration (LC50) of 1.7 to 1.2 mg V/L between pH 6 and 7 and then levelled off at around 1 mg V/L. When alkalinity (from 75 to 541 mg/L as CaCO<sub>3</sub>) and sulphate (from 54 to 394 mg/L) increased, the acute toxicity of V decreased slightly with LC(50)s changing from 0.6 to 1.6, and from 0.9 to 1.4, respectively. When the length of V exposure was extended (from 2 to 21 d), only an increase of sulphate from 135 to 480 mg/L caused a slight increase in V toxicity from a LC50 of 0.6 to 0.4 mg V/L, the opposite trend seen in the acute exposures. In addition, the influence of two OSPW representative mixtures of increasing sodium and sulphate, and increasing alkalinity and sulphate on V acute toxicity to *D. pulex* were evaluated; only the mixture of increasing sodium (from 18 to 536 mg/L) and sulphate (from 55 to 242 mg/L) caused a slight decrease in V acute toxicity (LC50 1.0-2.1 mg V/L). Evidence is presented that variations in surface water chemistry can affect V toxicity to daphnids, although only to a small degree (i.e. within a maximum factor of 2 in all cases evaluated here). These relationships should be considered when creating new water quality guidelines or local benchmarks for V.

**Ramsey, A.B., Faiia, A.M. & Szykiewicz, A. (2019) Eight years after the coal ash spill - Fate of trace metals in the contaminated river sediments near Kingston, eastern Tennessee. *Applied Geochemistry*, 104: 158-167.**

Keywords: Fly-Ash; Fathead Minnow; Selenium; Exposure; Release; Impact; Geochemistry & Geophysics

**Abstract:**

In December 2008, the failure of a coal ash retention pond at the Kingston Fossil Plant in eastern Tennessee, United States contaminated the Emory River and Clinch River located upstream of the Watts Bar Reservoir on the Tennessee River. Despite an extensive cleanup effort, further leaching of metals to river water from residual coal ash remains a cause of concern. Also, it is unknown whether coal ash has undergone substantial burial by younger river sediments. In order to address these uncertainties, in spring 2016 we collected six 30 cm long sediment cores from five contaminated and one uncontaminated portions of the river systems. The cores were subdivided into similar to 2-3 cm sediment layers, which were exposed to water and acid leaching for metal and metalloid analyses. The measured concentrations of arsenic are 10 times higher in the river sediments near the Kingston Plant compared to downstream locations. Using ratios of various metals (e.g., cadmium, chromium, selenium, vanadium) to arsenic, we have established that only arsenic and selenium in downstream sediments are predominantly sourced by coal ash (80-100%). For other metals (e.g., cadmium, chromium, vanadium) coal ash-derived contamination comprises < 20% of the total metal concentrations, which are likely of other anthropogenic origin. Under current

conditions, the ash from the 2008 spill appears to be buried by 13-18 cm of natural sediment in downstream locations. However, elevated ash and metal and metalloid concentrations are still present in the shallow sediments (0-3 cm) in a close proximity to the Kingston Plant, suggesting redistribution of coal ash from further upstream. Overall, much higher concentrations of metals and metalloids were observed in the acid leachates compared to smaller, if any, concentrations in water-soluble fractions, suggesting that they may not be easily released to the water column. Through comparisons of metal and metalloid concentrations in raw coal ash and river sediments that had been in the river for 2 years, it appears that their quantities are similar. This implies that the majority of coal ash associated metals and metalloids are not mobilized by river waters.

**Sabarathinam, C., Bhandary, H. & Al-Khalid, A. (2019) A geochemical analogy between the metal sources in Kuwait Bay and territorial sea water of Kuwait. *Environmental Monitoring and Assessment*, 191(3): 142.**

Keywords: Desalination; Domestic sewage; Dust fall; Heavy metal evaluation index; Pollution; Contamination; Effluents; Heavy metals; Petroleum analysis; Sewage; Suspended sediments; Distribution of metal; Heavy metal evaluations; Metal concentrations; Metal contamination; Metal sources; Oxidation reduction cycles; Predominant control; Seawater; aluminum; arsenic; barium; beryllium; boron; cadmium; chromium; cobalt; iron; lead; lithium; manganese; mercury; metal; molybdenum; nickel; petroleum; sea water; selenium; strontium; vanadium; zinc; heavy metal; adsorption; domestic waste; dust; geochemistry; leaching; marine pollution; spatial distribution; suspended sediment; Article; bay; comparative study; environmental factor; environmental parameters; geochemical analysis; geographic distribution; Kuwait; oxidation reduction reaction; seashore; sewage effluent; trend study; water analysis; water contamination; analysis; chemistry; environmental monitoring; sea; sediment; water pollutant; Kuwait Bay; Kuwait [Middle East]; Bays; Geologic Sediments; Metals, Heavy; Oceans and Seas; Water Pollutants, Chemical

**Abstract:**

The sea water serves as a source for desalination and shelter for dependent biota. To understand the sources of metal in Kuwait Bay and the open sea, samples were collected and analyzed for metals like B, Li, Sr, Hg, Pb, Ba, Fe, Zn, Mn, Be, Cd, Co, Cr, Ni, Se, V, Al, Mo, and As. The comparison of Bay and Seawater shows that most of the metals were higher in sea water. Samples were collected in two different transects in the territorial sea water (TSW), the northern, and the southern transects. The heavy metal evaluation index and degree of contamination calculated for Bay and TSW show that they are contaminated, and the degree was higher in TSW. The variation of metal concentration along the transects in TSW reflects three different behaviors; (1) few metals decrease from the shore, (2) few increase from the shore, and (3) others show no significant trend. The statistical analysis of the data shows a representation of five factors for bay water and six for TSW indicating the complexity in sources of metal in TSW. The analysis infers the metal contamination due to petroleum products, and oxidation-reduction cycles are predominant in TSW. But, tidal influence along with dustfall plays a key role in the metal contamination of bay waters. Apart from these, desalination rejects and domestic sewage effluents are common sources contributing metals to both the environment. It is also observed that the suspended sediments play a significant role in the leaching, adsorption, and distribution of metals. The extraneous process has a predominant control over the distribution of the metals in TSW than the Bay. © 2019, Springer Nature Switzerland AG.

**Signa, G., Calizza, E., Costantini, M.L., et al. (2019) Horizontal and vertical food web structure drives trace element trophic transfer in Terra Nova Bay, Antarctica. *Environmental Pollution*, 246: 772-781.**

Keywords: Biomagnification; Metal; Polar; Stable isotopes; Sympagic algae; Biogeochemistry; Biological materials; Drives; Dynamics; Ecology; Isotopes; Metals; Organic compounds; Sea ice; Trace elements; Benthic invertebrates; Carbon and nitrogen; Organic matter source; Primary consumers; Secondary consumers; Climate change; cadmium; carbon 13; chromium; cobalt; copper; lead; mercury; nickel; nitrogen 15; organic matter; stable isotope; trace element; vanadium; alga; bioaccumulation; carbon isotope; food web; nitrogen isotope; trophic structure; Antarctica; Article; benthos; bird; controlled study; dilution; fish; nonhuman; plankton; sediment; trophic level; zooplankton; animal; bay; Bayes theorem; biota; environmental monitoring; food chain; invertebrate; metabolism; procedures; water pollutant; East Antarctica; Ross Sea; Southern Ocean; Terra Nova Bay; algae; Aves; Invertebrata; Animals; Antarctic Regions; Bays; Fishes; Invertebrates; Water Pollutants, Chemical

#### **Abstract:**

Despite a vast amount of literature has focused on trace element (TE) contamination in Antarctica during the last decades, the assessment of the main pathways driving TE transfer to the biota is still an overlooked issue. This limits the ability to predict how variations in sea-ice dynamics and productivity due to climate change will affect TE allocation in the food web. Here, food web structure of Tethys Bay (Terra Nova Bay, Ross Sea, Antarctica) was first characterised by analysing carbon and nitrogen stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) in organic matter sources (sediment and planktonic, benthic and sympagic primary producers) and consumers (zooplankton, benthic invertebrates, fish and birds). Diet and trophic position were also characterised using Bayesian mixing models. Then, relationships between stable isotopes, diet and TEs (Cd, Cr, Co, Cu, Hg, Ni, Pb and V) were assessed in order to evaluate if and how horizontal (organic matter pathways) and vertical (trophic position) food web features influence TE transfer to the biota. Regressions between  $\log[\text{TE}]$  and  $\delta^{13}\text{C}$  revealed that the sympagic pathway drives accumulation of V in primary consumers and Cd and Hg in secondary consumers, and that a coupled benthic/pelagic pathway drives Pb transfer to all consumers. Regressions between  $\log[\text{TE}]$  and  $\delta^{15}\text{N}$  showed that only Hg biomagnifies across trophic levels, while all the others TEs showed a biodilution pattern, consistent with patterns observed in temperate food webs. Although the Cd behavior needs further investigations, the present findings provide new insights about the role of basal sources in the transfer of TEs in polar systems. This is especially important nowadays in light of the forecasted trophic changes potentially resulting from climate change-induced modification of sea-ice dynamics. © 2018 Elsevier Ltd Depiction of trace element transfer in the Antarctic food web highlighted an important role of both sympagic and pelagic pathways, suggesting that forecasted modification of sea-ice dynamics due to climate change may alter contaminant accumulation and biomagnification patterns. © 2018 Elsevier Ltd.

**Smalling, K.L., Anderson, C.W., Honeycutt, R.K., et al. (2019) Associations between environmental pollutants and larval amphibians in wetlands contaminated by energy-related brines are potentially mediated by feeding traits. *Environmental Pollution*, 248: 260-268.**

Keywords: Amphibian; Brines; Energy development; Metals; Prairie Pothole Region; Wetland; Aquatic organisms; Bioaccumulation; Chlorine compounds; Contamination; Histology; Selenium; Sodium compounds; Strontium; Sustainable development; Tissue; Vanadium; Volatile organic compounds; Wastewater disposal; Wetlands; Contamination history; Elevated concentrations; Environmental pollutants; Metals and metalloids; Physical chemical property; Prairie potholes; Sediments; antimony; chloride; hydrocarbon; lead; mercury; radioisotope; sodium; volatile organic compound; brine; concentration (composition); feeding behavior; heavy metal; larva; marine sediment; power generation; Ambystoma; Ambystoma

mavortium; Amphibia; Artemia; Article; biological trait; concentration (parameter); correlational study; energy yield; exposure; feeding; Montana; nonhuman; North Dakota; pollutant; Pseudacris; Pseudacris maculata; Rana pipiens; reduction (chemistry); salamander; waste water; water contamination; Williston Basin; Lithobates; Salamandroidea

**Abstract:**

Energy production in the Williston Basin, located in the Prairie Pothole Region of central North America, has increased rapidly over the last several decades. Advances in recycling and disposal practices of saline wastewaters (brines) co-produced during energy production have reduced ecological risks, but spills still occur often and legacy practices of releasing brines into the environment caused persistent salinization in many areas. Aside from sodium and chloride, these brines contain elevated concentrations of metals and metalloids (lead, selenium, strontium, antimony and vanadium), ammonium, volatile organic compounds, hydrocarbons, and radionuclides. Amphibians are especially sensitive to chloride and some metals, increasing potential effects in wetlands contaminated by brines. We collected bed sediment and larval amphibians (*Ambystoma mavortium*, *Lithobates pipiens* and *Pseudacris maculata*) from wetlands in Montana and North Dakota representing a range of brine contamination history and severity to determine if contamination was associated with metal concentrations in sediments and if metal accumulation in tissues varied by species. In wetland sediments, brine contamination was positively associated with the concentrations of sodium and strontium, both known to occur in oil and gas wastewater, but negatively correlated with mercury. In amphibian tissues, selenium and vanadium were associated with brine contamination. Metal tissue concentrations were higher in tadpoles that graze compared to predatory salamanders; this suggests frequent contact with the sediments could lead to greater ingestion of metal-laden materials. Although many of these metals may not be directly linked with energy development, the potential additive or synergistic effects of exposure along with elevated chloride from brines could have important consequences for aquatic organisms. To effectively manage amphibian populations in wetlands contaminated by saline wastewaters we need a better understanding of how life history traits, species-specific susceptibilities and the physical-chemical properties of metals co-occurring in wetland sediments interact with other stressors like chloride and wetland drying. Metals in wetland sediments were not associated with brines but larval amphibians' feeding traits mediate tissue-metal accumulation in wetlands contaminated by energy-related brines. © 2019.

**Soltani, N., Moore, F., Keshavarzi, B., et al. (2019) Potentially toxic elements (PTEs) and polycyclic aromatic hydrocarbons (PAHs) in fish and prawn in the Persian Gulf, Iran. *Ecotoxicology and Environmental Safety*, 173: 251-265.**

Keywords: Fish; Human health risk assessment; Persian Gulf; Polycyclic aromatic hydrocarbon; Potentially toxic element; Prawn; arsenic; cadmium; chromium; cobalt; copper; fluorene; lead; manganese; mercury; naphthalene; nickel; phenanthrene; selenium; potentially toxic element; toxic substance; unclassified drug; vanadium; zinc; heavy metal; concentration (composition); crustacean; food intake; hazard assessment; health risk; PAH; risk assessment; animal tissue; Article; bioaccumulation; controlled study; *Coptodon zillii*; food contamination; health hazard; Iran; *Leuciscus vorax*; *Liza abu*; maximum permissible dose; *Metapenaeus affinis*; muscle tissue; nonhuman; *Penaeus semisulcatus*; sea food; shrimp; adult; analysis; animal; child; Decapoda (Crustacea); environmental monitoring; estuary; human; Indian Ocean; river; water pollutant; Arabian Sea; Khuzestan; Musa Estuary; Shatt al Arab; *Leuciscus*; *Musa*; Animals; Estuaries; Fishes; Humans; Metals, Heavy; Polycyclic Aromatic Hydrocarbons; Rivers; Seafood; Water Pollutants, Chemical

**Abstract:**

This study aimed to speciate and quantify potentially toxic elements (PTEs) and polycyclic aromatic hydrocarbons (PAHs), in addition to estimate potential human health risk of PTEs (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn) through the consumption of three edible fish species (*Leuciscus vorax*, *Liza abu*, and *Coptodon zillii*) and two prawn species (*Metapenaeus affinis* and *Penaeus semisulcatus*) collected from Arvand River and Musa Estuary in the Persian Gulf. The concentration of As in prawn species exceeded permissible limit set by international organizations. PAHs were dominated by low molecular weight species such as naphthalene, phenanthrene, and fluorene but generally exhibited low mean concentrations in fish and prawn samples. The human health hazard posed by PTEs was assessed using methods that consider estimated daily intake (EDI), estimated weekly intake (EWI), target hazard quotients (THQ), and combined THQ. The results suggested that elevated As concentrations in almost all prawn samples may pose a probable health hazard to local inhabitants. © 2019 Elsevier Inc.

**Wang, J. (2019) Short-term geochemical investigation and assessment of dissolved elements from simulated ash reclaimed soil into groundwater. *Environmental Pollution*, 247: 302-311.**

Keywords: Ash reclaimed soil; Assessment; Groundwater; Leaching; Multivariate statistical analysis; Cluster analysis; Flow velocity; Fly ash; Geochemistry; Health risks; Multivariate analysis; Potable water; Quality control; Reclamation; Soils; Water quality; Dissolved element; Geochemical investigations; Geochemical partitioning; Leaching behavior; Reclaimed soil; Sampling stations; Land reclamation; aluminum; antimony; arsenic; cadmium; carbon monoxide; chromium; copper; ground water; iron; lead; magnesium; manganese; nickel; tin; vanadium; zinc; heavy metal; assessment method; multivariate analysis; soil remediation; Article; ash; concentration (parameter); environmental impact assessment; environmental monitoring; flow rate; geochemical analysis; simulation; water contamination; water pollutant; water sampling; analysis; chemistry; soil; soil pollutant; Coal Ash; Metals, Heavy; Soil Pollutants

**Abstract:**

A soil column migration trough was used to study the leaching behavior and geochemical partitioning of fifteen elements Al, As, Cr, Cu, Fe, Mg, Sn, Sb, Zn, V, Co, Mn, Pb, Ni and Cd in simulated ash reclaimed soil. According to the results of cluster analysis for the sampling stations, there were three clusters: Cluster 1 of 7 wells with relative good groundwater quality originated from the background control area, Cluster 2 of 9 wells with worst groundwater quality in the downstream parts of the simulated ash reclaimed soil, and Cluster 3 of 2 wells with representative of samples influenced by the combined effect of injection of leaching solution and the main current. Statistical analysis identified five factor types that accounted for 83.055% of the total variance, which declined in the order: ash-soil rate > leaching intensity > water depths > flow velocity > leaching time. As, Sb, Cd, Pb and Ni were the dominant contaminants. The water around ash reclaimed soil was unsuitable for drinking. As, Mn, Cd, Sb, Co and V were the largest contributors to health risks. Soils reclaimed with fly ash can consequently be a long-time source for the transfer of toxic elements into groundwater. © 2019 Elsevier Ltd.

**Windom, H.L. (2019) Elemental composition of suspended particles across the southeastern continental shelf off the coast of North Florida and South Georgia: Provenance, transport, fate and implications to mid-outer shelf water column processes. *Continental Shelf Research*, 178: 27-40.**

Keywords: Suspended particles; Trace metals; Alkaline earths; Rare earths; Transition metals; Southeastern US Atlantic shelf; Trace-Metal Composition; Atlantic Bight; Benthic

Foraminifera; Spatial; Variability; SR/CA Ratios; Ocean; Iron; Barium; Acantharians; Productivity; Oceanography

**Abstract:**

This paper reports on the chemistry of suspended particulates collected in waters of the southeastern US continental shelf off the coasts of North Florida and South Georgia. Approximately 350 suspended sediment samples were analyzed for particulate organic carbon and nitrogen (POC and PON), particulate aluminum and calcium and a suite of trace metals which included particulate alkaline earths (magnesium, strontium, barium), particulate rare earth metals (lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium and dysprosium), particulate transition metals (cobalt, copper, iron, manganese, nickel, scandium, titanium and vanadium) and others: particulate cadmium, zinc, thorium and uranium. The samples were collected in the fall of 1987 during a multidiscipline expedition (FLEX) focused on cross shelf exchange of water and materials during northward wind stress and fall Gulf Stream intrusions. Although samples were analyzed shortly after collection, archived data have not been previously presented. Results are interpreted with regard to how they relate to particle provenance, transport and fate. Results indicate that significant influence of terrestrial sources of suspended particles is limited to the inner shelf, however the concentrations of some metals, such as rare earths, appear to reflect this provenance across the entire shelf. Mid-outer shelf particles are dominated by re-suspended biogenic carbonates and biogenic organic carbon rich particles formed in response to Gulf Stream upwelled nutrients. Particulate trace element concentrations and primary production in mid-outer shelf waters are interpreted as a response to not only nutrient, but also trace metal enrichment of upwelled Gulf Stream water intruded onto the shelf. Based on particle chemistry, micro nutrients such as Fe in upwelled waters may be limiting in sustaining mid-outer shelf production. Other trace metals such as Sc appear to be enriched due to adsorption on organic rich particles. And the formation SrSO<sub>4</sub> particles, originating from Acantharian spicules, appear to create an environment for the precipitation of barite in outer shelf surface waters.

**Zhang, B., Wang, S., Diao, M., et al. (2019) Microbial Community Responses to Vanadium Distributions in Mining Geological Environments and Bioremediation Assessment. *Journal of Geophysical Research: Biogeosciences*, 124(3): 601-615.**

Available at: <http://www.cugb.edu.cn/uploadCms/file/20600/20190430112825708780.pdf>

Keywords: vanadium; biogeochemical process; bioremediation; microbial community; geological environment

**Abstract:**

Vanadium mining activities can cause contamination of the surrounding geological environment. Vanadium may exist in multiple matrices due to its migration and transformation, forming interactive relationships; however, the connection between vanadium distributions in multiple matrices and microbial community responses remains largely unknown. Vanadium is a redox-sensitive metal that can be microbiologically reduced and immobilized. To date, bioremediation of vanadium-contaminated environments by indigenous microorganisms has rarely been evaluated. This paper reports a systematic investigation into vanadium distributions and microbial communities in soils, water, and sediment from Panzhihua, China. Large vanadium contents of  $1130.1 \pm 9.8$  mg/kg and  $0.13 \pm 0.02$  mg/L were found in surface soil and groundwater. Vanadium in surface water tended to precipitate. Microbial communities isolated from similar environments were alike due to similarity in matrix chemistry whereas communities were distinct when compared to different matrices, with lower richness and diversity in groundwater. Proteobacteria was

distributed widely and dominated microbial communities within groundwater. Redundancy analysis shows that vanadium and nutrients significantly affected metal-tolerant bacteria. Long-term cultivation (240 days) suggests the possibility of vanadium bioremediation by indigenous microorganisms, within acid-soluble fraction. This active fraction can potentially release mobile vanadium with shifted redox conditions. Vanadium (V) was bio-reduced to less toxic, mobile vanadium (IV) primarily by enriched *Bacillus* and *Thauera*. This study reveals the biogeochemical fate of vanadium in regional geological environments and suggests a bioremediation pathway via native vanadium-reducing microbes.

## 8. MISCELLANEOUS

**Di Carlo, E., Boullemant, A. & Courtney, R. (2019) A field assessment of bauxite residue rehabilitation strategies. *Science of the Total Environment*, 663: 915-926.**

Keywords: Field sampling; Mine tailings; Plant-availability; Revegetation; Soil extraction; Alkalinity; Alumina; Aluminum oxide; Antennas; Nutrients; pH; Soil conservation; Soils; Sustainable development; Tailings; Trace elements; Vegetation; Elevated concentrations; Plant availability; Rehabilitation programs; Rehabilitation strategy; Soil physico-chemical properties; Soil pollution; aluminum; arsenic; calcium sulfate; chromium; iron; mercury; nickel; sodium; trace element; vanadium; assessment method; bauxite; concentration (composition); environmental risk; field survey; soil amendment; aluminum factory; Article; concentration (parameter); controlled study; ecosystem restoration; environmental sustainability; industrial waste; nutrient availability; physical chemistry; priority journal; soil property; soil quality; summer; waste disposal; winter

### **Abstract:**

Bauxite residue, the by-product of the alumina industry, is mainly stored in land-based bauxite residue disposal areas (BRDAs). Environmental concern has been raised due to the large volumes in stockpile, the high alkalinity of the material, as well as the presence of elevated concentrations of trace elements. If not adequately managed, BRDAs can act as a source of pollution. In order to minimize the environmental risk, revegetation is implemented to stabilize the residue against water and wind erosion. Currently, two main approaches are used: the use of amendments or the installation of a capping layer. However, few studies evaluating the long-term success and self-sustainability of the rehabilitation programs have been published. A series of field-established rehabilitation strategies reflecting both direct revegetation and revegetation on capping layer were assessed in terms of both soil and plant quality. Soil physico-chemical properties, including pseudo-total and plant-available fractions of nutrients and trace elements, were determined over a summer and winter seasons and aerial portions of vegetation were analysed for nutrients and trace elements. Failure to adequately lower alkalinity remains the major constraint to long-term rehabilitation success of bauxite residue. This is evidenced from poor soil properties in unamended residue and in residue capped with a shallow soil layer, as well from vegetation displaying excessive concentrations of certain elements. Certain elements exceeded typical ranges for non-contaminated soils (i.e. Cr, Fe, Na, Ni and V), with some showing excessive plant-available fractions (i.e. of Al, As, Cr, Hg and V). Vegetation analysis found excessive uptake of some elements (i.e. of Al, Na, Fe, Cr and V). Future attempts for bauxite residue rehabilitation should include both gypsum and organic amendments, while a capping layer may only be effective if either a deep layer (>1 m) is installed or if the underlying residue is sufficiently treated prior to capping. © 2019.

**Fajardo, C., Costa, G., Nande, M., et al. (2019) Heavy metals immobilization capability of two iron-based nanoparticles (nZVI and Fe<sub>3</sub>O<sub>4</sub>): Soil and freshwater bioassays to assess ecotoxicological impact. *Science of the Total Environment*, 656: 421-432.**

Keywords: Ecotoxicological bioassays; Heavy metals; Iron-based nanoparticles; Nanoremediation; Aquatic organisms; Biomarkers; Iron; Iron oxides; Magnetite; Metal nanoparticles; Remediation; Soil conservation; Soils; Toxicity; Vanadium compounds; Antagonistic interactions; *Caenorhabditis elegans*; Ecotoxicological bioassays; Ecotoxicological risks; Heavy metals pollution; Iron-based; Zero-valent iron nanoparticles; Soil pollution; cadmium; fresh water; iron nanoparticle; lead; ultrasmall superparamagnetic iron oxide; zinc; metal nanoparticle; bioassay; ecotoxicology; heavy metal; immobilization; nanoparticle; soil remediation; Article; ecotoxicity; mining; phytoplankton; priority journal; soil; toxicity testing; analysis; animal; chemistry; drug effect; *Microcystis*; procedures; risk assessment; *Scenedesmus*; sewage; soil pollutant; *Vibrio*; waste water; water pollutant; Animals; Soil Pollutants; Toxicity Tests; Waste Disposal, Fluid; Water Pollutants, Chemical

**Abstract:**

The contamination by heavy metals constitutes an environmental problem of great importance in the last decades, and demands of society for clean environments are increasingly evident. To achieve this goal, several strategies have appeared for the in situ remediation of soil contamination caused by heavy metals. This study evaluated two types of iron-based nanoparticles, zero-valent iron nanoparticles (nZVI) and Fe<sub>3</sub>O<sub>4</sub> nanoparticles, for the effective immobilization of heavy metals. Furthermore, we conducted a set of ecotoxicological bioassays: Microtox<sup>®</sup> Test, *Caenorhabditis elegans* Test, and Phytoplankton Toxicity Tests, on selected soil and aquatic test organisms to both, i) evaluate the potential ecotoxicological risks associated with nanoparticles treatment, and ii) to define sensitive organisms to be used as suitable bioindicators of heavy metals pollution. The application of 5% nZVI significantly reduced the amount of bioavailable heavy metals, which was effective from an ecotoxicity point of view as a reduction of the toxicity of was observed. Among the bioassays used, *C. elegans* seems the most effective reference organism in detecting changes in the toxicity of and therefore, *C. elegans* was found to be a sensitive heavy metals pollution bioindicator. When the Combination index (CI) was obtained to determine combined heavy metals interactions, the results indicated that toxicity would be higher than that expected for Pb, Cd and Zn individually considered, due to the proved antagonistic interactions of those toxicants. The obtained results suggested that nZVI nanoparticles are susceptible to be used as a soil remediation strategy for heavy metal pollution, although a short reactive lifespan must be considered, and therefore its effectiveness in long periods remains to be elucidated. © 2018.

**Feder, D., Gahan, L.R., McGeary, R.P., et al. (2019) The Binding Mode of an ADP Analogue to a Metallohydrolase Mimics the Likely Transition State. *Chembiochem*, 20(12): 1536-1540.**

Keywords: catalysis; metallohydrolases; osteoporosis; purple acid phosphatase; transition states; X-ray crystallography

**Abstract:**

Purple acid phosphatases (PAPs) are members of the large family of metallohydrolases, a group of enzymes that perform a wide range of biological functions, while employing a highly conserved catalytic mechanism. PAPs are found in plants, animals and fungi; in humans they play an important role in bone turnover and are thus of interest for developing treatments for osteoporosis. The majority of metallohydrolases use a metal-bound hydroxide to initiate catalysis, which leads to the formation of a proposed five-coordinate oxyphosphorane species in the transition state. In this work, we crystallized PAP from red kidney beans (rkbPAP) in the presence of both adenosine and vanadate. The in crystallo-formed vanadate analogue of ADP provides detailed insight into the binding mode of a PAP substrate, captured in a structure that mimics the putative five-coordinate transition state. Our observations not only provide unprecedented insight into the mechanism of metallohydrolases, but might also guide the

structure-based design of inhibitors for application in the treatment of several human illnesses. © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Fetter, N., Blichert-Toft, J., Telouk, P., et al. (2019) Extraction of Pb and Zn from crude oil for high-precision isotopic analysis by MC-ICP-MS. *Chemical Geology*, 511: 112-122.**

Keywords: Crude oil; Pb isotopes; Zn isotopes; MC-ICP-MS; Aqueous extraction; Lead; Metals; Ratios; Emulsions; Evolution; Vanadium; Zinc; Metalloids; Petroleum; Gasoline; Geochemistry & Geophysics

**Abstract:**

Radiogenic and stable isotopic tracing of crude oils has not so far been undertaken, largely because of the difficulties of dealing with the low trace element contents of oil samples for high-precision isotopic measurements. Here, we present a novel analytical protocol that allows for precise and accurate determination of radiogenic Pb and stable Zn isotopic compositions on as little as 5 ml of crude oil from a variety of geographically, geologically, and environmentally diverse settings. The 41 Pb and Zn samples measured to validate the new protocol were separated from their respective crude oils by liquid-liquid extraction into an aqueous phase readily handled in a clean laboratory for subsequent purification of Pb and Zn by standard anion-exchange column chromatography. Lead and Zn isotopic compositions on the same 5 ml sample of crude oil were obtained by MC-ICP-MS on 95% of the total extracted Pb and Zn, while elemental concentrations were measured by Q-ICP-MS on 5% aliquots. To the best of our knowledge, the present technique is the first efficient procedure for Pb and Zn isotopic analysis of crude oil, which, owing to the elimination of the organic fraction at the liquid-liquid extraction stage, does not require any specialized equipment, neither for the wet chemistry nor for the mass spectrometry. The high extraction yields of the method and the low detection limits and high sensitivity of, respectively, Q-ICP-MS and MC-ICP-MS permit analysis of very small sample quantities (down to 2 ng and 100 ng, respectively, of Pb and Zn for isotopic analysis, and a few hundred pg for abundance measurements). Reproducibility is on a par with routine state-of-the-art Pb and Zn isotopic measurements of other types of geological materials, while total procedural blanks for both elements are negligible relative to the amounts of Pb and Zn typically separated from crude oil.

**Fey, P., Bustamante, P., Bosserelle, P., et al. (2019) Does trophic level drive organic and metallic contamination in coral reef organisms? *Science of the Total Environment*, 667: 208-221.**

Keywords: Biomagnification; Bioreduction; Nitrogen stable isotope; PCBs; Pesticides; Serranidae; Trace elements; Insecticides; Polychlorinated biphenyls; Reefs; Zinc; Bio reductions; Coral reef communities; Metallic contamination; Metallic trace elements; Trace element concentrations; Organic pollutants; aldrin; cadmium; carbon monoxide; chlordecone; chromium; copper; dimpylate; endosulfan; heptachlor; iron; lead; manganese; mercury; nickel; nitrogen 15; organic compound; organic matter; organometallic compound; pesticide; selenium; trace element; vanadium; metal; polychlorinated biphenyl; bioaccumulation; coral reef; heavy metal; marine pollution; nitrogen isotope; organic pollutant; PCB; perciform; stable isotope; trophic level; Article; benthos; biomagnetism; bioremediation; concentration (parameter); controlled study; correlational study; geographic distribution; marine species; nonhuman; Pacific islands; predictive value; priority journal; water contamination; animal; aquatic species; bass; food chain; metabolism; New Caledonia; Polynesia; water pollutant; New Caledonia [Melanesia]; Switzerland; Valais; Anthozoa; Invertebrata; Animals; Aquatic Organisms; Coral Reefs; Metals; Organic Chemicals; Water Pollutants, Chemical

**Abstract:**

Metallic and organic pollutants constitute a serious threat for coral reef ecosystems, potentially affecting a great number of species interacting within complex trophodynamic processes. Pesticides, PCBs and trace elements were measured on coral reef communities of three Pacific islands (Moorea, Wallis and New Caledonia) in relation with  $\delta^{15}\text{N}$  values, a proxy of trophic level. Several potential sources of organic matter, benthic invertebrates and fish belonging to various trophic strategies were sampled at each island. Wallis and New Caledonia displayed, respectively, the highest concentrations of pesticides and trace elements. In the three islands, most trace element concentrations (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and V) decreased when  $\delta^{15}\text{N}$  was rising (i.e. bioreduction), whereas Hg and Se biomagnified with increasing  $\delta^{15}\text{N}$  values. Only few trace elements in some islands did not show any significant trend in relation with  $\delta^{15}\text{N}$  (i.e., Ag in New Caledonia, Zn in Wallis and As plus Zn in Moorea). PCBs concentrations showed a significant bioreduction in New Caledonia and in Moorea, but a significant biomagnification in Wallis. Aldrin and heptachlor were the only pesticides to show a similar significant bioreduction in the three islands. Other pesticides, such as chlordecone, diazinon, endosulfan I and II, heptachlor-epoxide A and B, lindane and pp'-DDE displayed contrasted patterns (e.g. chlordecone significantly biomagnified in New Caledonia, significantly bioreduced in Wallis and did not display any significant trend in Moorea). Finally, for unclear reasons, Moorea displayed only negative significant correlations between  $\delta^{15}\text{N}$  and all pesticides (except pp'-DDT). Our results highlight that trophic level, here assessed through  $\delta^{15}\text{N}$  values, is a good predictor of metallic trace elements biomagnification or bioreduction in coral reef organisms. However, at large spatial scale, trophic level relevance to predict pesticides and PCBs biomagnification or bioreduction should be considered with caution and studied in close relation with local characteristics. © 2019 Elsevier B.V.

**Gao, J-D., Zhang, J-L., Zhu, X., et al. (2019) Detailed surface analysis of V-defects in GaN films on patterned silicon(111) substrates by metal– organic chemical vapour deposition. *Journal of Applied Crystallography*, 52: 637-642.**

Keywords: Gallium nitride; Threading dislocations; Transmission electron microscopy; Chemical analysis; Chemical vapor deposition; Growth rate; High resolution transmission electron microscopy; III-V semiconductors; Organic chemicals; Silicon; Surface analysis; Chemical vapour deposition; Crystal face; Growth conditions; Growth mechanisms; Lateral growth; Patterned silicon; Spontaneous growth; Threading dislocation; Vanadium compounds

**Abstract:**

The growth mechanism of V-defects in GaN films was investigated. It was observed that the crystal faces of both the sidewall of a V-defect and the sidewall of the GaN film boundary belong to the same plane family of {1011}, which suggests that the formation of the V-defect is a direct consequence of spontaneous growth like that of the boundary facet. However, the growth rate of the V-defect sidewall is much faster than that of the boundary facet when the V-defect is filling up, implying that lateral growth of {1011} planes is not the direct cause of the change in size of V-defects. Since V-defects originate from dislocations, an idea was proposed to correlate the growth of V-defects with the presence of dislocations. Specifically, the change in size of the V-defect is determined by the growth rate around dislocations and the growth rate around dislocations is determined by the growth conditions. © 2019 International Union of Crystallography.

**Garg, N. & Kashyap, L. (2019) Joint effects of Si and mycorrhiza on the antioxidant metabolism of two pigeonpea genotypes under As (III) and (V) stress. *Environmental Science and Pollution Research*, 26(8): 7821-7839.**

Keywords: Arbuscular mycorrhiza; Arsenate; Arsenite; Ascorbate-glutathione pool; Oxidative burden; Silicon; antioxidant; biomass; concentration (composition); contaminated land; fungus; genotype; metabolism; oxidation; phytotoxicity; silica; soil pollution; vanadium; *Cajanus cajan*; Fungi; Pusa; *Rhizophagus*; arsenic; arsenic acid; arsenic acid derivative; arsenic trioxide; arsenous acid derivative; ascorbic acid; glutathione; *Cajanus*; Glomeromycota; mycorrhiza; physiology; plant development; plant root; soil pollutant; symbiosis; toxicity; Antioxidants; Arsenates; Arsenites; Mycorrhizae; Plant Roots; Soil Pollutants

**Abstract:**

Arsenic (As) is the most hazardous soil contaminant, which inactivates metabolic enzymes and restrains plant growth. To withstand As stress conditions, use of some alleviative tools, such as arbuscular mycorrhizal (AM) fungi and silicon (Si), has gained importance. Therefore, the present study evaluated comparative and interactive effects of Si and arbuscular mycorrhiza-*Rhizophagus irregularis* on phytotoxicity of arsenate (As V) and arsenite (As III) on plant growth, ROS generation, and antioxidant defense responses in pigeonpea genotypes (Tolerant-Pusa 2002; Sensitive-Pusa 991). Roots of As III treated plants accumulated significantly higher total As than As V supplemented plants, more in Pusa 991 than Pusa 2002, which corresponded to proportionately decreased plant growth, root to biomass ratio, and oxidative burst. Although Si nutrition and AM inoculations improved plant growth by significantly reducing As uptake and the resultant oxidative burst, AM was relatively more efficient in upregulating enzymatic and non-enzymatic antioxidant defense responses as well as ascorbate–glutathione pathway when compared with Si. Pusa 2002 was more receptive to Si nourishment due to its ability to establish more efficient mycorrhizal symbiosis, which led to higher Si uptake and lower As concentrations. Moreover, +Si+AM bestowed better metalloid resistance by further reducing ROS and strengthening antioxidants. Results demonstrated that the genotype with more efficient AM symbiosis in As-contaminated soils could accrue higher benefits of Si fertilization in terms of metalloid tolerance in pigeonpea. © 2019, Springer-Verlag GmbH Germany, part of Springer Nature.

**Griboff, J., Baroni, M.V., Horacek, M., et al. (2019) Multielemental + isotopic fingerprint enables linking soil, water, forage and milk composition, assessing the geographical origin of Argentinean milk. *Food Chemistry*, 283: 549-558.**

Keywords: Geographical origin; Isotopic fingerprint; Milk provenance; Trace elements; Potable water; Soils; Canonical correlation analysis; Environmental matrixes; Generalized procrustes analysis; Geographical origins; Milk composition; Production area; Isotopes; aluminum; arsenic; carbon 13; cobalt; drinking water; hydrogen; magnesium; mercury; molybdenum; nickel; nitrogen 15; oxygen 18; proton; rubidium; selenium; sodium; strontium; vanadium; isotope; metal; Argentina; Article; chemical procedures; chemometrics; correlation analysis; elemental analysis; food analysis; food composition; food web; forage; milk; soil; soil property; animal; chemistry; procedures; statistics and numerical data; Animals; Metals

**Abstract:**

The aim of this work was to verify the usefulness of multielemental and isotopic fingerprint to differentiate the origin of milk samples from different areas, linking milk fingerprint with those corresponding to soil, water, and forage. Samples from four production areas in Argentina were analysed: 26 elements,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ . Milk provenance was assessed using 16 variables (Na, Mg, Al, V, Co, Ni, As, Se, Rb, Sr, Mo, Hg,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  and K/Rb). Generalized Procrustes Analysis (GPA) demonstrated the consensus between soil, water, forage and milk, in addition to differences between studied areas. Canonical Correlation Analysis (CCA) demonstrated significant correlations between the milk-drinking water, milk-

forage, and milk-soil. So far, we report a feasible method to establish the milk provenance, assessing the follow up from environmental matrixes (soil + water) to dairy products through the food web (forage) by a combined chemical-isotopic fingerprint. © 2019 Elsevier Ltd.

**Halevas, E., Nday, C.M., Eleftheriadou, D., et al. (2019) Synthesis and encapsulation of V(IV,V) compounds in silica nanoparticles targeting development of antioxidant and antiradical nanomaterials. *Journal of Inorganic Biochemistry*, 194: 180-199.**

Keywords: Antioxidant-antiradical activity; Hydroxycarboxylic acid; Oxidative stress; Silica nanoparticles; Sol-gel encapsulation-release; Vanadium complex synthesis

**Abstract:**

The quest for effective treatments of oxidative stress has concentrated over the years on new nanomaterials with improved antioxidant and antiradical activity, thereby attracting broad research interest. In that regard, research efforts in our lab were launched to pursue such hybrid materials involving a) synthesis of silica gel matrices, b) evaluation of the suitability of atoxic matrices as potential carriers for the controlled release of V(IV)(VOSO<sub>4</sub>), V(V)(NaVO<sub>3</sub>) compounds and a newly synthesized heterometallic lithium-vanadium(IV,V) tetranuclear compound containing vanadium-bound hydroxycarboxylic 1,3-diamine-2-propanol-N,N',N'-tetraacetic acid (DPOT), and c) investigation of structural and textural properties of silica nanoparticles (NPs) by different and complementary characterization techniques, inquiring into the nature of the encapsulated vanadium species and their interaction with the siloxane matrix, collectively targeting novel antioxidant and antiradical nanomaterials biotechnology. The physicochemical characterization of the vanadium-loaded SiO<sub>2</sub> NPs led to the formulation of optimized material configuration linked to the delivery of the encapsulated antioxidant-antiradical load. Entrapment and drug release studies showed a) the competence of hybrid nanoparticles with respect to encapsulation efficiency of the vanadium compound (concentration dependence), b) congruence with the physicochemical features determined, and c) a well-defined release profile of NP load. Antioxidant properties and the free radical scavenging capacity of the new hybrid materials (containing VOSO<sub>4</sub>, NaVO<sub>3</sub>, and V-DPOT) were demonstrated through a) 2-diphenyl-1-picrylhydrazyl (DPPH) free radical, and b) intracellular-extracellular reactive oxygen species (ROS) assays, through UV-Visible spectroscopy techniques, collectively showing that the hybrid silica NPs (empty-loaded) could serve as an efficient platform for nanodrug formulations counteracting oxidative stress.

**Hamouda, R.A., Abd El-Mongy, M. & Eid, K.F. (2019) Comparative study between two red algae for biosynthesis silver nanoparticles capping by SDS: Insights of characterization and antibacterial activity. *Microbial Pathogenesis*, 129: 224-232.**

Keywords: Antibacterial; Capping AgNPs; Chlorella vulgaris; Red algae; biomaterial; dodecyl sulfate sodium; silver nanoparticle; vanadium; anti-infective agent; metal nanoparticle; silver; antibacterial activity; Article; biosynthesis; comparative study; concentration (parameter); controlled study; Corallina elongata; energy dispersive X ray spectroscopy; Escherichia coli; Fourier transform infrared spectroscopy; Gelidium amansii; Kocuria; Kocuria varians; Micrococcus; Micrococcus leutus; molecular stability; nonhuman; particle size; priority journal; red alga; scanning electron microscopy; surface plasmon resonance; transmission electron microscopy; ultraviolet spectroscopy; zeta potential; bacterium; chemistry; drug effect; drug stability; electron microscopy; metabolism; microbial sensitivity test; spectroscopy; ultrastructure; Anti-Bacterial Agents; Bacteria; Metal Nanoparticles; Microbial Sensitivity Tests; Microscopy, Electron; Rhodophyta; Sodium Dodecyl Sulfate; Spectrum Analysis

**Abstract:**

Biosynthesis silver nanoparticles (AgNPs) have received a lot of attention as a cytotoxic and antimicrobial activity against pathogenic bacteria. This study was carried out to evaluate the potential ability of red marine algae *Corallina elongata* and *Gelidium amansii* to biosynthesis AgNPs capping with Sodium Dodecyl Sulfate (SDS) and to determine its antibacterial efficacy. Characterization of capping AgNPs were determined by Ultra violet-Visible spectroscopy, Transmission electron microscope (TEM), Scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), Energy dispersive X-ray spectroscopy (EDX), Zeta potential and sizer. The results indicated that there is no variation change between capping AgNPs synthesis by two red algae in plasmon resonance peak and also both stable along 3 weeks. The capping nanoparticles size were range from 8 to 25 nm in the case of *G. amansii* and 12–20 nm *C. elongata*. The results were obtained from Fourier transforms infrared spectroscopy (FTIR) indicated that same metals are present in both algae except Vanadium (V) was present with *G. amansii*. Capping AgNPs biosynthesis by *C. elongata* had more toxicity to *Chlorella vulgaris* than that of synthesized by *G. amansii*. Capping AgNPs by SDS have been shown to enhance antibacterial activity against *Micrococcus leutus*, *Kocuria varians* and *Escherichia coli* ATCC 8739 compared to non-capping AgNPs. The antibacterial activity and toxicity of AgNPs is affected by concentrations of capping agent and the biomaterial (red algae) that used for synthesis. © 2019.

**Hopkins, S.S., Prytulak, J., Barling, J., et al. (2019) The vanadium isotopic composition of lunar basalts. *Earth and Planetary Science Letters*, 511: 12-24.**

Keywords: vanadium isotopes; moon formation; exposure age; cosmogenic effects; lunar basalt; irradiation; Comparative Planetary Mineralogy; Mare Basalts; Extinct Radioactivities; Oxidation-State; Cosmic-Rays; Earth; Moon; Fractionation; Mantle; Oxygen; Geochemistry & Geophysics

**Abstract:**

We present the first high-precision vanadium (V) isotope data for lunar basalts. Terrestrial magmatic rock measurements can display significant V isotopic fractionation (particularly during (Fe, Ti)oxide crystallisation), but the Earth displays heavy V (i.e. higher V-51/V-50) isotopic compositions compared to meteorites. This has been attributed to early irradiation of meteorite components or nucleosynthetic heterogeneity. The Moon is isotopically-indistinguishable from the silicate Earth for many refractory elements and is expected to be similar in its V isotopic composition. Vanadium isotope ratios and trace element concentrations were measured for 19 lunar basalt samples. Isotopic compositions are more variable (similar to 2.5 parts per thousand) than has been found thus far for terrestrial igneous rocks and extend to lighter values. Magmatic processes do not appear to control the V isotopic composition, despite the large range in oxide proportions in the suite. Instead, the V isotopic compositions of the lunar samples are lighter with increasing exposure age ( $t(e)$ ). Modelling nuclear cross-sections for V production and burnout demonstrates that cosmogenic production may affect V isotope ratios via a number of channels but strong correlations between V isotope ratios and  $t(e) \cdot [Fe]/[V]$  implicate Fe as the primary target element of importance. Similar correlations are found in the latest data for chondrites, providing evidence that most V isotope variation in chondrites is due to recent cosmogenic production via Fe spallation. Contrary to previous suggestions, there is no evidence for resolvable differences between the primary V isotopic compositions of the Earth, Moon, chondrites and Mars. (C) 2019 The Author(s). Published by Elsevier B.V.

**Huang, Z., Dai, X., Huang, Z., et al. (2019) Simultaneous and efficient photocatalytic reduction of Cr(VI) and oxidation of trace sulfamethoxazole under LED light by rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub> p-n heterojunction composite. *Chemosphere*, 221: 824-833.**

Keywords: Cr(VI); Intermediates; p-n heterojunction; Photocatalytic reduction; Sulfamethoxazole; Antibiotics; Bismuth compounds; Copper oxides; Detoxification; Heavy metals; Heterojunctions; Light emitting diodes; Liquid chromatography; Mass spectrometry; Oxidation; Photocatalytic activity; Pollution; Water treatment; Electrical conductivity; P-n heterojunctions; Photo catalytic degradation; Photogenerated charge; Triple-quadrupole mass spectrometry; Chromium compounds; chromium; copper oxide; graphene; bismuth; bismuth vanadium tetraoxide; chromium hexavalent ion; copper; cuprous oxide; vanadic acid; light effect; nanoparticle; photochemistry; photodegradation; pollution incidence; reduction; separation; sulfate; trace element; aqueous solution; Article; controlled study; crystal structure; doping; electric conductivity; environmental temperature; hydroxylation; light; light absorption; oxidation reduction reaction; photocatalysis; photosensitization; surface property; synthesis; triple quadrupole mass spectrometry; ultraviolet photoelectron spectroscopy; catalysis; chemistry; water pollutant; Oxidation-Reduction; Photochemical Processes; Vanadates; Water Pollutants, Chemical

**Abstract:**

Antibiotics and heavy metals often coexist in polluted environment, and the harm of combined pollution is greater than that of single pollution. In this study, a series of graphene supported p-n heterojunction rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub> composites are synthesized with different Cu<sub>2</sub>O doping for simultaneous detoxification of Cr(VI) and antibiotics. The obtained photocatalysts (rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub>) with proper loading amount of Cu<sub>2</sub>O shows the a high photocatalytic degradation activity for simultaneously efficient Cr(VI) reduction and sulfamethoxazole (SMZ) oxidation under LED light at neutral pH. The Cr(VI) was completely transformed to Cr(III) rather than simply Cr(VI) adsorbed on the surface of rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub>. The photocatalytic activity of composites can be attributed to excellent electrical conductivity of rGO and the p-n heterojunction between Cu<sub>2</sub>O and BiVO<sub>4</sub>, which promotes the spatial separation of photogenerated charges at the heterojunction boundary and inhibits of the photogenerated h<sup>+</sup> and e<sup>-</sup> recombination. It's confirmed that h<sup>+</sup>, [rad]O<sub>2</sub><sup>-</sup> and [rad]OH are the main reactive species for the photocatalytic SMZ oxidation, and the most important reactive species is h<sup>+</sup>. Finally, the tentative degradation pathways of SMZ are proposed based on the liquid chromatography-triple quadrupole mass spectrometry analysis. This work provides an effective approach for the treatment of water that contains SMZ and Cr(VI) under LED light. © 2019 Elsevier Ltd.

**King, T. & Sheridan, R. (2019) Determination of 27 elements in animal feed by inductively coupled plasma-mass spectrometry. *Journal of AOAC International*, 102(2): 434-444.**

Keywords: Animals; Inductively coupled plasma; Inductively coupled plasma mass spectrometry; Linearization; Nickel-Phosphorus; Preferred numbers; Veterinary medicine; Accuracy and precision; Accuracy and repeatabilities; Certified reference materials; Closed-vessel microwave digestion; National Institute of Standards and Technology; Performance characteristics; Potentially toxic elements; Single laboratory validations; Chemical contamination; element; analysis; animal; animal food; mass spectrometry; pet animal; Animal Feed; Elements; Pets

**Abstract:**

A method was developed to determine 27 elements (aluminum, arsenic, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorus, potassium, selenium, sodium, sulfur, vanadium, zinc, antimony, uranium, beryllium, thallium, and thorium) in animal feeds and pet foods using closed vessel microwave digestion and inductively coupled plasma-mass spectrometry. These elements can adversely affect animal health when amounts become excessive or deficient in

food. For potentially toxic elements, the target LOQ was determined to be 1/10 the lowest maximum tolerable level (MTL) for the most sensitive animal species. For nutritionally essential elements, the target LOQ was determined to be 1/10 the concentration that would be considered deficient in feed if that level is lower than 1/10 the lowest MTL. The targeted high end of the quantitation range was selected as twice the highest MTL. A single-laboratory validation (SLV) was performed to determine the accuracy and precision of the method, and the results were evaluated with respect to predetermined performance characteristics. The test materials used in the SLV included two National Institute of Standards and Technology certified reference materials, two Association of American Feed Control Officials (AAFCO) check samples, and one in-house previously analyzed feed sample. The concentrations of each element determined were the result of spiked analyte, incurred analyte, or a combination of spiked and incurred analyte. All samples were analyzed seven times on different days at  $2 \times$  LOQ and at the midrange concentration. For most data, the results of the SLV met or exceeded the criteria for accuracy and repeatability. For accuracy, K at the midrange level had a mean recovery of 95%, which is just below the low preferred accuracy threshold of 97%. For repeatability, all the  $2 \times$  LOQ CV r values were below the preferred values. Be, Cr, Ni, Na, Mn, and S all had midrange CV r values exceeding the preferred values. Be had the highest midrange CV r value of 9.93. Eight AAFCO check samples were also analyzed to determine the method's accuracy and repeatability for elements at the manufacturer's claimed levels. For accuracy, all results had z-scores  $<1.5$ . For repeatability, three CV r values from two AAFCO check samples were greater than the preferred limits. © 2019 AOAC International. All Rights Reserved.

**Lin, K., Li, P., Ma, J., et al. (2019) An automatic reserve flow injection method using vanadium (III) reduction for simultaneous determination of nitrite and nitrate in estuarine and coastal waters. *Talanta*, 195: 613-618.**

Keywords: Estuarine and coastal water; Nitrite and nitrate; Reserve flow injection analysis; Vanadium (III) chloride; Cadmium compounds; Chlorine compounds; Estuaries; Nitrates; Water injection; Analytical results; Coastal waters; Experimental parameters; Flow injection analysis; Flow injection method; Optimized conditions; Relative standard deviations; Simultaneous determinations; Vanadium compounds

**Abstract:**

An automatic reserve flow injection method using vanadium (III) as a reducing agent for the simultaneous determination of nitrite and nitrate in estuarine and coastal waters was reported for the first time. Vanadium (III) chloride was used as an environmentally friendly substitute to toxic cadmium for reducing nitrate to nitrite. The experimental parameters were optimized based on a univariate experimental design. The salinity effect of estuarine and coastal waters was carefully investigated. Under the optimized conditions, the detection limit of the proposed method was  $0.06 \mu\text{mol L}^{-1}$  and  $0.13 \mu\text{mol L}^{-1}$ , and the linearity was up to  $20 \mu\text{mol L}^{-1}$  and  $80 \mu\text{mol L}^{-1}$  for nitrite and nitrate detection, respectively. The relative standard deviations were below 1.5% ( $n = 7$ ). The recovery of spiked estuarine and coastal water samples varied from  $100.0 \pm 2.5\%$  to  $107.5 \pm 2.5\%$  for nitrite and  $90.7 \pm 0.3\%$  to  $98.0 \pm 1.0\%$  for nitrate. The sample throughput was approximately  $15 \text{ h}^{-1}$ . The analytical results obtained with the proposed method displayed good agreement with the classic copperized cadmium column reduction method. The automatic reserve flow injection method has been successfully applied to analyze the nitrite and nitrate in estuarine and coastal water samples. © 2018 Elsevier B.V.

**Liu, X., Guo, Z., Zhou, L., et al. (2019) Hierarchical biomimetic BiVO<sub>4</sub> for the treatment of pharmaceutical wastewater in visible-light photocatalytic ozonation. *Chemosphere*, 222: 38-45.**

Keywords: Biomimetic morphology; BiVO 4; Photocatalytic ozonation; Photogenerated hole; Synergies; Biomimetic processes; Bismuth compounds; Catalysts; Light; Mergers and acquisitions; Morphology; Oxalic acid; Ozone; Ozone water treatment; Ozonation; Photocatalytic activity; Reusability; Wastewater treatment; Advanced Oxidation Processes; BiVO<sub>4</sub>; Hydrothermal methods; Ozone concentration; Pharmaceutical wastewater; Photogenerated holes; Vanadium compounds; bismuth; penicillin derivative; vanadic acid; bismuth vanadium tetraoxide; catalysis; catalyst; concentration (composition); degradation; drug; hydroxyl radical; inorganic compound; light intensity; oxidation; ozonation; visible spectrum; wastewater; Article; biomimetics; controlled study; electric potential; photocatalysis; plant leaf; synergistic effect; volume; waste water management; chemistry; oxidation reduction reaction; photolysis; procedures; synthesis; waste water; water pollutant; Oxidation-Reduction; Penicillins; Vanadates; Water Pollutants, Chemical

**Abstract:**

Photocatalytic ozonation is an attractive advanced oxidation process for wastewater treatment, but highly active catalysts with strong response to visible light are urgently needed to push forward its practical application. In this study, a hierarchical biomimetic monoclinic bismuth vanadate (BiVO<sub>4</sub>) with leaves morphology was synthesized by a hydrothermal method, and employed as catalyst for oxalic acid and penicillin degradation in photocatalytic ozonation. The results show that the organics degradation was more efficient using leaves shaped BiVO<sub>4</sub> as catalyst than the bulk shaped one in photocatalytic ozonation and the synergy index is ranged from 2.8 to 3.3, indicating a superior positive synergistic effect between photocatalysis and ozonation. The higher activity of the leaves shaped BiVO<sub>4</sub> was probably attributed to the distinctive biomimetic morphology and preferable band structure with more negative CB potential. Mechanism studies suggested that the main reactive species were h<sup>+</sup> and [rad]OH for the degradation of persistent oxalic acid in photocatalytic ozonation. In addition, the effect of ozone concentration and inorganic ions and reusability of the material were also intensively investigated. © 2019 Elsevier Ltd.

**Sakpirom, J., Kantachote, D., Siripattanakul-Ratpukdi, S., et al. (2019) Simultaneous bioprecipitation of cadmium to cadmium sulfide nanoparticles and nitrogen fixation by *Rhodopseudomonas palustris* TN110. *Chemosphere*, 223: 455-464.**

Keywords: Bioprecipitation; Cadmium sulfide nanoparticle; Cysteine desulphydrase; Nitrogenase; Purple non-sulfur bacteria; Amides; Amines; Amino acids; Ammonia; Bacteria; Binary alloys; Biochemistry; Bioremediation; Cadmium chloride; Cadmium sulfide; Chlorine compounds; Fertilizers; Gene expression; II-VI semiconductors; Molybdenum alloys; Nitrogen fixation; Proteins; Stretching; Sulfur compounds; Synthesis (chemical); Vanadium alloys; Bioprecipitation; Fourier transform infrared spectra; Inhibitory concentration; Nitrogenase genes (nifH); *Rhodopseudomonas palustris*; CdS nanoparticles; aliphatic amine; amide; aromatic amine; cadmium; carbon; carbonyl derivative; cystathionine gamma lyase; iron; molybdenum; nanoparticle; nitrogen; vanadium; cadmium derivative; sulfide; biotransformation; enzyme activity; precipitation (chemistry); sulfate-reducing bacterium; Article; bacterial cell; biosynthesis; electron diffraction; Fourier transform infrared spectroscopy; growth inhibition; IC50; nonhuman; particle size; precipitation; room temperature; chemistry; drug effect; gene expression regulation; genetics; metabolism; *Rhodopseudomonas*; ultrastructure; Bacteria (microorganisms); Proteobacteria; Biodegradation, Environmental; Cadmium Compounds; Chemical Precipitation; Gene Expression Regulation, Enzymologic; Nanoparticles; Sulfides

**Abstract:**

This study investigated the abilities of a purple non-sulfur bacterium, *Rhodopseudomonas palustris* TN110 to bioremediate cadmium through the biosynthesis of CdS nanoparticles and

to fix nitrogen simultaneously. Under microaerobic-light conditions, *R. palustris* TN110 synthesized CdS nanoparticles. The produced CdS nanoparticles had a spherical shape and an average size of 4.85 nm. The Fourier transform infrared spectrum of the nanoparticles reveals the carbonyl groups, bending vibrations of the amide I and II bands of proteins, and C–N stretching vibrations of aromatic and aliphatic amines. These bands and groups suggest protein capping/binding on the surface of the nanoparticles. *R. palustris* TN110 converted 25.61% of 0.2 mM CdCl<sub>2</sub> to CdS nanoparticles under optimal conditions (pH 7.5, 30 °C and 3000 lux). The half maximal inhibitory concentration (IC<sub>50</sub>) value of the produced CdS nanoparticles was 1.76 mM. The produced CdS nanoparticles at IC<sub>50</sub> up-regulated two genes associated with nitrogen fixation: Mo-Fe nitrogenase gene (*nifH*) and V-Fe nitrogenase gene (*vnfG*) at 2.83 and 2.27 fold changes, respectively. On the contrary, the produced CdS nanoparticles slightly down-regulated Fe-Fe nitrogenase gene (*anfG*). The amounts of ammonia released by the strain support the gene expression results. *R. palustris* TN110 has great potential to serve concurrently as a cadmium bioremediation agent and a nitrogen fixer. The strain could be beneficial to paddy fields that are contaminated with Cd through run off from mining and chemical fertilizer applications. © 2019 Elsevier Ltd.

**Sanz-Robinson, J. & Williams-Jones, A.E. (2019) Zinc solubility, speciation and deposition: A role for liquid hydrocarbons as ore fluids for Mississippi Valley Type Zn-Pb deposits. *Chemical Geology*, 520: 60-68.**

Keywords: Zinc; Total acid number; Carboxylic acids; Mississippi Valley Type; Ore; Oil; Bitumen; Thermochemical sulphate reduction; Petroleum; Hydrocarbons; MVT; TSR; Sphalerite; Precipitation; Deposition; Redbeds; Brine; Biodegradation; Deposit; Base metals; Thermochemical Sulfate Reduction; Organic Geochemistry; Crude-Oil; Field; Constraints; Transport; Vanadium; Genesis; Acidity; Geochemistry & Geophysics

**Abstract:**

Although the ore fluid for Mississippi Valley Type (MVT) deposits is universally considered to be a basinal brine, the common occurrence of liquid hydrocarbons as inclusions in one of the ore minerals (sphalerite) raises the question of whether liquid hydrocarbons could play a role in metal transport. Here we explore the potential of liquid hydrocarbons to act as an ore fluid by determining the steady-state concentration of zinc in crude oil and evaluating the factors that promote its dissolution. To this end, zinc wires were reacted with a series of oils (labelled oils A, B and C) at 150, 200 and 250 degrees C, and the steady-state concentration of Zn was determined. Zinc concentrations were observed to increase with temperature and with the Total Acid Number (TAN) of the oils, the latter of which is strongly correlated to the carboxylic acid content of crude oil. Crude oil B, the highest TAN oil, dissolved 1700 +/- 0.8 ppm at 250 degrees C, which is comparable to the highest Zn concentration inferred to have been dissolved in brines interpreted to represent MVT ore fluids. X-ray Photoelectron Spectroscopic (XPS) analyses performed on the residual oil coating the zinc wires after the reaction supported the conclusion that Zn has a strong chemical affinity for carboxylic acids in crude oil. Finally, an experiment designed to precipitate sphalerite crystals from a Zn-rich synthetic oil at room temperature showed that sphalerite precipitation from liquid hydrocarbons proceeds efficiently in a carbonate-buffered, H<sub>2</sub>S-rich environment.

**Shen, H-Z., Yuan, C-S., Jing, G., et al. (2019) Chemisorption and kinetic mechanisms of elemental mercury on immobilized V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> at low temperatures. *Journal of Hazardous Materials*, 368: 819-829.**

Keywords: Elemental mercury (Hg<sup>0</sup>); Influential factors; Low temperature; Thermal adsorption and kinetic mechanisms; V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>; Adsorption; Catalysts; Chemisorption; Efficiency; Kinetics; Mass transfer; Mercury (metal); Temperature; Titanium compounds; Vanadium

pentoxide; Elemental mercury; Kinetic mechanism; Low temperatures; V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>; Mercury compounds; mercury; titanium dioxide; catalyst; concentration (composition); equipment; immobilization; inorganic compound; mercury (element); reaction kinetics; temperature effect; adsorption kinetics; Article; concentration (parameter); diffusion; model; reaction temperature

**Abstract:**

To investigate the effect of low temperature and catalyst filling pattern on the adsorption of Hg<sup>0</sup> by DeNO<sub>x</sub> equipment, the chemisorption and kinetic mechanisms of Hg<sup>0</sup> adsorption on 5–30%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> immobilized on glass beads at 100–160 °C were investigated. The effects of the reaction temperature, influent Hg<sup>0</sup> concentration, and V<sub>2</sub>O<sub>5</sub> doping amount on the adsorption efficiency and capacity for Hg<sup>0</sup> were explored. The active sites for Hg<sup>0</sup> adsorption were further identified. Additionally, the adsorption kinetics were modelled using the linear driving force approximation, Fick's diffusion model, and pseudo-second-order kinetic model. Finally, the influence of immobilization on the adsorption of Hg<sup>0</sup> was also investigated. Experimental results showed that the bridged oxygen atom of V-O-V played a key role in the adsorption of Hg<sup>0</sup>. The Hg<sup>0</sup> adsorption efficiencies decreased from >90% to 40% as the reaction temperature increased from 120 °C to 160 °C for 20%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, while the adsorptive capacities for Hg<sup>0</sup> were highly influenced by the influent Hg<sup>0</sup> concentration and V<sub>2</sub>O<sub>5</sub> doping amount. 20%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> had the highest adsorptive capacity of 2547 µg Hg<sup>0</sup>/g V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> at 160 °C. The kinetic results showed that the linear driving force approximation model fit the Hg<sup>0</sup> adsorption better than the other models. The diffusion resistance increased significantly for the immobilized catalysts because the external mass transfer coefficient decreased by more than 1200-fold. © 2019 Elsevier B.V.

**Tahir, M.B., Kiran, H. & Iqbal, T. (2019) The detoxification of heavy metals from aqueous environment using nano-photocatalysis approach: a review. *Environmental Science and Pollution Research*, 26(11): 10515-10528.**

Keywords: Heavy metals' remediation; Nanomaterials; Photocatalysis; Treatment technologies; bioremediation; catalysis; detoxification; electrochemical method; heavy metal; nanomaterial; performance assessment; public health

**Abstract:**

Heavy metals are discharged into aquatic environment and causes serious problems to the environment, human's health, and other organisms. The industrial effluents contain high concentration of heavy metals that should be treated by different technologies. Numerous technologies have been widely used for the remediation of heavy metals such as chemical precipitation, ion exchange, membrane filtration, adsorption, coagulation-flocculation, floatation, electrochemical treatment, bioremediation, and photocatalysis. Among these technologies, photocatalysis has gained much attention due to chemical, physical, and electrical properties of heterogeneous semiconductor nano-photocatalysis. Bismuth vanadate is an n-type semiconductor photocatalyst having 2.4 eV band gap that was widely used from several decades having three monoclinic, tetragonal, and tetragonal zircon structures, but it also have some limitation that can be overcome by modification with metals or non-metals to gain high removal efficiency of heavy metals. This modification can tune its photocatalytic properties like band gap, absorption capacity, and surface area resulting in high photocatalytic performance towards heavy metals detoxification. © 2019, Springer-Verlag GmbH Germany, part of Springer Nature.

**Tian, T., Sun, W., Xiong, X., et al. (2019) Novel "Z-pins like" vanadium rods prepared by solid phase sintering to improve ablation resistance of the C/C-ZrC-SiC composites. *Journal of the European Ceramic Society*, 39(4): 1696-1702.**

Keywords: C/C-ZrC-SiC composites; "Z-pins like" vanadium rods; Oxide compensator; Solid phase sintering; Self-healing capability; Microstructure; Oxidation; Mechanism; Behavior; Infiltration; Pyrolysis; Materials Science

**Abstract:**

Novel "Z-pins like" vanadium rods (V rods) were prepared as oxide compensators to improve ablation resistance of the C/C-ZrC-SiC composites. The microstructure and anti-ablation performance were investigated. Results show that the solid phase sintering promoted the formation of a good interface between the "Z-pins like" V rods and C/C-ZrC-SiC composites, and the generation of VC and Si<sub>3</sub>V<sub>5</sub> (anti-oxidant phases) in the "Z-pins like" V rods. The unique "Z-pins like" V rods changed the local oxidation rate, and flow regime of the formed vanadium oxide with high melting point. And the liquid vanadium oxide flowed radially to the surface of the C/C-ZrC-SiC replacing SiO<sub>2</sub> with the self-healing capability and effectively healed the holes and cracks. Finally, a dense and homogeneous zirconium/vanadium compound oxides film was generated to improve the ablation resistance of C/C-ZrC-SiC without any mass and thickness reduction.

**Tosti, L., van Zomeren, A., Pels, J.R., et al. (2019) Assessment of biomass ash applications in soil and cement mortars. *Chemosphere*, 223: 425-437.**

Keywords: Availability; Biomass ash; Cement; pH-dependent leaching; Regulations; Soil amendment; Biomass; Cements; Leaching; Mortar; Soil cement; Soil moisture; Trace elements; Beneficial utilizations; Biomass ashes; Conversion technology; Environmental assessment; Major and trace elements; PH-dependent; Soil pollution; antimony; arsenic; barium; cadmium; calcium; chloride; chromium; cobalt; copper; lead; molybdenum; nickel; phosphorus; potassium; selenium; sodium; sulfur; tin; vanadium; zinc; trace element; ash; pH; redox conditions; soil; Article; batch process; bottom ash; chemical composition; comparative study; controlled study; fly ash; gasification; analysis; building material; chemistry; pharmacology; soil pollutant; Coal Ash; Construction Materials; Soil Pollutants

**Abstract:**

The pH-dependent availability and leaching of major and trace elements was investigated for a wide range of biomass ash from different fuels and conversion technologies. A technical and environmental assessment of selected biomass ash for application in soil or cement mortars was performed, using both the total content and leaching of elements. A large variation in biomass ash composition, yet consistent pH dependent leaching patterns were observed for most elements and conversion technologies. Chromium showed a distinct behaviour which was hypothesized to reflect redox conditions during conversion of the biomass. The leaching based approach was found to provide a more realistic assessment of the availability of desired (i.e. nutrients) and undesired elements (i.e. contaminants) in soil systems. When applied to a reference soil at a rate of 2% by weight, the selected biomass ash increased the concentration of particularly Cr, Mo and Zn in soil solution to a level of concern. For cement applications, the release of Ba, Cr and Mo can become of concern during the second life stage, but the release was not attributed to the included biomass ash. Both soil and cement matrixes were found to control the release of elements such as Cu, V and Ni (soil) and As, Cr and Mo (cement) when compared to the released from pure biomass ash, underlining the importance of evaluating the availability and leaching of desired and undesired elements in the application scenario. Given current regulatory criteria, beneficial utilization of biomass ash in cement may be more

feasible than in soil, but regulatory criteria based on leaching rather than total content of elements may widen the application potential of biomass ash. © 2019 Elsevier Ltd.

**Wang, X., Zhao, Y., Zhang, D., et al. (2019) Dawson-type vanadium-substituted tungstophosphate-modified ITO electrode: Preparation, characterization and electrochemical determination of dopamine. *International Journal of Electrochemical Science*, 14(4): 3595-3609.**

Keywords: Composite film; Dopamine; Electrochemistry; Polyoxometalate

**Abstract:**

In this work, we describe a robust composite film-modified indium tin oxide (ITO) electrode with improved detection capabilities for an example neurotransmitter, dopamine (DA). The composite film was developed by the combination of a Dawson-type vanadium tungstophosphate,  $\alpha$ -K<sub>7</sub>P<sub>2</sub>W<sub>17</sub>VO<sub>62</sub>·18H<sub>2</sub>O (P<sub>2</sub>W<sub>17</sub>V), and cationic chitosan (CS) via a layer-by-layer (LbL) self-assembly technique. The composite film-modified electrode presents excellent electrochemical catalytic activity towards dopamine (DA) with a linear response over the range of  $1.25 \times 10^{-8}$  M to  $3.04 \times 10^{-4}$  M. The proposed system responds selectively to dopamine with a low detection limit of 0.18  $\mu$ M (S/N = 3), a high sensitivity of 0.23  $\mu$ A  $\mu$ M<sup>-1</sup> and a quick response time. As a result, the prepared composite film materials with these superior properties show promising applicability in electrochemical sensors. © 2019 The Authors.

**Zhang, X., Chen, T., Xu, Y., et al. (2019) Synthesis and characterization of environmentally friendly BiVO<sub>4</sub> yellow pigment by non-hydrolytic sol-gel route. *Journal of Sol-Gel Science and Technology*, 91(1): 127-137.**

Keywords: Pigment; Yellow; Bismuth vanadate; FT-IR; Non-hydrolytic sol-gel; Brilliant Yellow; Structural Variation; Ceramic Pigment; Performance; Color; Reflectance; Degradation; Deposition; Raman; Materials Science

**Abstract:**

Monoclinic bismuth vanadate (m-BiVO<sub>4</sub>) yellow pigments were synthesized by non-hydrolytic sol-gel (NHSG) route without any surfactants. The presence of Bi-O-V band in the sol and xerogel, indicates that the excellent atomic scale homogeneity could be reached. It is beneficial to achieve high purity m-BiVO<sub>4</sub> phase and submicron scale particles (738nm) with homogenous distribution at low temperature (400 degrees C), resulting in a brilliant yellow hue (b<sup>\*</sup>=71.18, h(ab)=89.73). These pigments have better chromatic performance than previously reported and commercially available BiVO<sub>4</sub> yellow pigments. Meanwhile, the cytotoxicity of the pigment was tested in *Mus musculus* skin melanoma cells, and showed nontoxic for human cells, indicating its potential application in the high quality paints for automotive and architectural finishes. [GRAPHICS]. Highlights BiVO<sub>4</sub> pigment was prepared via non-hydrolytic sol-gel method at 400 degrees C. It exhibited high purity and brilliant yellow hue (L<sup>\*</sup>=74.83, a<sup>\*</sup>=-0.34, b<sup>\*</sup>=71.18). The pigment has low cytotoxicity for human cells.

**Zhang, Y., Zhang, T.-., Dreisinger, D., et al. (2019) Recovery of vanadium from calcification roasted-acid leaching tailing by enhanced acid leaching. *Journal of Hazardous Materials*, 369: 632-641.**

Keywords: Leaching; Mine tailing; Recycling; Vanadium; Biomineralization; Calcination; Efficiency; Extraction; Tailings; Titanium; Atmospheric leaching; Environmental quality; Extraction efficiencies; Leaching experiments; Liquid to solid ratio; Mine tailings; Optimum conditions; Orthogonal experiment; calcium sulfate; chromium; iron; magnesium; sulfuric acid; acid activation; calcification; concentration (composition); pollutant removal;

temperature profile; acidity; Article; atmospheric pressure; calcification roasted acid leaching; chemical analysis; chemical composition; comparative study; concentration (parameter); Fourier transform infrared spectroscopy; high temperature; liquid; low temperature; metal recovery; particle size; reaction time; scanning electron microscopy; solid; solvent extraction; X ray diffraction; X ray photoemission spectroscopy

**Abstract:**

Vanadium contained tailing generated from the typical calcium roasting-acid leaching process is contaminant and waste of resource. Atmospheric and pressurized leaching were conducted and compared to recover the vanadium from the vanadium tailing and improve the tailing's environmental quality. Orthogonal experiments were designed and applied for the atmospheric leaching study. It is shown that the extraction efficiency of V changed from 29.6% to 43.5% while the extraction efficiency of Fe, Cr, Ti, Mg remained stable under 4% with variable atmospheric leaching conditions. In the pressurized leaching experiments, the effects of leaching temperature, H<sub>2</sub>SO<sub>4</sub> concentration, liquid to solid ratio and leaching time on the extraction of V, Fe, and Ti were investigated. Under the optimum conditions (the temperature of 413.15 K, H<sub>2</sub>SO<sub>4</sub> concentration of 300 g/L, liquid to solid ratio of 8:1 mL/g and the reaction time of 100 min), the extraction efficiencies of V, Fe, and Ti reached 91.7%, 60.1% and 46.5% respectively, a leach residue contains only 0.13% of stable vanadium was obtained. © 2019.

**Zhu, Y., Hou, Y., Wang, J., et al. (2019) Effect of SCR Atmosphere on the Removal of Hg<sub>0</sub> by a V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>/AC Catalyst at Low Temperature. *Environmental Science and Technology*, 53(9): 5521-5527.**

Keywords: Ammonia; Catalysts; Cerium oxide; Temperature; Vanadium pentoxide; Catalyst surfaces; Catalytic system; Competitive adsorption; Gas analyzers; Impregnation methods; Inhibiting effect; Low temperatures; Whole process; Mercury compounds; Xenox

**Abstract:**

A series of V<sub>2</sub>O<sub>5</sub>-xCeO<sub>2</sub>/AC (noted as V-Ce/AC) catalysts were synthesized by the impregnation method, which combined the advantage of AC and V-Ce. The effects of SCR atmosphere on Hg<sub>0</sub> removal were systematically investigated at low temperature. The experimental results indicated that NO had a positive effect on Hg<sub>0</sub> removal. In addition, an interesting experimental phenomenon was found that NH<sub>3</sub> also showed a positive effect on Hg<sub>0</sub> removal, which is different from many studies that have reported a negative effect of NH<sub>3</sub> on Hg<sub>0</sub> removal by other catalysts. NH<sub>3</sub>-TPD experiment showed that there was no apparent competition between NH<sub>3</sub> and Hg<sub>0</sub>. An FT-IR gas analyzer and in situ DRIFTS were used to study the mechanism for the effect of NH<sub>3</sub> on the catalyst surface and found that a small part of NH<sub>3</sub> was overoxidized to NO<sub>2</sub> in this catalytic system. O<sub>2</sub> acted as a promoter in the whole process of NO and Hg<sub>0</sub> removal. However, H<sub>2</sub>O showed an inhibiting effect on Hg<sub>0</sub> and NO removal over V-Ce/AC catalysts, which may be caused by the competitive adsorption of H<sub>2</sub>O and pollutants (NO and Hg<sub>0</sub>). Additionally, 1 V-8Ce/AC catalyst exhibited high stability (E<sub>Hg</sub> = 87.6%, E<sub>NO</sub> = 82.84%) after 72 h reaction in SCR atmosphere at 150 °C. © 2019 American Chemical Society.