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# Vanadium Health Research Programme: Recent Published Literature

October 2019 – December 2019

Report to Vanitec

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Prepared by: Ruth Bevan and Lini Ashdown
Reviewed by: Len Levy
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# Introduction

This report presents the bibliographic details of the 92 papers identified as being published during the period October 2019 to December 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

**Austin, C., Curtin, P., Curtin, A.*, et al.* (2019) Dynamical properties of elemental metabolism distinguish attention deficit hyperactivity disorder from autism spectrum disorder. *Translational Psychiatry,* 9(1): Article number 238.**
Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6760156/pdf/41398_2019_Article_567.pdf

**Abstract:**
Attention deficit hyperactivity disorder (ADHD) and autism spectrum disorder (ASD) are neurodevelopmental conditions of overlapping etiologies and phenotypes. For ASD, we recently reported altered elemental metabolic patterns in the form of short and irregular zinc and copper cycles. Here, we extend the application of these biomarkers of prenatal and early postnatal elemental metabolism to distinguish between individuals diagnosed with ADHD and/or ASD and neurotypical controls. We recruited twins discordant for ADHD, ASD and other neurodevelopmental diagnoses from national twin studies in Sweden (N = 74) diagnosed according to DSM-5 clinical consensus and standardized psychiatric instruments. Detailed temporal profiles of exposure to 10 metals over the prenatal and early childhood periods were measured using tooth biomarkers. We used recurrence quantification analysis (RQA) to characterize properties of cyclical metabolic patterns of these metals. Regularity (determinism) and complexity (entropy) of elemental cycles was consistently reduced in ADHD for cobalt, lead, and vanadium (determinism: cobalt, β = −0.03, P = 0.017; lead, β = −0.03, P = 0.016; and vanadium, β = −0.03, P = 0.01. Entropy: cobalt, β = −0.13, P = 0.017; lead, β = −0.18, P = 0.016; and vanadium, β = −0.15, P = 0.008). Further, we found elemental pathways and dynamical features specific to ADHD vs ASD, and unique characteristics associated with ADHD/ASD combined presentation. Dysregulation of cyclical processes in elemental metabolism during prenatal and early postnatal development not only encompasses pathways shared by ADHD and ASD, but also comprise features specific to either condition. © 2019, The Author(s).

**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.**
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412019302272/pdfft?md5=7290cbba319f215f81f9d6e6a852e9e3&pid=1-s2.0-S0160412019302272-main.pdf
Keywords: Essential metals; Zinc; Lung cancer; Cohort study; Telomere attrition; Gene expression.

**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 [β (95% CI) = −0.73 (−1.27, −0.19)]. These effects were pronounced among males. In particularly, zinc could regulate the expressions of 8 cancer-related genes, including *SOD1*, *APE*, *TP53BP1*, *WDR33*, *LAPTM4B*, *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.

**Cheng, Y., Nathanail, C.P. & Ja'afaru, S.W. (2019) Generic assessment criteria for human health risk management of agricultural land scenario in Jiangsu Province, China. *Science of the Total Environment,* 697**.

Keywords: Agricultural land; China; CLEA model; Generic Assessment Criteria; Jiangsu Province

**Abstract:**

The widespread of agricultural soil pollution in China is posing great risks to food safety and human health. Lack of human health-based generic assessment criteria (GAC) for Chinese agricultural land makes it impossible to efficiently screen and assess the risks unless site-specific risk assessments being carried out, which are both time-consuming and costly. This paper has thus derived the first set human health-based generic assessment criteria (GAC) for 13 substances of concern (including isomers) using the CLEA model for agricultural land scenario in Jiangsu province of China. As there is no authoritative human health risk assessment model in China yet, this paper has determined and demonstrated the applicability of the CLEA model to Chinese agricultural land exposure scenarios. The derived GAC are generally less stringent than the current two Chinese standards (i.e. GB 15618-2018, GB36600-2018) for most substances except for five substances (including cadmium, nickel, alpha-HCH, beta-HCH and gamma-HCH) for which the oral background intake accounts for 50% of the Total Daily Intake. This indicates that the two Chinese soil quality standards maybe over conservative, and oral background intake (i.e. MDIoral) can be a critical parameter when deriving regional GAC for Chinese agricultural land scenarios. Since there is a notable regional difference in MDIoral for some of the substances of concern, as well as in the vegetable consumption rates and vegetable varieties consumed, it is considered necessary to derive GAC for other provinces of China for agricultural land scenario, to further examine the sensitivity of MDIoral on GAC. In addition, the 13 substances of concern in this paper are some of the most prevalent contaminants in agricultural soils in China, but GAC for some emerging new contaminants, such as thallium, vanadium, should also be derived in further research. © 2019 Elsevier B.V.

**Cho, J., Bing, S.J., Kim, A.*, et al.* (2019) Jeju ground water containing vanadium induces normal T cell development and immune activation in chronically stressed mice. *Molecular Biology Reports,* 46(4): 4443-4452.**

Keywords: Jeju ground water; Chronic stress; Immune activation; T cell development; animal-models; depression; susceptibility; cytokines; anxiety; system; mouse; Biochemistry & Molecular Biology

**Abstract:**
Containing high concentration of vanadium served by the volcanic bedrock, Jeju ground water has long been known for various implicit health benefits including immune-promotion. Exposure to stress has been reported to be associated with immunosuppression such as reducing lymphocyte population or antibody production due to stress hormones. In this study, we aimed at evaluating the effects of Jeju ground water on chronically stressed mice. C57BL/6 mice were subjected to various stressors such as restraint stress, water swimming stress, heat stress, acoustic stress, and Jeju ground water was supplied for 28days with two different concentrations, S1 (vanadium 15-20 mu g/l, pH 8.3) and S2 (vanadium 20-25 mu g/l, pH 8.5). Treatment with Jeju ground water increased CD4(+)CD8(-) or CD4(-)CD8(+) single-positive thymocytes. It also increased the proliferation of splenocytes and the populations of CD4(+) T cells, CD45R/B220(+) B cells, CD11b(+) macrophages or Gr-1(+) granulocytes in spleen. In addition, the production of IgG was increased in chronically stressed mice by treatment with Jeju ground water. These results suggest vanadium-rich Jeju ground water may be helpful in T cell development in thymus and immune cell proliferation and its function in spleen against chronic stress.

**Figueroa-Lara, J.J., Murcia-González, J.M., García-Martínez, R.*, et al.* (2019) Effect of platform subway depth on the presence of Airborne PM2.5, metals, and toxic organic species. *Journal of Hazardous Materials,* 377: 427-436.**
Keywords: Depth; Metals; PAHs; PM2.5; Subway.

**Abstract:**
PM2.5 that have been related to public health risks, were collected during two seasons with High-Vol samplers in platforms of a Mexican subway station, which interconnects through transfers three lines having different depths. The objective was to study the influence of depth on the PM2.5 concentrations and their species. PM2.5 concentrations in cold-dry and warm-dry seasons presented statistical differences, being in average 57 and 66 μgm−3 respectively, in the shallower line 9; 90 μgm−3 and 111 μgm−3 in line 1; and 104 and 122 μgm−3in the deepest line 7. During the cold-dry season and warm-dry season PM2.5concentrations in the subway environment were respectively up to 3.5 times and up to 5 times greater than in the ambient air. Like PM2.5, metals analyzed with an OES-ICP presented higher concentrations in deeper lines as well as PAHs quantified with CG-MS, which ranged from 4.5 to 11.7 ngm−3. High PM2.5, metals and organic toxic concentrations found in deeper lines of the subway environment represent a risk for commuters endorsing the need for ventilation systems to reduce them. Zn, Pb, V and Ni in subway particles presented the highest solubility in artificial lysosomal fluid suggesting high bioavailability in the lung fluids. © 2019 Elsevier B.V.

**Galon-Negru, A.G., Olariu, R.I. & Arsene, C. (2019) Size-resolved measurements of PM2.5 water-soluble elements in Iasi, north-eastern Romania: Seasonality, source apportionment and potential implications for human health. *Science of the Total Environment,* 695.**
Available at:
https://www.sciencedirect.com/science/article/pii/S0048969719337866/pdfft?md5=8406f3ebb8ab38c9ff5e0098346a1364&pid=1-s2.0-S0048969719337866-main.pdf
Keywords: Emission sources; Fine particle; Health risks; Positive matrix factorization; Water-soluble metals

**Abstract:**
The present paper reports the first size-resolved element measurements in the PM2.5 fraction collected throughout 2016 in the Iasi urban area in north-eastern Romania. Concentrations of water-soluble elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cu, Cr, Fe, Ga, Mg, Mn, Mo, Ni, Pb,

Rb, Se, Sr, Te, Ti, U, V, Zn) were determined using inductively coupled plasma mass spectrometry. Several water-soluble heavy metals (Al, Fe, Zn, As, Cr, Pb) exhibit clear seasonal patterns with maxima over the cold season and minima over the warm season. Elements as Al, Fe, Mg, Zn, Ni, Mn, and Cu present the highest levels in the PM2.5 fraction, indicating significant contributions from soil-dust resuspension or brake lining and tires. Clear fine mode size-dependent distributions were observed for anthropogenic source-origin elements (Pb, Zn, Cd, V, etc.) due to an acidity-driven metals dissolution process. Positive matrix factorization, concentration weighted trajectory and bivariate polar plot analyses were applied to the entire PM2.5 database. Based on relative concentrations of various elements, five factors associated with specific sources were identified. The most important contributions to the total PM2.5 mass concentration (during the total period) come from secondary formation of the ammonium sulfate form (~44%) and from nitrate (~37%). Resuspended dust accounts for a contribution of about 16%, while biomass burning mixed with NaCl salt/sea-salt sources contribute as much as ~3%. Traffic and industrial sources seem to yield little contribution (<0.05%). An assessment investigation of non-carcinogenic and carcinogenic health risks revealed water-soluble arsenic and chromium (VI) as elements with the largest incremental carcinogenic risks. Both metals have traffic and industrial related sources and therefore it is believed that in the future, at the local/regional level, these sources should receive attention by implementing appropriate emission control measures. 

**Gutierrez-Gonzalez, E., Garcia-Esquinas, E., de Larrea-Baz, N.F.*, et al.* (2019) Toenails as biomarker of exposure to essential trace metals: A review. *Environmental Research,* 179(Pt A): 108787.**

Keywords: Biomarker; Biomonitoring; Essential trace essential metals; Exposure; Systematic review; Toenail.

**Abstract:**

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

studies makes the validation of the usage of toenails as biomarkers of exposure to these elements difficult. Standardization of sample collection, quality control, analytical techniques and reporting procedures might facilitate further research focused on the clear understanding of the significance of essential levels in this promising matrix and would enhance its utility in epidemiological research.

**Hu, J., Peng, Y., Zheng, T.*, et al.* (2018) Effects of trimester-specific exposure to vanadium on ultrasound measures of fetal growth and birth size: a longitudinal prospective prenatal cohort study. *The Lancet.Planetary Health,* 2(10): e427-e437.**
Available at:
https://www.sciencedirect.com/science/article/pii/S2542519618302109/pdfft?md5=c660b708e6b659723b2e2b72cbdaad79&pid=1-s2.0-S2542519618302109-main.pdf
Keywords: Adult; Birth Weight/drug effects; China; Dose-Response Relationship, Drug; Environmental Pollutants/adverse effects; Female; Fetal Development/drug effects; Humans; Longitudinal Studies; Male; Maternal Exposure/adverse effects; Nonlinear Dynamics; Pregnancy; Pregnancy Trimesters/drug effects; Prospective Studies; Ultrasonography, Prenatal; Vanadium/adverse effects; Young Adult

**Abstract:**
BACKGROUND: Identification of windows of heightened vulnerability to environmental factors has substantial public health implications. Prenatal exposure to vanadium has been linked to adverse birth outcomes; however, critical windows for such exposure during fetal growth remain unknown. We aimed to assess trimester-specific associations of vanadium exposure with ultrasound measures of fetal growth and birth size in a Chinese longitudinal cohort. METHODS: The present study was embedded in our ongoing prospective prenatal cohort study at the Wuhan Women and Children Medical Care Center (Wuhan, Hubei, China). Pregnant women were eligible for inclusion if they provided signed informed consent and were less than 16 weeks pregnant with a single gestation, and agreed to take in-person interviews, undergo ultrasound examinations, and provide blood and urine samples. We collected urine samples and measured urinary vanadium concentrations using inductively coupled plasma mass spectrometry. We calculated SD scores for ultrasound-measured biparietal diameter, head circumference, occipitofrontal diameter, abdominal circumference, femur length, and estimated fetal weight at 16, 24, and 31 weeks of gestation. We applied linear regressions with generalised estimating equations to estimate associations of urinary vanadium concentrations in each trimester with ultrasound-measured fetal growth parameters or neonatal size at birth. FINDINGS: As of Oct 12, 2016, we recruited 3075 women who were non-smokers and non-drinkers during pregnancy, provided up to three urine samples during the first, second, and third trimesters, and gave birth to live singletons without birth defects. We excluded women who did not provide information on ultrasound measurements (n=20) or who only had one ultrasound measurement of fetal crown-rump length at the first trimester (n=14). We excluded another 16 women because they had missing values for confounding variables, leaving 3025 women retained in the study. Every doubling of urinary vanadium concentration in the first trimester was associated with a significant increase in femur length (adjusted percentage change 6.4%, 95% CI 0.7 to 12.1) at 16 weeks of gestation and reductions in biparietal diameter (-4.2%, -8.2 to -0.1), head circumference (-6.0%, -10.1 to -1.9), occipitofrontal diameter (-5.7%, -9.9 to -1.5), and abdominal circumference (-5.3%, -9.4 to -1.2) at 31 weeks of gestation. Every doubling of urinary vanadium concentration in the second trimester was significantly associated with reductions in SD scores for head circumference (-7.2%, -14.1 to -0.3) and abdominal circumference (-6.9%, -13.8 to -0.1) at 31 weeks of gestation. The highest quartile of urinary vanadium concentration (>1.18 mug/L) in the first trimester, when compared with the lowest quartile

(</=0.60 mug/L), was associated with a mean decrease in birthweight of 12.6 g (95% CI 2.5-22.8; ptrend=0.0055) and a mean decrease in ponderal index of 0.07 kg/m(3) (0.01-0.12; ptrend=0.0053). Moreover, newborns with restricted birth size had higher vanadium exposure in the first and third trimesters. INTERPRETATION: Vanadium might be toxic to humans and impair fetal growth. The first, early second, and late third trimesters could be critical windows for heightened vulnerability to vanadium for fetal growth. Our findings require further investigation in other populations. FUNDING: National Key R&D Plan of China, National Natural Science Foundation of China, and Fundamental Research Funds for the Central Universities, Huazhong University of Science and Technology.

**Kambunga, S.N., Candeias, C., Hasheela, I.*, et al.* (2019) The geochemistry of geophagic material consumed in Onangama Village, Northern Namibia: a potential health hazard for pregnant women in the area. *Environmental Geochemistry and Health,* 41(5): 1987-2009.**
Keywords: Geochemistry; Geophagy; Pregnant women; Termite mound soils.

**Abstract:**
Ingestion of geophagic materials might affect human health and induce diseases by different ways. The purpose of this study is to determine the geochemical composition of geophagic material consumed especially by pregnant women in Onangama Village, Northern Namibia and to assess its possible health effects. X-ray fluorescence and inductively coupled plasma mass spectrometry were used in order to determine the major, and trace elements as well as anions concentrations of the consumed material. The geochemical analysis revealed high concentrations of aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), potassium (K), sodium (Na), and silica (Si); and trace elements including arsenic (As), chromium (Cr), mercury (Hg), nickel (Ni) and vanadium (V) as well as sulphate (SO4(2-)), nitrate (NO3(-)), and nitrite (NO2(-)) anions comparing to the recommended daily allowance for pregnant women. The pH for some of the studied samples is alkaline, which might increase the gastrointestinal tract pH (pH 1) revealed that Al and Mn might be a potential risk for human consumption. Based on the results obtained from the geochemical analysis, the consumption of the studied material might present a potential health risk to pregnant women including concomitant detrimental maternal and foetal effects.

**Kilic, S. (2019) Survey of trace elements in bottled natural mineral waters using ICP-MS. *Environmental Monitoring and Assessment,* 191(7): 452.**
Keywords: Bottled natural mineral water; ICP-MS; Trace elements; drinking-water; metal contamination; spectrometry; toxicity; chromium; Turkey; Environmental Sciences & Ecology.

**Abstract:**
This study monitors the elemental composition of different brands of bottled natural mineral waters marketed in Turkey and discusses compositional parameters. Natural mineral water samples were analyzed for cesium (Cs), rubidium (Rb), thallium (Tl), cobalt (Co), arsenic (As), chromium (Cr), lead (Pb), gallium (Ga), vanadium (V), silver (Ag), cadmium (Cd), uranium (U), thorium (Th), and molybdenum (Mo) by inductively coupled plasma mass spectrometry (ICP-MS). Method trueness was confirmed by using 1640A natural water certified reference materials purchased from Laboratory of the Government Chemist (LGC). The linearity, limit of detection, limit of quantification, repeatability, and recovery (%) were assessed. Method validation data and results obtained from the certified reference material suggested that the method could be applied to determine elemental contaminants of the samples. Cd, Tl, Ag, and Th could not be determined (< LOD) in the samples. Pb, Cs, Co, Rb, Ga, V, U, As, Cr, and Mo were determined in samples. The results were compared with elemental standards for natural mineral waters set according to the World Health Organization and United States

Environmental Protection Agency, and the concentrations of all metals did not exceed these values.

**López-Valdez, N., Guerrero-Palomo, G., Rojas-Lemus, M.*, et al.* (2019) The role of the non-ciliated bronchiolar cell in tolerance to inhaled vanadium of the bronchiolar epithelium. *Histology and Histopathology,* : 18165.**
Available at: https://www.hh.um.es/Articles-Proofs/18-165-manuscript.pdf

**Abstract:**
The Non-Ciliated Bronchiolar Cell (NCBC) is responsible for the defense and maintenance of the bronchiolar epithelium. Several cellular defense mechanisms have been associated with an increase in the secretion of CC16 and changes in the phenotype of the cell; these mechanisms could be linked to tolerance to the damage due to exposure to inhaled Particulate Matter (PM) of the epithelium. These defense mechanisms have not been sufficiently explored. In this article, we studied the response of the NCBC to inhaled vanadium, an element which adheres to PM. This response was measured by the changes in the phenotype of the NCBC and the secretion of CC16 in a mouse model. Mice were exposed in two phases to different vanadium concentrations; 1.27 mg/m³ in the first phase and 2.56 mg/m³ in the second phase. Mice were sacrificed on the 2nd, 4th, 5th, 6th and 8th weeks. In the second phase, we observed the following: sloughing of the NCBC, hyperplasia and small inflammatory foci remained without changes and that the expression of CC16 was higher in this phase than in phase I. We also observed a change in the phenotype with a slow decrease in both phases. The increase in the secretion of CC16 and the phenotype reversion could be due to the anti-inflammatory activity of CC16. The changes observed in the second phase could be attributed to the tolerance to inhaled vanadium.

**Lui, K.H., Jones, T., BeruBe, K.*, et al.* (2019) The effects of particle-induced oxidative damage from exposure to airborne fine particulate matter components in the vicinity of landfill sites on Hong Kong. *Chemosphere,* 230: 578-586.**
Keywords: Landfills; PM2.5; Ambient air; Landfill composites; Oxidative potential; AROMATIC-HYDROCARBONS PAHS; POSITIVE MATRIX FACTORIZATION; FREE-RADICAL; ACTIVITY; AIR-POLLUTION; PHYSICOCHEMICAL CHARACTERIZATION; SEASONAL-VARIATIONS; TRANSITION-METALS; ORGANIC-CARBON; AEROSOLS; China; Environmental Sciences & Ecology.

**Abstract:**
The physical, chemical and bioreactivity characteristics of fine particulate matter (PM2.5) collected near (<1 km) two landfill sites and downwind urban sites were investigated. The PM2.5 concentrations were significantly higher in winter than summer. Diurnal variations of PM2.5 were recorded at both landfill sites. Soot aggregate particles were identified near the landfill sites, which indicated that combustion pollution due to landfill activities was a significant source. High correlation coefficients (r) implied several inorganic elements and water-soluble inorganic ions (vanadium (V), copper (Cu), chloride (Cl-), nitrate (NO3-), sodium (Na) and potassium (K)) were positively associated with wind flow from the landfill sites. Nevertheless, no significant correlations were also identified between these components against DNA damage. Significant associations were observed between DNA damage and some heavy metals such as cadmium (Cd) and lead (Pb), and total Polycyclic Aromatic Hydrocarbons (PAHs) during the summer. The insignificant associations of DNA damage under increased wind frequency from landfills suggested that the PM2.5 loading from sources such as regional sources was possibly an important contributing factor for DNA damage. This outcome warrants the further development of effective and source-specific landfill management

regulations for particulate matter production control to the city. (C) 2019 Elsevier Ltd. All rights reserved.

**Ma, L., Abuduwaili, J. & Liu, W. (2019) Spatial Distribution and Health Risk Assessment of Potentially Toxic Elements in Surface Soils of Bosten Lake Basin, Central Asia. *International Journal of Environmental Research and Public Health,* 16(19): 10.3390/ijerph16193741.**
Available at: https://www.mdpi.com/1660-4601/16/19/3741/pdf
Keywords: arid land; classical linear model; geographically weighted regression; influencing factors; soil geochemistry.

**Abstract:**
A geographically weighted regression and classical linear model were applied to quantitatively reveal the factors influencing the spatial distribution of potentially toxic elements of forty-eight surface soils from Bosten Lake basin in Central Asia. At the basin scale, the spatial distribution of the majority of potentially toxic elements, including: cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), thallium (Tl), vanadium (V), and zinc (Zn), had been significantly influenced by the geochemical characteristics of the soil parent material. However, the arsenic (As), cadmium (Cd), antimony (Sb), and mercury (Hg) have been influenced by the total organic matter in soils. Compared with the results of the classical linear model, the geographically weighted regression can significantly increase the level of simulation at the basin spatial scale. The fitting coefficients of the predicted values and the actual measured values significantly increased from the classical linear model (Hg: r(2) = 0.31; Sb: r(2) = 0.64; Cd: r(2) = 0.81; and As: r(2) = 0.68) to the geographically weighted regression (Hg: r(2) = 0.56; Sb: r(2) = 0.74; Cd: r(2) = 0.89; and As: r(2) = 0.85). Based on the results of the geographically weighted regression, the average values of the total organic matter for As (28.7%), Cd (39.2%), Hg (46.5%), and Sb (26.6%) were higher than those for the other potentially toxic elements: Cr (0.1%), Co (4.0%), Ni (5.3%), V (0.7%), Cu (18.0%), Pb (7.8%), Tl (14.4%), and Zn (21.4%). There were no significant non-carcinogenic risks to human health, however, the results suggested that the spatial distribution of potentially toxic elements had significant differences.

**Mohammed Nawi, A., Chin, S. & Jamal, R. (2020) Simultaneous analysis of 25 trace elements in micro volume of human serum by inductively coupled plasma mass spectrometry (ICP-MS). *Practical Laboratory Medicine,* 18: e00142.**
Available at:
https://www.sciencedirect.com/science/article/pii/S2352551719300277/pdfft?md5=dd3be8165f6bd1f83c558a5de5239966&pid=1-s2.0-S2352551719300277-main.pdf
Keywords: Trace element; Acid digestion; Serum; ICP-MS.

**Abstract:**
Introduction In recent years, trace elements have gained importance as biomarkers in many chronic diseases. Unfortunately, the requirement for sample volume increases with the extent of investigation either for diagnosis or elucidating the mechanism of the disease. Here, we describe the method development and validation for simultaneous determination of 25 trace elements (lithium [Li], beryllium [Be], magnesium [Mg], aluminium [Al], vanadium [V], chromium [Cr], manganese [Mn], iron [Fe], cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], gallium [Ga], arsenic [As], selenium [Se], rubidium [Rb], strontium [Sr], silver [Ag], cadmium [Cd], caesium [Cs], barium [Ba], mercury [Hg], thallium [Tl], lead [Pb], uranium [U]) using only 20 µL of human serum. Methods Serum samples were digested with nitric acid and hydrochloric acid (ratio 1:1, v/v) and analysed by inductively coupled plasma–mass spectrometry (ICP-MS). Seronorm®, a human-derived serum control material was used as

quality control samples. Results The coefficient of variations for both intra- and inter-day precisions were consistently <15% for all elements. The validated method was later tested on 30 human serum samples to evaluate its applicability. Conclusion We have successfully developed and validated a precise and accurate analytical method for determining 25 trace elements requiring very low volume of human serum. ".

**Muñoz, A.A., Klock-Barría, K., Sheppard, P.R.*, et al.* (2019) Multidecadal environmental pollution in a mega-industrial area in central Chile registered by tree rings. *Science of the Total Environment,* 696: 133915.**
Keywords: Baseline; Cupressus macrocarpa; Dendrochemistry; Industrial pollution; Trace metals.

**Abstract:**
One of the most polluted areas in Chile is the Ventanas Industrial Area (VIA; 32.74°S / 71.48°W), which started in 1958 and today comprises around 16 industries in an area of ca. 4 km2. A lack of consistent long-term instrumental records precludes assessing the history of contamination in the area and also limits the evaluation of mitigation actions taken since the late 1980s. Here, we use dendrochemistry as an environmental proxy to analyze environmental changes over several decades at the VIA. We present chemical measurements of tree rings from planted, exotic Cupressus macrocarpa growing near the VIA with 4-year resolution over a period of 52 years (1960–2011). These data provide unprecedented information on regional anthropogenic pollution and are compared with a tree-ring elemental record of 48 years (1964–2011) from the Isla Negra (INE) control site not exposed to VIA emissions. For the 48 years of overlap between both sites, higher concentrations of Zn, V, Co, Cd, Ag, Fe, Cr, and Al were especially registered after the year 2000 at VIA compared to INE for the periods under study. Concentrations of Pb, Cu, As, Fe, Mo, Cr, and Zn increased through time, particularly over the period 1980–1990. Decontamination plans activated in 1992 appear to have had a positive effect on the amount of some elements, but the chemical concentration in the tree rings suggest continued accumulation of pollutants in the environment. Only after several years of implementation of the mitigation measures have some elements tended to decrease in concentration, especially at the end of the evaluated period. Dendrochemistry is a useful tool to provide a long-term perspective of the dynamics of trace metal pollution and represents a powerful approach to monitor air quality variability to extend the instrumental records back in time. © 2019 Elsevier B.V.

**Nadal, M., García, F., Schuhmacher, M.*, et al.* (2019) Metals in biological tissues of the population living near a hazardous waste incinerator in Catalonia, Spain: Two decades of follow-up. *Environmental Research,* 176.**
Keywords: Autopsy tissues; Blood; Dietary intake; Hair; Hazardous waste incinerator; Human biomonitoring; Metals.

**Abstract:**
During the period 1996–1998, a hazardous waste incinerator (HWI) was built in Constantí (Tarragona County, Catalonia, Spain). Because of the potential adverse effects of toxic emissions, mainly metals and dioxins and furans, waste incinerators in general have been an important cause of concern for the public opinion. For that reason, to assess its environmental impact on the surroundings, as well as the potential human health risks of the HWI, environmental and biological monitoring studies have been carried out since 1996–1998, when the baseline concentrations were established. This article summarizes all the results corresponding to metals in biological tissues of the population living near the HWI, two decades after the construction of the facility. In 1996–1998, the baseline concentrations of a

number of elements (As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sn, Tl and V) were determined in samples of hair, blood and autopsy tissues (bone, brain, liver, lung and kidney) of subjects living in the area. In successive 5-year periods, new surveys were conducted to periodically measure the levels of metals in the same biological tissues. The daily dietary intake of these metals was also estimated for the population of the area. The results of this surveillance program do no suggest additional adverse health risks of metals for the population living near the HWI. However, special attention should be paid to Cr, due not only to the increases of this element observed in most analyzed biological tissues, but also in its dietary intake. © 2019 Elsevier Inc.

**Parker, G.J., Ong, C.H., Manges, R.B.*, et al.* (2019) A Novel Method of Collecting and Chemically Characterizing Milligram Quantities of Indoor Airborne Particulate Matter. *Aerosol and Air Quality Research,* 19: 2387-2395.**
Available at:
http://aaqr.org/article/download?articleId=8006&path=/files/article/8006/3_AAQR-19-04-OA-0182_2387-2395.pdf
Keywords: Indoor air; Particulate matter; Electrostatic precipitation; Metals.

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

**Parviainen, A., Casares-Porcel, M., Marchesi, C.*, et al.* (2019) Lichens as a spatial record of metal air pollution in the industrialized city of Huelva (SW Spain). *Environmental Pollution,* 253: 918-929.**
Keywords: Cu smelter; Industrial activity; Lichen Xanthoria parietina; Metal emissions; Urban area.

**Abstract:**
Extreme concentrations of potentially toxic elements in lichens in urban areas surrounding industrial estates imply severe air pollution and a potential health risk to residents. © 2019 Elsevier Ltd Huelva is a highly industrialized city in SW Spain hosting, among others, a Cu smelter, a phosphate fertilizer plant, a power plant, and oil refineries. This study aims to evaluate metal concentrations in lichens as bioindicators of atmospheric pollution in the impacted urban areas. Xanthoria parietina species from Huelva and nearby villages, as well as reference samples from remote, non-contaminated urban areas, were analyzed for trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Sr, As, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Er, Tm, Yb, Lu, Pb, Th, U) using Inductively Coupled Plasma-Mass Spectrometry; and for major elements (Ca, K,

Mg, P, and S) by Inductively Coupled Plasma-Optical Emission Spectrometry after acid digestion. The metal composition of X. parietina exhibits spatial distribution patterns with extremely elevated concentrations (Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U, and S) in the surroundings of the industrial estates to 1 km from the pollution sources. However, air pollution persists in the urban areas up to 4 km away, as the mean concentrations of Cu, Zn, As, Cd, Sb and S remained considerably elevated in comparison to the reference samples. Though rigorous source apportionment analysis was not the aim of this study, a good positive correlation of our results with metal abundances in ambient particulate matter and in pollution sources points to the Cu smelter as the main source of pollution. Hence, the severe air pollution affecting Huelva and nearby urban areas may be considered a serious health risk to local residents. © 2019 Elsevier Ltd.

**Requia, W.J., Coull, B.A. & Koutrakis, P. (2019) The influence of spatial patterning on modeling PM2.5 constituents in Eastern Massachusetts. *Science of the Total Environment,* 682: 247-258.**

Keywords: Air pollution; Cluster analysis; Geostatistical interpolation; PM2.5 components.

**Abstract:**
Geostatistical exposure methods for air pollution have inherent uncertainties, resulting in varying levels of exposure misclassification. In this study, we propose that areas representing clusters of PM2.5 elements are potential predictor variables to be included in spatial models for particle composition. The inclusion of these clusters may minimize the exposure misclassification. We evaluated the influence of spatial patterning on modeling of 10 components of ambient PM2.5, which included Al, Cu, Fe, K, Ni, Pb, S, Ti, V, and Zn. This study was performed in three stages. First, we applied a hybrid approach (combination of Empirical Bayesian Kriging and land use regression) to estimate spatial variability for each one of the 10 components of ambient PM2.5. In this stage, we accounted for numerous predictors representing land use, transportation, demographic, and geographical characteristics. In the second stage, we applied the same hybrid approach adding clusters of each PM2.5 component to the set of predictor variables. The clusters here were estimated by a multivariate clustering approach based on k means. Finally, in the last stage, we compared the estimates obtained from the model without clusters (first stage) and the model with clusters (second stage). Overall, our findings suggest significant influence of spatial clusters on modeling some PM2.5 components. We observed that the clusters may affect the error of the prediction values and especially the proportion of explained variance for most of the PM2.5 constituents evaluated in this study. The model with cluster presented a better performance for all PM2.5 components, except for Pb, which the R2 value decreased 8.51% when we included the clusters in the analysis; and for V, which the R2 value did not change with the clusters. Models for Cu and Fe explained the highest concentration variance. The R2 value for the model without cluster was 0.55 for both pollutants. When we accounted for clusters, R2 value increased 13 and 7% for Cu (R2 = 0.62) and Fe (R2 = 0.59), respectively. The models for K and S presented the lowest performance for both models with and without cluster (although the model with cluster improved substantially the R2 values). Better knowledge of the influence of spatial patterns on air pollution modeling should be of interest to policy makers to devise future strategies to improve human exposure assessment to air particulates while controlling for spatial patterns of ambient PM2.5 elemental concentration. © 2019 Elsevier B.V.

**Requia, W.J., Coull, B.A. & Koutrakis, P. (2019) Multivariate spatial patterns of ambient PM2.5 elemental concentrations in Eastern Massachusetts. *Environmental Pollution,* 252: 1942-1952.**

Keywords: Air pollution; Cluster analysis; Particle composition; PM2.5.

**Abstract:**
Understanding the factors that affect spatial differences in PM2.5 composition is crucial for implementing emissions control and health policies. Although previous studies have explored modeling of spatial patterns as a tool to improve human exposure assessment, little work has employed a multivariate clustering approach to identify spatial patterns in particle composition. In this study, we used this approach to assess the spatial patterns of ambient PM2.5 elemental concentrations in Eastern Massachusetts in the United States. To distinguish one cluster of sites from another, we considered air pollution sources and geodemographic variables. We evaluated spatial patterns for 11 elemental components of ambient PM2.5, which included S, K, Ca, Fe, Zn, Cu, Ti, Al, Pb, V, and Ni. The analyses for S, Ca, Cu, Ti, Al, and Pb resulted in: 2 clusters for Fe, Zn, V, and Ni; 3 clusters; and for 12 clusters for K. Overall, our findings suggest substantial variation of clusters among PM2.5 components. In addition, land use, population density, and daily traffic were used as variables to more effectively characterize clusters of sites. We used R2 values to estimate the effectiveness of each variable in characterizing clusters. Larger R2 values indicate better the discrimination among the sites. For example, population density had the highest R2 value when the analysis was performed for S, Ca, Zn, Ti, Al, Pb, and V; land use presented the highest R2 value for Cu, V, and Ni; and, traffic showed the highest R2 value for PM2.5 mass concentration. This study improves the ability to model both the between- and within-area variability of source emissions and pollution regime, using concentrations of PM2.5 components. There is substantial variation of clusters among PM2.5 components, suggesting that public policies for emission controls and public health need to be tailored to address the specific contributing variables. © 2019 Elsevier Ltd.

**Smith, M.R., Fernandes, J., Hu, X.*, et al.* (2019) Metabolome-Wide Association Study of Vanadium Exposure Reveals Exacerbated Fatty Acid Oxidation in Human Plasma and Human Lung Fibroblasts. *Free Radical Biology and Medicine,* 145: S54-S54.** Abstract presented at the 26th Annual Meeting of the Society-for-Redox-Biology-and-Medicine (SFRBM), Las Vegas, November 2--23, 2019.
Keywords: Biochemistry & Molecular Biology; Endocrinology & Metabolism.

**Sun, X., Liu, W., Zhang, B.*, et al.* (2019) Maternal Heavy Metal Exposure, Thyroid Hormones, and Birth Outcomes: A Prospective Cohort Study. *Journal of Clinical Endocrinology & Metabolism,* 104(11): 5043-5052.**
Keywords: early-pregnancy; cadmium exposure; arsenic exposure; lead-exposure; fetal-growth; vanadium; weight; iodine; dysfunction; gestation; Endocrinology & Metabolism

**Abstract:**
Context: Maternal thyroid hormones during pregnancy play a critical role in fetal development. However, whether maternal heavy metal exposure affects their thyroid hormones and the effects on fetal growth are still unclear. Objective: To explore the effect of heavy metal exposure on maternal thyroid hormones and the potential mediation role of thyroid hormones on birth outcomes. Methods: Concentrations of heavy metals in urine samples and thyroid hormones in blood samples of 675 pregnant women were measured during early pregnancy in a cohort study conducted in China. Multivariable linear regressions were applied to explore the associations of maternal urinary heavy metal levels with both maternal thyroid hormones and birth outcomes. Mediation analyses were performed to assess the mediation role of thyroid hormones in these associations. Results: Maternal urinary vanadium (V) exhibited an inverse association with free T3 (FT3) and FT3/free T4 (FT4) ratio levels. Urinary arsenic (As) and lead (Pb) had inverse relationships with FT3. We also observed

the positive associations of maternal FT3 and FT3/FT4 ratio with birthweight. The mediation analyses suggested that 5.33% to 30.57% of the associations among V, As, and Pb levels and birth size might be mediated by maternal FT3 or FT3/FT4 ratio. Conclusions: We have shown that maternal exposures to V, As, and Pb at early pregnancy were associated with decreased maternal FT3 or FT3/FT4 ratio, which might contribute to reduced birthweight. Mediation analyses indicated that maternal thyroid hormone was a possible mediator of the association between urinary heavy metals and birth size.

**Teixeira, R.A., de Souza, E.S., de Lima, M.W.*, et al.* (2019) Index of geoaccumulation and spatial distribution of potentially toxic elements in the Serra Pelada gold mine. *Journal of Soils and Sediments,* 19(7): 2934-2945.**
Keywords: Bismuth; Contamination; Enrichment factor; Gold digging; Lithium; Tellurium; Tin; heavy-metals; soils; mercury; environment; sediments; exposure; province; vanadium; risk; Environmental Sciences & Ecology; Agriculture.

**Abstract:**
Purpose -The concentration and spatial distribution of many potentially toxic elements (PTEs) have not been studied in the mining areas of tropical soils in the Amazon. The objective of this study was to evaluate the concentrations and spatial distribution of Al, Bi, Fe, Li, Sn, Sr, Te, Ti, and V in an area influenced by artisanal gold (Au) mining and chemical attributes related to soil fertility. Materials and methods - The study area is located in Serra Pelada, on the east bank of the Brazilian Amazon, in the state of Para. A total of 104 soil samples were collected with different forms of use: residential areas, agricultural, forest, and mining areas. 0.5g of soil previously sieved at 0.15mm was weighed to determine the pseudo total contents of the PTEs. The soil was mixed to 9mL of concentrated HNO3 and to 3mL of concentrated HCl; then, this solution was digested in microwave according to the EPA method 3051A (Test Methods for Evaluating Solid Waste 1-30, 2007). The digested extracts were filtered on blue filter paper and diluted with ultrapure water to the final volume of 50mL. The pseudo total contents of Al, Bi, Fe, Li, Sn, Sr, Te, Ti, and V were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).Results and discussion -The pseudo total concentrations of Al, Bi, Fe, Li, Sn, Sr, Te, Ti, and V were high, considering the natural occurrence in the soils. The levels of Li, Sn, Sr, Te, and V did not differ between them as forms of soil use, while the levels of Al, Bi, Fe, and Ti were higher in residential and/or agricultural areas. The spatial distribution maps of the elements showed that the material removed from the pit is not a major source of contamination. In the residential areas, the exploitation of the Au in the backyards provided greater surface accumulation. The accumulated geography index shown by Bi, Li, Sn, Sr, and Te varied from moderately contaminated to highly contaminated. Conclusions -The pseudo total contents of the potentially toxic elements (PTEs) are high, characterizing a scenario of diffuse contamination and geoaccumulation of Bi, Li, Sn, Sr, and Te caused by anthropogenic activities. The mine pit opened during the initial exploration of the mine is not the only one contaminated by PTEs, the exploitation of tailings, backyards, and agricultural areas were other forms of environmental contamination.

**Tsai, M.S., Chen, M.H., Lin, C.C.*, et al.* (2019) Children's environmental health based on birth cohort studies of Asia (2) - air pollution, pesticides, and heavy metals. *Environmental Research,* 179(Pt A): 108754.**
Keywords: Air pollution; Asia; Birth cohort; Heavy metals; Pesticides.

**Abstract:**
The life style and child raising environment in Asia are quite different compared with Western countries. Besides, the children's environmental threats and difficulties in conducting studies

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

**Weissmannová, H.D., Mihočová, S., Chovanec, P.*, et al.* (2019) Potential ecological risk and human health risk assessment of heavy metal pollution in industrial affected soils by coal mining and metallurgy in Ostrava, Czech Republic. *International Journal of Environmental Research and Public Health,* 16(22).**
Available at: https://www.mdpi.com/1660-4601/16/22/4495/pdf
Keywords: Ecological risk; Heavy metals; Human health risk; Pollution assessment; Soils

**Abstract:**
The heavy metal pollution of soils has become serious environmental problem, mainly in localities with high industrialization and rapid growth. The purpose of this detailed research was to determine the actual status of heavy metal pollution of soils and an assessment of heavy metal pollution in a highly industrialized city, Ostrava, with a history of long-term impacts from the metallurgy industry and mining. The ecological risks to the area was subsequently also assessed. The heavy metals Cd, Hg, Cu, Mn, Pb, V, Zn, Cr and Fe were determined in top-soils (0–20 cm) using atomic absorption spectrometry (F AAS, GF AAS) from three areas with different anthropogenic loads. The obtained data expressed as mean metal concentrations were very varied among the sampled soils and values of all analyzed metal concentrations were higher than its background levels. To identify the ecological risk and assessment of soil pollution, various pollution indices were calculated, such as single pollution indices (Igeo, CF, EF, PI) and total complex indices (IPI, PLI, PINemerow, Cdeg, mCdeg, Er and PERI). The identification of pollution sources was assessed using Pearson's correlation analysis and multivariate methods (HCA, PCA/FA). The obtained results confirmed three major groups of metals (Fe–Cr, Pb–Cu and Mn–V). A human health risk was identified in the case of Pb, Cd and Cr, and the HI value of V for children also exceeded 1. © 2019 by the authors. Licensee MDPI, Basel, Switzerland.

**Williams, A.L., Gollapudi, B., Pace, N.D.*, et al.* (2019) Comment on "Concentrations of vanadium in urine and seminal plasma in relation to semen quality parameters, spermatozoa DNA damage and serum hormone levels," by Wang et al. *Science of the Total Environment,* 685: 772-774.**
Keywords: Vanadium; DNA damage; sex hormones; sperm; fertility; university-students; reference values; sperm counts; comet assay; area; men; ratios; health; risk; Environmental Sciences & Ecology.

**Wu, Y., Li, G., Yang, Y.*, et al.* (2019) Pollution evaluation and health risk assessment of airborne toxic metals in both indoors and outdoors of the Pearl River Delta, China. *Environmental Research,* 179.**
Keywords: Health risk assessment; Indoor and outdoor pollution; Pearl river delta; Toxic metals.

**Abstract:**
Background: Industries developed cities in the Pearl River Delta (PRD) are suffering serious atmospheric metals pollution, in which, people's health risks after inhaling particulate matter (PM) with airborne toxic metals might be rising. This study provides the latest and comprehensive pollution profiles of toxic metals both from indoors and outdoors in PRD. Method: Total 22 pairs of indoor and outdoor total suspended particulates (TSP), PM10 and PM2.5 samples in residential area were synchronously sampled and investigated in detail within 9 main cities of the PRD, China. The concentrations of the Zn, Pb, Mn, Ni, As, V, Sb and Cd in the samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). Health risk assessment via inhalation of residents was estimated by EPA recommended model with exposure parameters of Chinese population indoor and outdoor activity pattern. Results: The trends followed as Zn > Pb ≈ Mn > Ni > As > V > Sb ≈ Cd for both indoors and outdoors. Investigated metals were found to be dominantly distributed in PM2.5 for both indoors and outdoors. The concentrations of outdoor PM and the most of metals were significantly higher than those of indoors. The results concluded that toxic metals might be from regional emission, such as Pb from ceramic factory, Ni from motor factory and V from oil combustion of ship. In health risk assessments, LCR is higher than 1.00E-06 for adults, while contrary to children in the PRD. Among four carcinogenic metals, LCR of As and Cd are higher than 1.00E-06 in some cities. In addition, HI below one for both adults and children in the PRD. Conclusions: Outdoor metals concentrations are related to local industry types, while indoor metals are mainly from outdoor. Health risk assessments indicated that adults suffered unsafe cancer risk from metals, especially As and Cd in some cities, while both adults and children did not suffer non-carcinogenic risks. © 2019 Elsevier Inc.

# 2. HEALTH EFFECTS

**Austin, C., Curtin, P., Curtin, A.*, et al.* (2019) Dynamical properties of elemental metabolism distinguish attention deficit hyperactivity disorder from autism spectrum disorder. *Translational Psychiatry,* 9(1): Article number 238.**
Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6760156/pdf/41398_2019_Article_567.pdf

**Abstract:**
Attention deficit hyperactivity disorder (ADHD) and autism spectrum disorder (ASD) are neurodevelopmental conditions of overlapping etiologies and phenotypes. For ASD, we recently reported altered elemental metabolic patterns in the form of short and irregular zinc and copper cycles. Here, we extend the application of these biomarkers of prenatal and early postnatal elemental metabolism to distinguish between individuals diagnosed with ADHD and/or ASD and neurotypical controls. We recruited twins discordant for ADHD, ASD and other neurodevelopmental diagnoses from national twin studies in Sweden (N = 74) diagnosed according to DSM-5 clinical consensus and standardized psychiatric instruments. Detailed temporal profiles of exposure to 10 metals over the prenatal and early childhood periods were measured using tooth biomarkers. We used recurrence quantification analysis (RQA) to characterize properties of cyclical metabolic patterns of these metals. Regularity (determinism) and complexity (entropy) of elemental cycles was consistently reduced in

ADHD for cobalt, lead, and vanadium (determinism: cobalt, β = −0.03, P = 0.017; lead, β = −0.03, P = 0.016; and vanadium, β = −0.03, P = 0.01. Entropy: cobalt, β = −0.13, P = 0.017; lead, β = −0.18, P = 0.016; and vanadium, β = −0.15, P = 0.008). Further, we found elemental pathways and dynamical features specific to ADHD vs ASD, and unique characteristics associated with ADHD/ASD combined presentation. Dysregulation of cyclical processes in elemental metabolism during prenatal and early postnatal development not only encompasses pathways shared by ADHD and ASD, but also comprise features specific to either condition. © 2019, The Author(s).

**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.**
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412019302272/pdfft?md5=7290cbba319f215f81f9d6e6a852e9e3&pid=1-s2.0-S0160412019302272-main.pdf
Keywords: Essential metals; Zinc; Lung cancer; Cohort study; Telomere attrition; Gene expression.

**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 [β (95% CI) = −0.73 (−1.27, −0.19)]. These effects were pronounced among males. In particularly, zinc could regulate the expressions of 8 cancer-related genes, including *SOD1*, *APE*, *TP53BP1*, *WDR33*, *LAPTM4B*, *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.

**Gomez-Tomas, A., Pumarega, J., Alguacil, J.*, et al.* (2019) Concentrations of trace elements and KRAS mutations in pancreatic ductal adenocarcinoma. *Environmental and Molecular Mutagenesis,* 60(8): 693-703.**
Keywords: KRAS oncogene; etiology; pancreatic ductal adenocarcinoma; pancreatic neoplasm; trace elements.

**Abstract:**

Trace elements are a possible risk factor for pancreatic ductal adenocarcinoma (PDAC). However, their role in the occurrence and persistence of KRAS mutations remains unstudied. There appear to be no studies analyzing biomarkers of trace elements and KRAS mutations in any human cancer. We aimed to determine whether patients with KRAS mutated and nonmutated tumors exhibit differences in concentrations of trace elements. Incident cases of PDAC were prospectively identified in five hospitals in Spain. KRAS mutational status was determined through polymerase chain reaction from tumor tissue. Concentrations of 12 trace elements were determined in toenail samples by inductively coupled plasma mass spectrometry. Concentrations of trace elements were compared in 78 PDAC cases and 416 hospital-based controls (case-control analyses), and between 17 KRAS wild-type tumors and 61 KRAS mutated tumors (case-case analyses). Higher levels of iron, arsenic, and vanadium were associated with a statistically nonsignificant increased risk of a KRAS wild-type PDAC (OR for higher tertile of arsenic = 3.37, 95% CI 0.98-11.57). Lower levels of nickel and manganese were associated with a statistically significant higher risk of a KRAS mutated PDAC (OR for manganese = 0.34, 95% CI 0.14-0.80). Higher levels of selenium appeared protective for both mutated and KRAS wild-type PDAC. Higher levels of cadmium and lead were clear risk factors for both KRAS mutated and wild-type cases. This is the first study analyzing biomarkers of trace elements and KRAS mutations in any human cancer. Concentrations of trace elements differed markedly between PDAC cases with and without mutations in codon 12 of the KRAS oncogene, thus suggesting a role for trace elements in pancreatic and perhaps other cancers with such mutations. Environ. Mol. Mutagen. 2019. (c) 2019 Wiley Periodicals, Inc.

**Hu, J., Peng, Y., Zheng, T.*, et al.* (2018) Effects of trimester-specific exposure to vanadium on ultrasound measures of fetal growth and birth size: a longitudinal prospective prenatal cohort study. *The Lancet.Planetary Health,* 2(10): e427-e437.**
Available at:
https://www.sciencedirect.com/science/article/pii/S2542519618302109/pdfft?md5=c660b708e6b659723b2e2b72cbdaad79&pid=1-s2.0-S2542519618302109-main.pdf
Keywords: Adult; Birth Weight/drug effects; China; Dose-Response Relationship, Drug; Environmental Pollutants/adverse effects; Female; Fetal Development/drug effects; Humans; Longitudinal Studies; Male; Maternal Exposure/adverse effects; Nonlinear Dynamics; Pregnancy; Pregnancy Trimesters/drug effects; Prospective Studies; Ultrasonography, Prenatal; Vanadium/adverse effects; Young Adult

**Abstract:**
BACKGROUND: Identification of windows of heightened vulnerability to environmental factors has substantial public health implications. Prenatal exposure to vanadium has been linked to adverse birth outcomes; however, critical windows for such exposure during fetal growth remain unknown. We aimed to assess trimester-specific associations of vanadium exposure with ultrasound measures of fetal growth and birth size in a Chinese longitudinal cohort. METHODS: The present study was embedded in our ongoing prospective prenatal cohort study at the Wuhan Women and Children Medical Care Center (Wuhan, Hubei, China). Pregnant women were eligible for inclusion if they provided signed informed consent and were less than 16 weeks pregnant with a single gestation, and agreed to take in-person interviews, undergo ultrasound examinations, and provide blood and urine samples. We collected urine samples and measured urinary vanadium concentrations using inductively coupled plasma mass spectrometry. We calculated SD scores for ultrasound-measured biparietal diameter, head circumference, occipitofrontal diameter, abdominal circumference, femur length, and estimated fetal weight at 16, 24, and 31 weeks of gestation. We applied linear regressions with generalised estimating equations to estimate associations of urinary vanadium concentrations in each trimester with ultrasound-measured fetal growth

parameters or neonatal size at birth. FINDINGS: As of Oct 12, 2016, we recruited 3075 women who were non-smokers and non-drinkers during pregnancy, provided up to three urine samples during the first, second, and third trimesters, and gave birth to live singletons without birth defects. We excluded women who did not provide information on ultrasound measurements (n=20) or who only had one ultrasound measurement of fetal crown-rump length at the first trimester (n=14). We excluded another 16 women because they had missing values for confounding variables, leaving 3025 women retained in the study. Every doubling of urinary vanadium concentration in the first trimester was associated with a significant increase in femur length (adjusted percentage change 6.4%, 95% CI 0.7 to 12.1) at 16 weeks of gestation and reductions in biparietal diameter (-4.2%, -8.2 to -0.1), head circumference (-6.0%, -10.1 to -1.9), occipitofrontal diameter (-5.7%, -9.9 to -1.5), and abdominal circumference (-5.3%, -9.4 to -1.2) at 31 weeks of gestation. Every doubling of urinary vanadium concentration in the second trimester was significantly associated with reductions in SD scores for head circumference (-7.2%, -14.1 to -0.3) and abdominal circumference (-6.9%, -13.8 to -0.1) at 31 weeks of gestation. The highest quartile of urinary vanadium concentration (>1.18 mug/L) in the first trimester, when compared with the lowest quartile (</=0.60 mug/L), was associated with a mean decrease in birthweight of 12.6 g (95% CI 2.5-22.8; ptrend=0.0055) and a mean decrease in ponderal index of 0.07 kg/m(3) (0.01-0.12; ptrend=0.0053). Moreover, newborns with restricted birth size had higher vanadium exposure in the first and third trimesters. INTERPRETATION: Vanadium might be toxic to humans and impair fetal growth. The first, early second, and late third trimesters could be critical windows for heightened vulnerability to vanadium for fetal growth. Our findings require further investigation in other populations. FUNDING: National Key R&D Plan of China, National Natural Science Foundation of China, and Fundamental Research Funds for the Central Universities, Huazhong University of Science and Technology.

**Kambunga, S.N., Candeias, C., Hasheela, I.*, et al.* (2019) The geochemistry of geophagic material consumed in Onangama Village, Northern Namibia: a potential health hazard for pregnant women in the area. *Environmental Geochemistry and Health,* 41(5): 1987-2009.**
Keywords: Geochemistry; Geophagy; Pregnant women; Termite mound soils.

**Abstract:**
Ingestion of geophagic materials might affect human health and induce diseases by different ways. The purpose of this study is to determine the geochemical composition of geophagic material consumed especially by pregnant women in Onangama Village, Northern Namibia and to assess its possible health effects. X-ray fluorescence and inductively coupled plasma mass spectrometry were used in order to determine the major, and trace elements as well as anions concentrations of the consumed material. The geochemical analysis revealed high concentrations of aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), potassium (K), sodium (Na), and silica (Si); and trace elements including arsenic (As), chromium (Cr), mercury (Hg), nickel (Ni) and vanadium (V) as well as sulphate (SO4(2-)), nitrate (NO3(-)), and nitrite (NO2(-)) anions comparing to the recommended daily allowance for pregnant women. The pH for some of the studied samples is alkaline, which might increase the gastrointestinal tract pH (pH 1) revealed that Al and Mn might be a potential risk for human consumption. Based on the results obtained from the geochemical analysis, the consumption of the studied material might present a potential health risk to pregnant women including concomitant detrimental maternal and foetal effects.

**Koubaa, F.G., Abdennabi, R., Soussi Ben Salah, A.*, et al.* (2019) Microwave extraction of Salvia officinalis essential oil and assessment of its GC-MS identification and protective**

**effects versus vanadium-induced nephrotoxicity in Wistar rats models.** ***Archives of Physiology and Biochemistry,*** **125(5): 404-413.**
Keywords: Metavanadate; Salvia officinalis; antioxidant enzyme activities; kidney.

**Abstract:**
In this study, we assess the impact of Salvia officinalis essential oil on renal toxicity induced by vanadium in rats. The animals were exposed to either ammonium metavanadate (5 mg/kg body weight) or the combination of vanadium and S. officinalis essential oil (15 mg EO/kg body weight) for 10 days. Vanadium induced significant renal damage, demonstrated by increased plasma levels of urea and creatinine. A marked increase in lipid peroxidation markers and carbonyl protein levels with a significant decrease in enzymatic antioxidants (SOD), catalase (CAT), and glutathione peroxidase (GPx) was also observed in vanadium-treated rats. Histopathological studies also showed vanadium-induced alterations. Concomitant administration of sage essential oil significantly restored biochemical markers and pathological lesions. This protective effect seems to be due to the richness of this extract in beta-caryophyllene, limonene, carvacrol, caryophyllene, borneol and alpha-pinene, and alpha-pinene and alpha-thujene. These rates are determined by GC MS.

**Scibior, A. & Kurus, J. (2019) Vanadium and Oxidative Stress Markers - In Vivo Model: A Review.** ***Current Medicinal Chemistry,*** **26(29): 5456-5500.**
Keywords: Animals; Antioxidants; Biomarkers/analysis/metabolism; Free Radicals/analysis; Humans; Lipid Peroxidation/drug effects; Oxidative Stress/drug effects; Reactive Oxygen Species/analysis/metabolism; Vanadium/chemistry/pharmacology; Vanadium; animal studies; interactions; lipid peroxidation (LPO); magnesium; oxidative stress markers; reactive oxygen species (ROS).

**Abstract:**
This review article is an attempt to summarize the current state of knowledge of the impact of Vanadium (V) on Oxidative Stress (OS) markers in vivo. It shows the results of our studies and studies conducted by other researchers on the influence of different V compounds on the level of selected Reactive Oxygen Species (ROS)/Free Radicals (FRs), markers of Lipid peroxidation (LPO), as well as enzymatic and non-enzymatic antioxidants. It also presents the impact of ROS/peroxides on the activity of antioxidant enzymes modulated by V and illustrates the mechanisms of the inactivation thereof caused by this metal and reactive oxygen metabolites. It also focuses on the mechanisms of interaction of V with some nonenzymatic compounds of the antioxidative system. Furthermore, we review the routes of generation of oxygen-derived FRs and non-radical oxygen derivatives (in which V is involved) as well as the consequences of FR-mediated LPO (induced by this metal) together with the negative/ positive effects of LPO products. A brief description of the localization and function of some antioxidant enzymes and low-molecular-weight antioxidants, which are able to form complexes with V and play a crucial role in the metabolism of this element, is presented as well. The report also shows the OS historical background and OS markers (determined in animals under V treatment) on a timeline, collects data on interactions of V with one of the elements with antioxidant potential, and highlights the necessity and desirability of conducting studies of mutual interactions between V and antioxidant elements.

**Smith, M.R., Fernandes, J., Hu, X.*, et al.* (2019) Metabolome-Wide Association Study of Vanadium Exposure Reveals Exacerbated Fatty Acid Oxidation in Human Plasma and Human Lung Fibroblasts.** ***Free Radical Biology and Medicine,*** **145: S54-S54.** Abstract presented at the 26th Annual Meeting of the Society-for-Redox-Biology-and-Medicine (SFRBM), Las Vegas, November 2--23, 2019.

Keywords: Biochemistry & Molecular Biology; Endocrinology & Metabolism.

**Sun, X., Liu, W., Zhang, B.*, et al.* (2019) Maternal Heavy Metal Exposure, Thyroid Hormones, and Birth Outcomes: A Prospective Cohort Study. *Journal of Clinical Endocrinology & Metabolism,* 104(11): 5043-5052.**
Keywords: early-pregnancy; cadmium exposure; arsenic exposure; lead-exposure; fetal-growth; vanadium; weight; iodine; dysfunction; gestation; Endocrinology & Metabolism

**Abstract:**
Context: Maternal thyroid hormones during pregnancy play a critical role in fetal development. However, whether maternal heavy metal exposure affects their thyroid hormones and the effects on fetal growth are still unclear. Objective: To explore the effect of heavy metal exposure on maternal thyroid hormones and the potential mediation role of thyroid hormones on birth outcomes. Methods: Concentrations of heavy metals in urine samples and thyroid hormones in blood samples of 675 pregnant women were measured during early pregnancy in a cohort study conducted in China. Multivariable linear regressions were applied to explore the associations of maternal urinary heavy metal levels with both maternal thyroid hormones and birth outcomes. Mediation analyses were performed to assess the mediation role of thyroid hormones in these associations. Results: Maternal urinary vanadium (V) exhibited an inverse association with free T3 (FT3) and FT3/free T4 (FT4) ratio levels. Urinary arsenic (As) and lead (Pb) had inverse relationships with FT3. We also observed the positive associations of maternal FT3 and FT3/FT4 ratio with birthweight. The mediation analyses suggested that 5.33% to 30.57% of the associations among V, As, and Pb levels and birth size might be mediated by maternal FT3 or FT3/FT4 ratio. Conclusions: We have shown that maternal exposures to V, As, and Pb at early pregnancy were associated with decreased maternal FT3 or FT3/FT4 ratio, which might contribute to reduced birthweight. Mediation analyses indicated that maternal thyroid hormone was a possible mediator of the association between urinary heavy metals and birth size.

**Tabrizian, K., Esmaeilei, M., Hashemzaei, M.*, et al.* (2019) Protective Effects of Aminoguanidine against Sodium Metavanadate-Induced Spatial Memory Retention Impairment in Morris Water Maze. *Pharmaceutical Sciences,* 25(2): 93-99.**
Available at:
https://pdfs.semanticscholar.org/6aa6/7e0a817bb725593e9a42b91a3fd532e5ed39.pdf
Keywords: Sodium metavanadate; Inducible Nitric Oxide Synthase; Morris water maze; Spatial memory; nicotine-bucladesine combination; nitric-oxide production; long-term; potentiation; intrahippocampal infusion; vanadium; inhibition; hippocampus; involvement; inhalation; expression; Pharmacology & Pharmacy.

**Abstract:**
Background: Vanadium is a potential neurotoxic agent widely distributed in the environment. Understanding the neurotoxic mechanisms of vanadium on learning and memory seems necessary. Methods: We investigated the time-dependent (1-week, 2- week and 4-week) effects of sodium metavanadate (SMV) (25 mg/kg/day; pre-training oral administration) and 4-day intraperitonealperhao injections of aminoguanidine (AG) as a selective inducible nitric oxide synthase inhibitor (10, 50, and 100 mg/kg) on spatial memory retention in Morris water maze. Animals were trained for 4 days and tested 48 h after the last training trial. Results: The data showed that 4-week oral pre-treatment with SMV (25 mg/kg/day) induced spatial memory retention deficits and decreased the time spent in the target quadrant. We found that 4-day administration of different doses of AG during training trials significantly decreased the time and distance of finding the hidden platforms. Additionally, SMV-induced spatial

memory retention impairments were prevented in animals received combined SMV (25 mg/kg/day, 4 weeks) and AG (10 mg/kg/day, 4 days). Conclusion: Our findings showed the protective role of AG on SMV-induced spatial memory retention deficits.

**Tsai, M.S., Chen, M.H., Lin, C.C.*, et al.* (2019) Children's environmental health based on birth cohort studies of Asia (2) - air pollution, pesticides, and heavy metals. *Environmental Research,* 179(Pt A): 108754.**
Keywords: Air pollution; Asia; Birth cohort; Heavy metals; Pesticides.

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

**Williams, A.L., Gollapudi, B., Pace, N.D.*, et al.* (2019) Comment on "Concentrations of vanadium in urine and seminal plasma in relation to semen quality parameters, spermatozoa DNA damage and serum hormone levels," by Wang et al. *Science of the Total Environment,* 685: 772-774.**
Keywords: Vanadium; DNA damage; sex hormones; sperm; fertility; university-students; reference values; sperm counts; comet assay; area; men; ratios; health; risk; Environmental Sciences & Ecology.

**Wu, Y., Li, G., Yang, Y.*, et al.* (2019) Pollution evaluation and health risk assessment of airborne toxic metals in both indoors and outdoors of the Pearl River Delta, China. *Environmental Research,* 179.**
Keywords: Health risk assessment; Indoor and outdoor pollution; Pearl river delta; Toxic metals.

**Abstract:**
Background: Industries developed cities in the Pearl River Delta (PRD) are suffering serious atmospheric metals pollution, in which, people's health risks after inhaling particulate matter (PM) with airborne toxic metals might be rising. This study provides the latest and comprehensive pollution profiles of toxic metals both from indoors and outdoors in PRD. Method: Total 22 pairs of indoor and outdoor total suspended particulates (TSP), PM10 and PM2.5 samples in residential area were synchronously sampled and investigated in detail

within 9 main cities of the PRD, China. The concentrations of the Zn, Pb, Mn, Ni, As, V, Sb and Cd in the samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). Health risk assessment via inhalation of residents was estimated by EPA recommended model with exposure parameters of Chinese population indoor and outdoor activity pattern. Results: The trends followed as Zn > Pb ≈ Mn > Ni > As > V > Sb ≈ Cd for both indoors and outdoors. Investigated metals were found to be dominantly distributed in PM2.5 for both indoors and outdoors. The concentrations of outdoor PM and the most of metals were significantly higher than those of indoors. The results concluded that toxic metals might be from regional emission, such as Pb from ceramic factory, Ni from motor factory and V from oil combustion of ship. In health risk assessments, LCR is higher than 1.00E-06 for adults, while contrary to children in the PRD. Among four carcinogenic metals, LCR of As and Cd are higher than 1.00E-06 in some cities. In addition, HI below one for both adults and children in the PRD. Conclusions: Outdoor metals concentrations are related to local industry types, while indoor metals are mainly from outdoor. Health risk assessments indicated that adults suffered unsafe cancer risk from metals, especially As and Cd in some cities, while both adults and children did not suffer non-carcinogenic risks. 

# 3. BIOLOGICAL MECHANISMS

**Althumairy, D., Murakami, H.A., Zhang, D.*, et al.* (2020) Effects of vanadium(IV) compounds on plasma membrane lipids lead to G protein-coupled receptor signal transduction. *Journal of Inorganic Biochemistry,* 203: 110873.**

Keywords: Vanadium; G-protein-coupled receptor; BMOV; Signal transduction; Vanadyl; Plasma membrane rafts; Luteinizing hormone receptor.

**Abstract:**
Luteinizing hormone receptors (LHR), expressed at physiological numbers 85,000 receptors per cell) are found in larger clusters in polarized homo-transfer fluorescence resonance energy transfer (homo-FRET) studies that were not affected by either hCG or vanadium compounds. Intracellular cyclic adenylate monophosphate (cAMP) levels indicate that only clustered LHR are active and produce the intracellular second messenger, cAMP. When LHR are over-expressed, cell signaling is unaffected by binding of hCG or vanadium compounds. To confirm the existence of intact complex, the EPR spectra of vanadium compounds in cell media were obtained using 1 mM BMOV, BEOV or VOSO4. These data were used to determine intact complex in a 10 μM solution and verified by speciation calculations. Effects of BMOV and BEOV samples were about two-fold greater than those of aqueous vanadium(IV) making it likely that intact vanadium complex are responsible for effects of LHR function. This represents a new mechanism for activation of a G protein-coupled receptor; perturbations in the lipid bilayer by vanadium compounds lead to aggregation and accumulation of physiological numbers of LHR in membrane raft domains where they initiate signal transduction and production of cAMP, a second messenger involved in signaling. ".

**Barkarmo, S., Ostberg, A.K., Johansson, C.B.*, et al.* (2018) Inflammatory cytokine release from human peripheral blood mononuclear cells exposed to polyetheretherketone and titanium-6 aluminum-4 vanadium in vitro. *Journal of Biomaterials Applications,* 33(2): 245-258.**

Keywords: Biocompatible Materials/adverse effects; Cytokines/immunology; Humans; Inflammation/etiology/immunology; Ketones/adverse effects; Leukocytes, Mononuclear/drug effects/immunology; Polyethylene Glycols/adverse effects; Titanium/adverse effects; Polyetheretherketone; cytokines; in vitro; inflammatory mediators; titanium-6 aluminum-4 vanadium.

**Abstract:**
Objective To investigate the cytokine expression profiles of blood cells exposed to polyetheretherketone and titanium-6 aluminum-4 vanadium materials in vitro. Materials and methods Coin-shaped samples composed of titanium-6 aluminum-4 vanadium, polyetheretherketone, and blasted polyetheretherketone were manufactured. The surfaces of the coins were characterized using optical interferometry, scanning electron microscopy, and contact angle measurements. Peripheral blood mononuclear cells collected from 10 blood donors were cultured for one, three, and six days in the presence or absence of the coins, and then assayed for cytokine production. Quantification of the peripheral blood mononuclear cells attached to the coins was performed using confocal microscopy after immunofluorescence staining. Results The machined titanium-6 aluminum-4 vanadium coins had a smoother surface topography compared to the machined polyetheretherketone and blasted polyetheretherketone. The highest mean contact angle was noted for the blasted polyetheretherketone, followed by the machined polyetheretherketone and titanium-6 aluminum-4 vanadium. The peripheral blood mononuclear cells produced significantly more proinflammatory cytokines when exposed to the polyetheretherketone surface compared to the titanium-6 aluminum-4 vanadium surface, while the blasted polyetheretherketone induced the highest level of proinflammatory cytokine release from the peripheral blood mononuclear cells. Significantly more cells attached to both polyetheretherketone surfaces, as compared to the titanium-6 aluminum-4 vanadium surface. Conclusion Polyetheretherketone induces a stronger inflammatory response from peripheral blood mononuclear cells than does titanium-6 aluminum-4 vanadium. Surface topography has an impact on cytokine release from peripheral blood mononuclear cells.

**Cho, J., Bing, S.J., Kim, A.*, et al.* (2019) Jeju ground water containing vanadium induces normal T cell development and immune activation in chronically stressed mice. *Molecular Biology Reports,* 46(4): 4443-4452.**
Keywords: Jeju ground water; Chronic stress; Immune activation; T cell development; animal-models; depression; susceptibility; cytokines; anxiety; system; mouse; Biochemistry & Molecular Biology

**Abstract:**
Containing high concentration of vanadium served by the volcanic bedrock, Jeju ground water has long been known for various implicit health benefits including immune-promotion. Exposure to stress has been reported to be associated with immunosuppression such as reducing lymphocyte population or antibody production due to stress hormones. In this study, we aimed at evaluating the effects of Jeju ground water on chronically stressed mice. C57BL/6 mice were subjected to various stressors such as restraint stress, water swimming stress, heat stress, acoustic stress, and Jeju ground water was supplied for 28days with two different concentrations, S1 (vanadium 15-20 mu g/l, pH 8.3) and S2 (vanadium 20-25 mu g/l, pH 8.5). Treatment with Jeju ground water increased CD4(+)CD8(-) or CD4(-)CD8(+) single-positive thymocytes. It also increased the proliferation of splenocytes and the populations of CD4(+) T cells, CD45R/B220(+) B cells, CD11b(+) macrophages or Gr-1(+) granulocytes in spleen. In addition, the production of IgG was increased in chronically stressed mice by treatment with Jeju ground water. These results suggest vanadium-rich Jeju ground water may be helpful in T cell development in thymus and immune cell proliferation and its function in spleen against chronic stress.

**Gomez-Tomas, A., Pumarega, J., Alguacil, J.*, et al.* (2019) Concentrations of trace elements and KRAS mutations in pancreatic ductal adenocarcinoma. *Environmental and Molecular Mutagenesis,* 60(8): 693-703.**

Keywords: KRAS oncogene; etiology; pancreatic ductal adenocarcinoma; pancreatic neoplasm; trace elements.

**Abstract:**

Trace elements are a possible risk factor for pancreatic ductal adenocarcinoma (PDAC). However, their role in the occurrence and persistence of KRAS mutations remains unstudied. There appear to be no studies analyzing biomarkers of trace elements and KRAS mutations in any human cancer. We aimed to determine whether patients with KRAS mutated and nonmutated tumors exhibit differences in concentrations of trace elements. Incident cases of PDAC were prospectively identified in five hospitals in Spain. KRAS mutational status was determined through polymerase chain reaction from tumor tissue. Concentrations of 12 trace elements were determined in toenail samples by inductively coupled plasma mass spectrometry. Concentrations of trace elements were compared in 78 PDAC cases and 416 hospital-based controls (case-control analyses), and between 17 KRAS wild-type tumors and 61 KRAS mutated tumors (case-case analyses). Higher levels of iron, arsenic, and vanadium were associated with a statistically nonsignificant increased risk of a KRAS wild-type PDAC (OR for higher tertile of arsenic = 3.37, 95% CI 0.98-11.57). Lower levels of nickel and manganese were associated with a statistically significant higher risk of a KRAS mutated PDAC (OR for manganese = 0.34, 95% CI 0.14-0.80). Higher levels of selenium appeared protective for both mutated and KRAS wild-type PDAC. Higher levels of cadmium and lead were clear risk factors for both KRAS mutated and wild-type cases. This is the first study analyzing biomarkers of trace elements and KRAS mutations in any human cancer. Concentrations of trace elements differed markedly between PDAC cases with and without mutations in codon 12 of the KRAS oncogene, thus suggesting a role for trace elements in pancreatic and perhaps other cancers with such mutations. Environ. Mol. Mutagen. 2019. (c) 2019 Wiley Periodicals, Inc.

**Griffin, E., Levina, A. & Lay, P.A. (2019) Vanadium(V) tris-3,5-di-tert-butylcatecholato complex: Links between speciation and anti-proliferative activity in human pancreatic cancer cells. *Journal of Inorganic Biochemistry,* 201: 110815.**

Keywords: Cytotoxicity; Human serum albumin; Intratumoral injections; Pancreatic cancer; Speciation; Vanadium.

**Abstract:**

Vanadium complexes are intensively tested for anti-cancer activities, particularly for the novel treatment protocols involving injections of cytotoxic compounds directly into the tumor. This approach is increasingly applied to difficult-to-treat cancers, such as pancreatic cancer. The first study of in-vitro anti-cancer properties of a rare stable non-oxido V(V) complex, (NH4)[V(dtbc)3], where dtbcH2 is 3,5-di-tert-butylcatechol, was performed by a combination of end-point viability assays and real-time (IncuCyte) proliferation and cytotoxicity assays in human pancreatic cancer (PANC-1) cells. An improved synthetic procedure led to a nearly quantitative yield of the complex under ambient conditions. Reactions of (NH4)[V(dtbc)3] either in polar organic solvents or in neutral aqueous media led to the formation of V(V)-oxido-catecholato intermediates (characterized by electrospray mass spectrometry) that were responsible for its anti-proliferative and cytotoxic (apoptotic or necrotic) activity (IC50, 3.5-18muMV in 72h assays). These results demonstrate the link between solution speciation and biological activity of V complexes. Reaction of (NH4)[V(dtbc)3] with human serum albumin (HSA) in aqueous media led to the formation of protein-bound V(V) oxido-catecholato species that showed high anti-proliferative activity (IC50 ~10muMV) combined

with low cytotoxicity. Formation of HSA adducts of hydrophobic V complexes, such as (NH4)[V(dtbc)3], is a promising way to achieve their sustained delivery to cancer tumors.

**Hou, C.C., Liang, H.Y., Pan, Y.H.*, et al.* (2019) Vanadium compounds induced damage of human umbilical vein endothelial cells and the protective effect of berberine. *Biometals : An International Journal on the Role of Metal Ions in Biology, Biochemistry, and Medicine,* 32(5): 785-794.**

Keywords: Berberine; Endothelial nitric oxide synthase; Human umbilical vein endothelial cells; Reactive oxygen species; Vanadium compounds.

**Abstract:**

This study was conducted to investigate the damage caused by vanadium compounds and to explore the protective effects of berberine (BBR) in human umbilical vein endothelial cells (HUVECs). BBR is a biologically active small molecule found in Coptis rhizome, a remedy used in traditional Chinese medicine to treat diabetes. BBR has also been shown to lower blood glucose in diabetic patients. MTT assay was performed to observe the influence of bis(acetylacetonato)-oxidovanadium [VO(acac)2] or sodium metavanadate (NaVO3) and BBR on viability of HUVECs. The monolayer permeability of the HUVECs was assessed by measuring the transendothelial electrical resistance (TER). The endothelial nitric oxide synthase (eNOS) activity was detected by ELISA. Flow cytometry was performed to detect the generation of reactive oxygen species (ROS). The results showed that the viability of HUVECs was decreased by treatment with vanadium compounds 50-400 muM in a concentration-dependent manner, while 0.01-1 muM BBR effectively protected HUVECs from the inhibitory effects of vanadium compounds on cell viability. Also 100 and 200 muM VO(acac)2 induced high permeability and decreased eNOS activity in HUVECs. While 0.01-1 muM BBR showed no improvement in the permeability, and failed to reverse the VO(acac)2-induced changes of eNOS activity, but BBR treatment increased the eNOS activity in control cells. The addition of 200 muM VO(acac)2 significantly induced ROS generation in HUVECs, while 0.01 or 0.1 muM BBR reversed the change of ROS. In summary, BBR has protective effects in HUVECs damage induced by vanadium compounds, which is not mediated by eNOS, but related to reduced intracellular ROS.

**Kim, U.J., Lee, B.H. & Lee, K.H. (2019) Neuroprotective effects of a protein tyrosine phosphatase inhibitor against hippocampal excitotoxic injury. *Brain Research,* 1719: 133-139.**

Keywords: Excitotoxicity; Kainic acid; Organotypic hippocampal slice culture; Sodium orthovanadate; Survival signal.

**Abstract:**

Neuronal excitotoxicity is the neuronal cell death arising from prolonged exposure to glutamate and the associated excessive influx of ions into the cell. Sodium orthovanadate (Na3VO4,) competitively inhibits the protein tyrosine phosphatases that affect intracellular protein phosphorylation. No study has examined the role of protein tyrosine phosphatases in kainic acid (KA)-induced excitotoxic injury using sodium orthovanadate. Thus, the present study was conducted to determine the neuroprotective effects of sodium orthovanadate on KA-induced neuronal death in organotypic hippocampal slice culture. We also performed an in vivo electrophysiology study in Sprague-Dawley rats to observe the function of surviving cells after sodium orthovanadate treatment in KA-induced excitotoxicity. Rats were anaesthetized with sodium pentobarbital and KA was injected unilaterally in CA3 of the hippocampus by microinjection-cannula. Neuronal cell death, as assessed by propidium iodide uptake, was reduced by 10 and 25 μM sodium orthovanadate treatment (24 and 48 h)

compared with the KA-only group. Sodium orthovanadate enhanced survival signals by increasing levels of phospho-Akt and superoxide dismutase. In addition, sodium orthovanadate treatment reduced calcineurin level for neuronal protection, which regulates activation of cellular calcium caused by KA-induced injury. In vivo results showed that sodium orthovanadate treatment elicited resistance to KA-induced behavior seizures and significantly reduced the duration of epileptiform discharges. In addition, sodium orthovanadate treatment (25 mM) significantly prevented the increase in power spectra induced by KA injection. These results suggest that sodium orthovanadate decreases the acute effects of KA, thereby inducing neuroprotective effects with reduced reactive oxygen species and cellular Ca2+. Thus, sodium orthovanadate may protect hippocampal neurons against excitotoxicity, and surviving neurons may function to reduce seizures. © 2019 Elsevier B.V.

**Li, J., Jiang, M., Zhou, H.*, et al.* (2019) Vanadium Dioxide Nanocoating Induces Tumor Cell Death through Mitochondrial Electron Transport Chain Interruption. *Global Challenges,* 3(3): 1800058.**
Available at: https://onlinelibrary.wiley.com/doi/epdf/10.1002/gch2.201800058
Keywords: anticancer; charge transfer; functional coatings and films; mitochondria; vanadium dioxide.

**Abstract:**
A biomaterials surface enabling the induction of tumor cell death is particularly desirable for implantable biomedical devices that directly contact tumor tissues. However, this specific antitumor feature is rarely found. Consequently, an antitumor-cell nanocoating comprised of vanadium dioxide (VO2) prepared by customized reactive magnetron sputtering has been proposed, and its antitumor-growth capability has been demonstrated using human cholangiocarcinoma cells. The results reveal that the VO2 nanocoating is able to interrupt the mitochondrial electron transport chain and then elevate the intracellular reactive oxygen species levels, leading to the collapse of the mitochondrial membrane potential and the destruction of cell redox homeostasis. Indeed, this chain reaction can effectively trigger oxidative damage in the cholangiocarcinoma cells. Additionally, this study has provided new insights into designing a tumor-cell-inhibited biomaterial surface, which is modulated by the mechanism of mitochondria-targeting tumor cell death.

**Liu, J., Li, K., Zhou, J.*, et al.* (2019) Bisperoxovanadium induces M2-type macrophages and promotes functional recovery after spinal cord injury. *Molecular Immunology,* 116: 56-62.**
Keywords: Acellular spinal cord; Bisperoxovanadium; M2-type macrophages; PTEN; Spinal cord injury.

**Abstract:**
Macrophages can be polarized towards either a classically activated pro-inflammatory (M1) state, or alternatively towards an activated anti-inflammatory (M2) state. M1 cells are activated by ligands of toll-like receptor (TLR) or interferon (IFN)-γ and have a toxic effect, whereas M2 cells are activated by interleukin (IL)-4, IL-10, and IL-13 and have a regenerative effect in vitro and in vivo. Previously studies have shown that these cells play an important role in the inflammatory responses following spinal cord injury (SCI). Mechanistically, the role of PTEN in the regulation of macrophage polarization has yet to be fully elucidated. In the present study, we first evaluated the expression of PTEN in macrophages after SCI. We found that PTEN expression was accumulated in the macrophages after the SCI surgery. Knock-down of PTEN or inhibition of phospho-PTEN with bpV(pic) in RAW264.7 cells resulted in increased M2 polarization and decreased M1 polarization. In a rat model of SCI, grafts containing bpV(pic) reduced spinal tissue cavitation and promoted locomotor improvement, while

combining grafts of bpV(pic) and acellular spinal cord (ASC) scaffolds showed a better effect. Moreover, grafts containing bpV(pic) enhanced M2 polarization and decreased M1 polarization in the macrophages during SCI. Thus, we have established that PTEN is critical for the polarization of macrophages and the functional recovery of SCI. Targeting PTEN enhances the macrophages towards to M2 polarization and promoting the functional recovery in SCI, and this suggest that PTEN may be a future therapeutic target for SCI treatment. © 2019 Elsevier Ltd.

**López-Valdez, N., Guerrero-Palomo, G., Rojas-Lemus, M.*, et al.* (2019) The role of the non-ciliated bronchiolar cell in tolerance to inhaled vanadium of the bronchiolar epithelium. *Histology and Histopathology,* : 18165.**
Available at: https://www.hh.um.es/Articles-Proofs/18-165-manuscript.pdf

**Abstract:**
The Non-Ciliated Bronchiolar Cell (NCBC) is responsible for the defense and maintenance of the bronchiolar epithelium. Several cellular defense mechanisms have been associated with an increase in the secretion of CC16 and changes in the phenotype of the cell; these mechanisms could be linked to tolerance to the damage due to exposure to inhaled Particulate Matter (PM) of the epithelium. These defense mechanisms have not been sufficiently explored. In this article, we studied the response of the NCBC to inhaled vanadium, an element which adheres to PM. This response was measured by the changes in the phenotype of the NCBC and the secretion of CC16 in a mouse model. Mice were exposed in two phases to different vanadium concentrations; 1.27 mg/m³ in the first phase and 2.56 mg/m³ in the second phase. Mice were sacrificed on the 2nd, 4th, 5th, 6th and 8th weeks. In the second phase, we observed the following: sloughing of the NCBC, hyperplasia and small inflammatory foci remained without changes and that the expression of CC16 was higher in this phase than in phase I. We also observed a change in the phenotype with a slow decrease in both phases. The increase in the secretion of CC16 and the phenotype reversion could be due to the anti-inflammatory activity of CC16. The changes observed in the second phase could be attributed to the tolerance to inhaled vanadium.

**Scibior, A. & Kurus, J. (2019) Vanadium and Oxidative Stress Markers - In Vivo Model: A Review. *Current Medicinal Chemistry,* 26(29): 5456-5500.**
Keywords: Animals; Antioxidants; Biomarkers/analysis/metabolism; Free Radicals/analysis; Humans; Lipid Peroxidation/drug effects; Oxidative Stress/drug effects; Reactive Oxygen Species/analysis/metabolism; Vanadium/chemistry/pharmacology; Vanadium; animal studies; interactions; lipid peroxidation (LPO); magnesium; oxidative stress markers; reactive oxygen species (ROS).

**Abstract:**
This review article is an attempt to summarize the current state of knowledge of the impact of Vanadium (V) on Oxidative Stress (OS) markers in vivo. It shows the results of our studies and studies conducted by other researchers on the influence of different V compounds on the level of selected Reactive Oxygen Species (ROS)/Free Radicals (FRs), markers of Lipid peroxidation (LPO), as well as enzymatic and non-enzymatic antioxidants. It also presents the impact of ROS/peroxides on the activity of antioxidant enzymes modulated by V and illustrates the mechanisms of the inactivation thereof caused by this metal and reactive oxygen metabolites. It also focuses on the mechanisms of interaction of V with some nonenzymatic compounds of the antioxidative system. Furthermore, we review the routes of generation of oxygen-derived FRs and non-radical oxygen derivatives (in which V is involved) as well as the consequences of FR-mediated LPO (induced by this metal) together with the negative/

positive effects of LPO products. A brief description of the localization and function of some antioxidant enzymes and low-molecular-weight antioxidants, which are able to form complexes with V and play a crucial role in the metabolism of this element, is presented as well. The report also shows the OS historical background and OS markers (determined in animals under V treatment) on a timeline, collects data on interactions of V with one of the elements with antioxidant potential, and highlights the necessity and desirability of conducting studies of mutual interactions between V and antioxidant elements.

**Sibiya, S., Msibi, B., Khathi, A.*, et al.* (2019) The effect of dioxidovanadium complex (V) on hepatic function in streptozotocin-induced diabetic rats. *Canadian Journal of Physiology and Pharmacology,* 97(12): 1169-1175.**
Keywords: C-reactive protein; dysfonctionnement hepatique; hyperglycaemia; hyperglycemie; liver dysfunction; liver function marker enzymes; marqueurs enzymatiques du fonctionnement hepatique; oxidative stress; proteine C reactive; stress oxydatif.

**Abstract:**
Diabetics are susceptible to hepatic dysfunction risks due to hyperglycaemia and insulin therapy. Conventional diabetes treatments improve glycaemic control; however, hepatic hazards associated with these agents remains a challenge. Accordingly, this study sought to investigate the effect of a dioxidovanadium complex (V) on the hepatic function in streptozotocin-induced diabetic rats. Sprague-Dawley rats (240-250 g) were divided into 4 groups (n = 6): nondiabetic control, diabetic control, insulin-treated, and vanadium complex groups. The dioxidovanadium (10, 20, and 40 mg/kg) was administered twice every 2nd day for 5 weeks and blood glucose concentration was monitored weekly. At the end of the experimental period, all the experimental groups were sacrificed, and then the lipid profile, liver superoxide dismutase, glutathione peroxidase and malondialdehyde, plasma alanine aminotransferase and aspartate aminotransferase, and C-reactive protein (CRP) concentration were measured. The administration of dioxidovanadium significantly alleviated hyperglycaemia with concomitant attenuation in oxidative stress as evidenced by reduced malondialdehyde concentrations. Furthermore, vanadium complex abolished diabetes-induced dyslipidaemia. Lastly, vanadium complex administration attenuated the increase in alanine aminotransferase, aspartate aminotransferase, and plasma C-reactive protein. These findings suggest that this metallo-compound (dioxidovanadium) may ameliorate liver dysfunction often observed in diabetes.

# 4. USES OF VANADIUM

**Bakhshi Aliabad, H., Khanamani Falahati-Pour, S., Ahmadirad, H.*, et al.* (2018) Vanadium complex: an appropriate candidate for killing hepatocellular carcinoma cancerous cells. *Biometals : An International Journal on the Role of Metal Ions in Biology, Biochemistry, and Medicine,* 31(6): 981-990.**
Available at:
https://link.springer.com/content/pdf/10.1007%2Fs10534-018-0139-x.pdf
Keywords: Animals; Antineoplastic Agents/chemical synthesis/chemistry/pharmacology; Carcinoma, Hepatocellular/drug therapy/pathology; Cell Death/drug effects; Cell Proliferation/drug effects; Dose-Response Relationship, Drug; Drug Screening Assays, Antitumor; Hep G2 Cells; Humans; Liver Neoplasms/drug therapy/pathology; Mice; Organometallic Compounds/chemical synthesis/chemistry/pharmacology; Structure-Activity Relationship; Vanadium/chemistry/pharmacology; Cytotoxicity; HepG2 cells; Hepatocellular carcinoma; L929 cells; Vanadium complex.

**Abstract:**

Hepatocellular carcinoma (HCC) is a prevalent human malignancy which its drug resistance is increasing world-wide. This project was designed to assess the anti-cancer effects of 4-bromo-2-(((5-chloro-2-hydroxyphenyl) imino) methyl) phenol ([IV(L)] complex) on the HepG2 cell line and also L929 cells, as normal cells. HepG2 and L929 cells were cultured in RPMI culture medium and the survival rates of the cells were determined after 24 and 48 h using MTT assay to find IC50 concentration of vanadium m, [IV(L)] complex. The early apoptosis and necrosis/late apoptosis were determined by means of annexin V/PI apoptosis detection kit. The results revealed that vanadium m, [IV(L)] complex induce early apoptosis higher in HepG2 cell line than L929 cells. The rates of necrosis/late apoptosis were also induced in HepG2 cells more than L929 cells. Based on the results, vanadium m, [IV(L)] complex might be considered as a safe new drug for treatment of HCC with low side effects on control liver cells.

**Bergeron, A., Kostenkova, K., Selman, M.*, et al.* (2019) Enhancement of oncolytic virotherapy by vanadium(V) dipicolinates. *Biometals,* 32(3): 545-561.**
Keywords: Oncolytic virus; Vanadium; Cancer; Dipicolinate derivatives; Vanadium(V); Coordination complexes; or-equal-to; in-vivo; reverse micelles; multicomponent polyanions; anticancer activity; aqueous chemistry; vanadyl sulfate; complexes; NMR; speciation; Biochemistry & Molecular Biology.

**Abstract:**
Oncolytic viruses rewire the immune system and can lead to long-lasting antitumor defenses against primary and metastatic tumors. However, results from clinical studies have shown heterogeneity in responses suggesting that multiplexed approaches may be necessary to consistently generate positive outcomes in patients. To this end, we explored the combination of oncolytic rhabdovirus VSV51 with vanadium(V) dipicolinate derivatives, which have already been explored for their antidiabetic properties in animal models. The combination of vanadium-based dipicolinate compounds with VSV51 significantly increased viral replication and cytotoxicity in the human renal cell carcinoma cell line 786-0. The effects of three vanadium(V)-dipicolinate coordination complexes ([VO(2)dipic](-), [VO(2)dipic-OH](-) and [VO(2)dipic-Cl](-) with -OH or -Cl in the para position) were compared to that of the simple salts using spectroscopy and speciation profiles. Like the vanadate salts and the vanadyl cation, all dioxovanadium(V) dipicolinate complexes tested were found to increase viral infection and cytotoxicity when used in combination with VSV51. Viral sensitization is dependent on the vanadium since free dipicolinate ligands exerted no effect on viral infection and viability. The ability of these complexes to interact with interfaces and the stability of the complexes were evaluated under physiological conditions. Results indicate that these complexes undergo hydrolysis in cell culturemedia thereby generating vanadate. The vanadium dipicolinate derivatives in the context of immunovirotherapy shares similarities with previous studies exploring the antidiabetic properties of the compounds. The synergy between vanadium compounds and the oncolytic virus suggests that these compounds may be valuable in the development of novel and effective pharmaco-viral therapies.

**Cho, J., Bing, S.J., Kim, A.*, et al.* (2019) Jeju ground water containing vanadium induces normal T cell development and immune activation in chronically stressed mice. *Molecular Biology Reports,* 46(4): 4443-4452.**
Keywords: Jeju ground water; Chronic stress; Immune activation; T cell development; animal-models; depression; susceptibility; cytokines; anxiety; system; mouse; Biochemistry & Molecular Biology
**Abstract:**
Containing high concentration of vanadium served by the volcanic bedrock, Jeju ground water has long been known for various implicit health benefits including immune-promotion.

Exposure to stress has been reported to be associated with immunosuppression such as reducing lymphocyte population or antibody production due to stress hormones. In this study, we aimed at evaluating the effects of Jeju ground water on chronically stressed mice. C57BL/6 mice were subjected to various stressors such as restraint stress, water swimming stress, heat stress, acoustic stress, and Jeju ground water was supplied for 28days with two different concentrations, S1 (vanadium 15-20 mu g/l, pH 8.3) and S2 (vanadium 20-25 mu g/l, pH 8.5). Treatment with Jeju ground water increased CD4(+)CD8(-) or CD4(-)CD8(+) single-positive thymocytes. It also increased the proliferation of splenocytes and the populations of CD4(+) T cells, CD45R/B220(+) B cells, CD11b(+) macrophages or Gr-1(+) granulocytes in spleen. In addition, the production of IgG was increased in chronically stressed mice by treatment with Jeju ground water. These results suggest vanadium-rich Jeju ground water may be helpful in T cell development in thymus and immune cell proliferation and its function in spleen against chronic stress.

**Dias Moreira, L.d.P., Piovezana Gomes, J.V., Mattar, J.B.*, et al.* (2019) Potential of trace elements as supplements for the metabolic control of Type 2 Diabetes Mellitus: A systematic review. *Journal of Functional Foods,* 57: 317-327.**
Available at: http://www.posnutricao.ufv.br/wp-content/uploads/2019/05/POTENTIAL-OF-TRACE-ELEMENTS-AS-SUPPLEMENTS-FOR-THE-METABOLIC-CONTROL-OF-TYPE-2-DIABETES-MELLITUS-A-SYSTEMATIC-REVIEW.pdf
Keywords: Glycemie profile; Oxidative stress; Lipid profile; Inflammation; Oligo-elements; induced oxidative stress; high-fat diet; oral zinc supplementation; activated protein-kinase; chromium-picolinate; glycemic control; insulin; sensitivity; gene-expression; kidney tissue; nitric-oxide; Food Science & Technology; Nutrition & Dietetics.

**Abstract:**
The objective of this review was to understand the role of trace elements in the form of supplements in metabolic control of Type 2 Diabetes Mellitus (T2DM). A systematic research was performed following PRISMA recommendations. Although 3236 studies were identified, only 18 studies composed of nine animal studies and nine clinical studies were included in this review. The included trace elements were Chromium (Cr), Selenium (Se), Zinc (Zn) and Vanadium (V). The time, dose and type of supplement varied among the studies. Se, Cr, Zn and V improved glycemic profile and antioxidant status while Se, Cr and Zn affected lipid profile. Se and Zn supplementation improved endothelial function. Also, Se modified inflammatory profile. In general, cautious supplementation of trace elements promotes the metabolic control of T2DM.

**Gunasinghe, M.A., Kim, A.T. & Kim, S.M. (2019) Inhibitory Effects of Vanadium-Binding Proteins Purified from the Sea Squirt Halocynthia roretzi on Adipogenesis in 3T3-L1 Adipocytes. *Applied Biochemistry and Biotechnology,* 189(1): 49-64.**
Keywords: Adipogenesis; Sea squirt; Vanadium-binding proteins; ACTIVATED RECEPTOR-GAMMA; C/EBP-ALPHA; PPAR-GAMMA; DIFFERENTIATION; FAT; MECHANISMS; EXPRESSION; EXTRACT; BALANCE; BROWN; Biochemistry & Molecular Biology; Biotechnology & Applied Microbiology.

**Abstract:**
The inhibitory effects of vanadium-binding proteins (VBPs) from the blood plasma and the intestine of sea squirt on adipogenesis in 3T3-L1 adipocytes were examined. 3T3L-1 cells treated with VBP (blood plasma) decreased markedly the lipid content in maturing pre-adipocytes in a dose-dependent manner, whereas VBP (intestine) did not show significant effects on lipid accumulation. Both VBPs did not have significant effect on cell viability. In

order to demonstrate the anti-adipogenic effects of VBP (blood plasma), the expressions of several adipogenic transcription factors and enzymes were investigated by Reverse Transcriptase-Polymerase Chain Reaction. VBP (blood plasma) down-regulated the expressions of transcription factors; PPAR-gamma, C/EBP-alpha, SREBP1, and FAS, but did not have significant effects on the expressions of lipolytic enzymes; HSL and LPL. Both the crude and purified VBPs significantly increased the mRNA levels of Wnt10b, FZ1, LRP6, and beta-catenin, while decreased the expression of GSK-3 beta. Hence, VBP (blood plasma) inhibited adipogenesis by activating WNT/beta-catenin pathway via the activation of Wnt10b. Based on the findings, VBP (blood plasma) decreased lipid accumulation which was mediated by decreasing adipogenesis, not by lipolysis. Therefore, VBP (blood plasma) could be used to treat obesity.

**Kim, U.J., Lee, B.H. & Lee, K.H. (2019) Neuroprotective effects of a protein tyrosine phosphatase inhibitor against hippocampal excitotoxic injury. *Brain Research,* 1719: 133-139.**
Keywords: Excitotoxicity; Kainic acid; Organotypic hippocampal slice culture; Sodium orthovanadate; Survival signal.

**Abstract:**
Neuronal excitotoxicity is the neuronal cell death arising from prolonged exposure to glutamate and the associated excessive influx of ions into the cell. Sodium orthovanadate (Na3VO4,) competitively inhibits the protein tyrosine phosphatases that affect intracellular protein phosphorylation. No study has examined the role of protein tyrosine phosphatases in kainic acid (KA)-induced excitotoxic injury using sodium orthovanadate. Thus, the present study was conducted to determine the neuroprotective effects of sodium orthovanadate on KA-induced neuronal death in organotypic hippocampal slice culture. We also performed an in vivo electrophysiology study in Sprague-Dawley rats to observe the function of surviving cells after sodium orthovanadate treatment in KA-induced excitotoxicity. Rats were anaesthetized with sodium pentobarbital and KA was injected unilaterally in CA3 of the hippocampus by microinjection-cannula. Neuronal cell death, as assessed by propidium iodide uptake, was reduced by 10 and 25 μM sodium orthovanadate treatment (24 and 48 h) compared with the KA-only group. Sodium orthovanadate enhanced survival signals by increasing levels of phospho-Akt and superoxide dismutase. In addition, sodium orthovanadate treatment reduced calcineurin level for neuronal protection, which regulates activation of cellular calcium caused by KA-induced injury. In vivo results showed that sodium orthovanadate treatment elicited resistance to KA-induced behavior seizures and significantly reduced the duration of epileptiform discharges. In addition, sodium orthovanadate treatment (25 mM) significantly prevented the increase in power spectra induced by KA injection. These results suggest that sodium orthovanadate decreases the acute effects of KA, thereby inducing neuroprotective effects with reduced reactive oxygen species and cellular Ca2+. Thus, sodium orthovanadate may protect hippocampal neurons against excitotoxicity, and surviving neurons may function to reduce seizures. © 2019 Elsevier B.V.

**Kumar, A., Dixit, A., Sahoo, S.*, et al.* (2020) Crystal structure, DNA crosslinking and photo-induced cytotoxicity of oxovanadium(IV) conjugates of boron-dipyrromethene. *Journal of Inorganic Biochemistry,* 202: 110817.**
Available at:
https://www.sciencedirect.com/science/article/pii/S0162013419305057/pdfft?md5=1dad4ffbccda9ddc1e8f0897324345cd&pid=1-s2.0-S0162013419305057-main.pdf
Keywords: Vanadium; Bioinorganic chemistry; DNA crosslink; Photodynamic therapy; Crystal

structure

**Abstract:**
Cis-dichloro-oxovanadium(IV) complexes [VO(L1/L2)Cl2], where L1 is N-(4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4ʎ4,5ʎ4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-10-yl)benzyl)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine in 1 and L2 is N-(4-(5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-5H-4ʎ4,5ʎ4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-10-yl)benzyl)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine in 2) having 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene as boron-dipyrromethene (BODIPY) appended dipicolylamine bases were prepared, characterized and their photocytotoxicity studied. X-ray crystal structure of 1 showed distorted octahedral geometry with a VIVON3Cl2 core having Cl-V-Cl angle of 91.93(4)°. The complexes showed variable solution conductivity properties. They were non-electrolytes in dry DMF at 25 °C but showed 1:1 electrolytic behavior in an aqueous medium due to dissociation of one chloride ligand as evidenced from the mass spectral study. Complexes 1 and 2 showed absorption bands at 500 and 535 nm, respectively. The calf thymus DNA melting study revealed their interaction through DNA crosslinking on exposure to light which was further confirmed from the alkaline agarose gel electrophoresis using plasmid supercoiled pUC19 DNA. Complex 2 showed disruption of the mitochondrial membrane potential in the JC-1 (1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachloroimidacarbocyanine iodide) assay. The complexes were photocytotoxic in visible light (400–700 nm, power: 10 J cm−2) in cervical cancer HeLa and breast cancer MCF-7 cells. Complex 2 having a photoactive diiodo-boron-dipyrromethene moiety gave a singlet oxygen quantum yield (ΦΔ) value of ~0.6. It showed singlet oxygen mediated apoptotic photodynamic therapy activity with remarkably low IC50 (half maximal inhibitory concentration) value of ~0.15 μM. The cis-disposition of chlorides gave a cis-divacant 4-coordinate intermediate structure from the density functional theory (DFT) study thus mimicking the DNA crosslinking property of cisplatin. ".

**Leon, I.E., Ruiz, M.C., Franca, C.A., *et al.* (2019) Metvan, bis(4,7-Dimethyl-1,10-phenanthroline)sulfatooxidovanadium(IV): DFT and Spectroscopic Study-Antitumor Action on Human Bone and Colorectal Cancer Cell Lines. *Biological Trace Element Research,* 191(1): 81-87.**
Keywords: Oxidovanadium(IV); Metvan; DFT calculations; FTIR spectrum; Human bone and colorectal cancer cell lines; normal coordinate analysis; infra-red spectra; vanadium; 1,10-phenanthroline; complexes; sulfatooxovanadium(iv); phenanthrolines; assignment; ligands; Biochemistry & Molecular Biology; Endocrinology & Metabolism.
**Abstract:**
The complex bis(4,7-dimethyl-1,10-phenantroline)sulfatooxidovanadium(IV), commonly known as Metvan, was prepared using a known synthetic procedure. Its optimized molecular structure was obtained by DFT calculations, as it was impossible to grow single crystals adequate for a crystallographic study. The complex was also characterized by a detailed analysis of its infrared spectrum, supported by the theoretical calculations, and also by some data derived from its Raman spectrum. In addition, cytotoxicity studies were performed using human osteosarcoma (MG-63) and human colorectal adenocarcinoma (HT-29) cell lines. The results show that Metvan impaired cell viability of both cancer cell lines in a low concentration range (0.25-5.0 mu M).

**Li, J., Jiang, M., Zhou, H., *et al.* (2019) Vanadium Dioxide Nanocoating Induces Tumor Cell Death through Mitochondrial Electron Transport Chain Interruption. *Global Challenges,* 3(3): 1800058.**
Available at: https://onlinelibrary.wiley.com/doi/epdf/10.1002/gch2.201800058

Keywords: anticancer; charge transfer; functional coatings and films; mitochondria; vanadium dioxide.

**Abstract:**
A biomaterials surface enabling the induction of tumor cell death is particularly desirable for implantable biomedical devices that directly contact tumor tissues. However, this specific antitumor feature is rarely found. Consequently, an antitumor-cell nanocoating comprised of vanadium dioxide (VO2) prepared by customized reactive magnetron sputtering has been proposed, and its antitumor-growth capability has been demonstrated using human cholangiocarcinoma cells. The results reveal that the VO2 nanocoating is able to interrupt the mitochondrial electron transport chain and then elevate the intracellular reactive oxygen species levels, leading to the collapse of the mitochondrial membrane potential and the destruction of cell redox homeostasis. Indeed, this chain reaction can effectively trigger oxidative damage in the cholangiocarcinoma cells. Additionally, this study has provided new insights into designing a tumor-cell-inhibited biomaterial surface, which is modulated by the mechanism of mitochondria-targeting tumor cell death.

**Liu, J., Li, K., Zhou, J.*, et al.* (2019) Bisperoxovanadium induces M2-type macrophages and promotes functional recovery after spinal cord injury. *Molecular Immunology,* 116: 56-62.**
Keywords: Acellular spinal cord; Bisperoxovanadium; M2-type macrophages; PTEN; Spinal cord injury.

**Abstract:**
Macrophages can be polarized towards either a classically activated pro-inflammatory (M1) state, or alternatively towards an activated anti-inflammatory (M2) state. M1 cells are activated by ligands of toll-like receptor (TLR) or interferon (IFN)-γ and have a toxic effect, whereas M2 cells are activated by interleukin (IL)-4, IL-10, and IL-13 and have a regenerative effect in vitro and in vivo. Previously studies have shown that these cells play an important role in the inflammatory responses following spinal cord injury (SCI). Mechanistically, the role of PTEN in the regulation of macrophage polarization has yet to be fully elucidated. In the present study, we first evaluated the expression of PTEN in macrophages after SCI. We found that PTEN expression was accumulated in the macrophages after the SCI surgery. Knock-down of PTEN or inhibition of phospho-PTEN with bpV(pic) in RAW264.7 cells resulted in increased M2 polarization and decreased M1 polarization. In a rat model of SCI, grafts containing bpV(pic) reduced spinal tissue cavitation and promoted locomotor improvement, while combining grafts of bpV(pic) and acellular spinal cord (ASC) scaffolds showed a better effect. Moreover, grafts containing bpV(pic) enhanced M2 polarization and decreased M1 polarization in the macrophages during SCI. Thus, we have established that PTEN is critical for the polarization of macrophages and the functional recovery of SCI. Targeting PTEN enhances the macrophages towards to M2 polarization and promoting the functional recovery in SCI, and this suggest that PTEN may be a future therapeutic target for SCI treatment. © 2019 Elsevier Ltd.

**Lountos, G.T., Zhao, X.Z., Kiselev, E.*, et al.* (2019) Identification of a ligand binding hot spot and structural motifs replicating aspects of tyrosyl-DNA phosphodiesterase I (TDP1) phosphoryl recognition by crystallographic fragment cocktail screening. *Nucleic Acids Research,* 47(19): 10134-10150.**

**Abstract:**
Tyrosyl DNA-phosphodiesterase I (TDP1) repairs type IB topoisomerase (TOP1) cleavage complexes generated by TOP1 inhibitors commonly used as anticancer agents. TDP1 also

removes DNA 3' end blocking lesions generated by chain-terminating nucleosides and alkylating agents, and base oxidation both in the nuclear and mitochondrial genomes. Combination therapy with TDP1 inhibitors is proposed to synergize with topoisomerase targeting drugs to enhance selectivity against cancer cells exhibiting deficiencies in parallel DNA repair pathways. A crystallographic fragment screening campaign against the catalytic domain of TDP1 was conducted to identify new lead compounds. Crystal structures revealed two fragments that bind to the TDP1 active site and exhibit inhibitory activity against TDP1. These fragments occupy a similar position in the TDP1 active site as seen in prior crystal structures of TDP1 with bound vanadate, a transition state mimic. Using structural insights into fragment binding, several fragment derivatives have been prepared and evaluated in biochemical assays. These results demonstrate that fragment-based methods can be a highly feasible approach toward the discovery of small-molecule chemical scaffolds to target TDP1, and for the first time, we provide co-crystal structures of small molecule inhibitors bound to TDP1, which could serve for the rational development of medicinal TDP1 inhibitors. Published by Oxford University Press on behalf of Nucleic Acids Research 2019.

**Mohanty, M., MAURYA, S.K., Banerjee, A.*, et al.* (2019) In vitro cytotoxicity and catalytic evaluation of dioxidovanadium (V) complexes in azohydrazone ligand environment. *New Journal of Chemistry,* 43(45): 17680-17695.**

**Abstract:**
Three new anionic dioxidovanadium(V) complexes $(HNEt_3)[VO_2(L)^{1-3}]$ (**1–3**) of tridentate binegative aroylhydrazone ligands containing the azobenzene moiety were synthesized and structurally characterized. The aroylhydrazone ligands ($\mathbf{H_2L^{1-3}}$) were derived from the condensation of 5-(arylazo) salicylaldehyde derivatives with the corresponding aroyl hydrazides. All the synthesized ligands and metal complexes were successfully characterized by several physicochemical techniques, namely, elemental analysis, electrospray ionization mass spectrometry, spectroscopic methods (IR, UV-vis and NMR), and cyclic voltammetry. Single-crystal X-ray diffraction crystallography of **1–3** revealed five-coordinate geometry, where the ligand coordinates to the metal centre in a binegative tridentate O, N, O coordinating anion and two oxido-O atoms, resulting in distortion towards the square pyramidal structure. The complexes were further evaluated for their *in vitro* cytotoxicity against HeLa and HT-29 cancer cell lines. All the complexes manifested a cytotoxic potential that was found to be comparable with that of clinically referred drugs, while complex 3 proved to be the most cytotoxic among the three complexes for both cell lines, which may be due to the synergistic effect of the naphthyl substituent in the azohydrazone ligand environment coordinated to the vanadium metal. The synthesized complexes **1–3** were probed as catalysts for the oxidative bromination of thymol and styrene as a functional mimic of vanadium haloperoxidases (VHPOs). All the reactions provided high percentages of conversion (>90%) with a high turnover frequency (TOF) in the presence of the catalysts **1–3**. In particular, for the oxidative bromination of thymol, the percentage of conversion and TOF were in the ranges of 98–99% and 5380–7173 ($h^{-1}$), respectively. Besides, 3 bearing the naphthyl substituent showed the highest TOF among all the complexes for the oxidative bromination of both thymol and styrene.

**Noriega, L., Castro, M., Perez-Aguilar, J.*, et al.* (2019) Oxidovanadium (V) complexes as promising anticancer photosensitizers. *Journal of Inorganic Biochemistry,* 203: 110862.**
Keywords: Oxido-vanadium(V) complexes; Photosensitizer; Photodynamic therapy; Density; Functional Theory calculations; Anticancer activity.

**Abstract:**

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

**Pisano, M., Arru, C., Serra, M.*, et al.* (2019) Antiproliferative activity of vanadium compounds: effects on the major malignant melanoma molecular pathways. *Metallomics : Integrated Biometal Science,* 11(10): 1687-1699.**

**Abstract:**
Malignant melanoma (MM) is the most fatal skin cancer, whose incidence has critically increased in the last decades. Recent molecular therapies are giving excellent results in the remission of melanoma but often they induce drug resistance in patients limiting their therapeutic efficacy. The search for new compounds able to overcome drug resistance is therefore essential. Vanadium has recently been cited for its anticancer properties against several tumors, but only a few data regard its effect against MM. In a previous work we demonstrated the anticancer activity of four different vanadium species towards MM cell lines. The inorganic anion vanadate(v) (VN) and the oxidovanadium(iv) complex [VO(dhp)2] (VS2), where dhp is 1,2-dimethyl-3-hydroxy-4(1H)-pyridinonate, showed IC50 values of 4.7 and 2.6 muM, respectively, against the A375 MM cell line, causing apoptosis and cell cycle arrest. Here we demonstrate the involvement of Reactive Oxygen Species (ROS) production in the pro-apoptotic effect of these two V species and evaluate the activation of different cell cycle regulators, to investigate the molecular mechanisms involved in their antitumor activity. We establish that VN and VS2 treatments reduce the phosphorylation of extracellular-signal regulated kinase (ERK) by about 80%, causing the deactivation of the mitogen activated protein kinase (MAPK) pathway in A375 cells. VN and VS2 also induce dephosphorylation of the retinoblastoma protein (Rb) (VN 100% and VS2 90%), together with a pronounced increase of cyclin-dependent kinase inhibitor 1 p21 (p21Cip1) protein expression up to 1800%. Taken together, our results confirm the antitumor properties of vanadium against melanoma cells, highlighting its ability to induce apoptosis through generation of ROS and cell cycle arrest by counteracting MAPK pathway activation and strongly inducing p21Cip1 expression and Rb hypo-phosphorylation.

**Sibiya, S., Msibi, B., Khathi, A.*, et al.* (2019) The effect of dioxidovanadium complex (V) on hepatic function in streptozotocin-induced diabetic rats. *Canadian Journal of Physiology and Pharmacology,* 97(12): 1169-1175.**

Keywords: C-reactive protein; dysfonctionnement hepatique; hyperglycaemia; hyperglycemie; liver dysfunction; liver function marker enzymes; marqueurs enzymatiques du fonctionnement hepatique; oxidative stress; proteine C reactive; stress oxydatif.

**Abstract:**

Diabetics are susceptible to hepatic dysfunction risks due to hyperglycaemia and insulin therapy. Conventional diabetes treatments improve glycaemic control; however, hepatic hazards associated with these agents remains a challenge. Accordingly, this study sought to investigate the effect of a dioxidovanadium complex (V) on the hepatic function in streptozotocin-induced diabetic rats. Sprague-Dawley rats (240-250 g) were divided into 4 groups (n = 6): nondiabetic control, diabetic control, insulin-treated, and vanadium complex groups. The dioxidovanadium (10, 20, and 40 mg/kg) was administered twice every 2nd day for 5 weeks and blood glucose concentration was monitored weekly. At the end of the experimental period, all the experimental groups were sacrificed, and then the lipid profile, liver superoxide dismutase, glutathione peroxidase and malondialdehyde, plasma alanine aminotransferase and aspartate aminotransferase, and C-reactive protein (CRP) concentration were measured. The administration of dioxidovanadium significantly alleviated hyperglycaemia with concomitant attenuation in oxidative stress as evidenced by reduced malondialdehyde concentrations. Furthermore, vanadium complex abolished diabetes-induced dyslipidaemia. Lastly, vanadium complex administration attenuated the increase in alanine aminotransferase, aspartate aminotransferase, and plasma C-reactive protein. These findings suggest that this metallo-compound (dioxidovanadium) may ameliorate liver dysfunction often observed in diabetes.

**Suzuki, M.K., Martins, D.A., Costa, M.T.*, et al.* (2018) Ions release Evaluation and Changes in Mini-implant Orthodontic Surface. *The Journal of Contemporary Dental Practice,* 19(8): 910-917.**

Keywords: Bone Screws; Containment of Biohazards; Corrosion; Dental Alloys/chemistry; Dental Implants; Humans; Immersion; In Vitro Techniques; Ions; Materials Testing; Microscopy, Electron, Scanning; Saliva, Artificial/pharmacology; Surface Properties/drug effects; Time Factors; Artificial saliva; Ions Laboratory research.

**Abstract:**
AIM: To evaluate, in vitro, the mini-implant surface changes and the release of ions after immersion in artificial saliva during follow-up of 60 and 120 days. MATERIALS AND METHODS: As for the surface features, examined in a scanning electron microscope (SEM), before and after immersion in artificial saliva, there was a rough and uneven surface, suggestive of corrosion areas for the two trademarks evaluated after 120 days of immersion. The extracts generated in artificial saliva analysis were submitted to energy dispersive spectroscopy to identify the solid corrosion products produced on the surfaces of miniscrews. RESULTS: Both SIN miniscrews and Neodent brands were observed to release minimal quantities of silver ions, chromium, iron, nickel, titanium, and vanadium. Regarding titanium, this index varied from 88.84% in the control group of Neodent brand, and 91.29% in the control group of SIN brand. For the aluminum content, the quantities ranged from 4.91% in group immersed for 60 days in Neodent brand to 8.71% for the SIN control group. Considering vanadium, the index ranged from 2.65% in the group immersed for 120 days to 4.53% in the control group, both for Neodent brand. Statistically significant differences in iron ion were observed between the control group and the miniscrews brand SIN after 60 and 120 days and for Neodent after 60 days of immersion. The titanium ions suffered statistically significant decrease for both brands after 120 days of storage when compared with the control group. CONCLUSION: The studied miniscrews showed results consistent with the biosafety of alloys for use, in vivo. CLINICAL SIGNIFICANCE: The knowledge of the physical/chemical state of corrosion products released in the oral cavity is very important for the toxicological assessment of metal alloys used in dental miniscrews.

**Zegke, M., Spencer, H.L.M. & Lord, R.M. (2019) Fast, Facile and Solvent-Free Dry-Melt Synthesis of Oxovanadium(IV) Complexes: Simple Design with High Potency towards Cancerous Cells. *Chemistry (Weinheim an Der Bergstrasse, Germany),* 25(53): 12275-12280.**
Keywords: Animals; Antineoplastic Agents/chemical synthesis/chemistry/pharmacology; Cattle; Cisplatin/chemistry/toxicity; Coordination Complexes/chemical synthesis/chemistry/pharmacology; Humans; Serum Albumin, Bovine/chemistry/metabolism; Solvents; Vanadium/chemistry; antitumor agents; bioinorganic chemistry; coordination compounds; solid-state synthesis; vanadium.

**Abstract:**
A range of oxobis(phenyl-1,3-butanedione) vanadium(IV) complexes have been successfully synthesized from cheap starting materials and a simple and solvent-free one-pot dry-melt reaction. This direct, straightforward, fast and alternative approach to inorganic synthesis has the potential for a wide range of applications. Analytical studies confirm their successful synthesis, purity and solid-state coordination, and we report the use of such complexes as potential drug candidates for the treatment of cancer. After a 24 hour incubation of A549 lung carcinoma cells with the compounds, they reveal cytotoxicity values elevenfold greater than cisplatin and remain non-toxic towards normal cell types. Additionally, the complexes are stable over a range of physiological pH values and show the potential for interactions with bovine serum albumin.

**Zhou, L., Yi, Y., Yuan, Q.*, et al.* (2018) VAOS, a novel vanadyl complexes of alginate saccharides, inducing apoptosis via activation of AKT-dependent ROS production in NSCLC. *Free Radical Biology & Medicine,* 129: 177-185.**
Keywords: A549 Cells; Alginates/chemical synthesis/pharmacology; Animals; Antineoplastic Agents/chemical synthesis/pharmacology; Apoptosis/drug effects/genetics; Carcinoma, Non-Small-Cell Lung/drug therapy/genetics/metabolism/pathology; Cell Survival/drug effects; Female; Gene Expression Regulation, Neoplastic; Humans; Lung Neoplasms/drug therapy/genetics/metabolism/pathology; Mice; Mice, Inbred BALB C; Mice, Nude; PTEN Phosphohydrolase/antagonists & inhibitors/genetics/metabolism; Phosphorylation; Protein Tyrosine Phosphatase, Non-Receptor Type 1/genetics/metabolism; Proto-Oncogene Proteins c-akt/genetics/metabolism; RNA, Small Interfering/genetics/metabolism; Reactive Oxygen Species/agonists/metabolism; Signal Transduction; Tumor Burden/drug effects; Vanadates/chemical synthesis/pharmacology; Xenograft Model Antitumor Assays; AKT; Non-small cell lung cancer; PTEN; ROS; Vanadyl alginate oligosaccharides.

**Abstract:**
Previous studies have confirmed that protein tyrosine phosphatase 1B (PTP1B) can promote tumour progression in non-small cell lung cancer (NSCLC). Vanadyl alginate oligosaccharides (VAOS) is a new coordination compounds that possesses a good PTP1B inhibitory activity. However, the potent anticancer efficacy of VAOS in human NSCLC requires further study. In this study, VAOS exhibited effective inhibitory effects in NSCLC both in cultured cells and in a xenograft mouse model. VAOS was further identified to induce NSCLC cell apoptosis through activating protein kinase B (AKT) to elevate intracellular reactive oxygen species (ROS) levels by increasing in oxygen consumption and impairing the ROS-scavenging system. Neither silencing of PTP1B by siRNA nor transient overexpression of PTP1B had an effect on the AKT phosphorylation triggered by VAOS, indicating that PTP1B inhibition was not involved in VAOS-induced apoptosis. Through phosphorus colorimetric assay, we demonstrated that VAOS notably inhibited phosphatase and tensin homologue deleted on chromosome 10 (PTEN) dephosphorylation activity, another member of the protein tyrosine phosphatases (PTPases)-upstream factor of AKT. Interestingly, PTEN knockdown sensitized cells to VAOS,

whereas ectopic expression of PTEN markedly rescued VAOS-mediated lethality. In vivo, VAOS treatment markedly reduced PTEN activity and tumour cell burden with low systemic toxicity. Thus, our data not only provided a new therapeutic drug candidate for NSCLC, but presented new understanding into the pharmacological research of VAOS.

# 5. ENVIRONMENTAL EFFECTS in PLANTS and SOIL

**Aihemaiti, A., Jiang, J., Gao, Y.*, et al.* (2019) The effect of vanadium on essential element uptake of Setaria viridis' seedlings. *Journal of Environmental Management,* 237: 399-407.**
Keywords: Biodegradation, Environmental; Poaceae; Seedlings; Soil; Soil Pollutants; Trace Elements; Vanadium; Accumulation; BCF; Essential element; Plant growth; Setaria viridis.

**Abstract:**
High concentrations of vanadium, a ubiquitous element in the environment, in growing media leads to deformation of root structure and leaf chlorosis and necrosis, consequently affecting the translocations of nutrients and essential elements. However, the effects of vanadium on essential element uptake, and the interactions of essential elements in the presence of vanadium, remain incompletely understood. To elucidate the effects of different concentrations of vanadium on major and trace essential elements and plant growth, a native plant species growing in a vanadium mining area, Setaria viridis (dog tail's grass), was incubated in solutions containing 0-55.8mg/L vanadium. The shoot accumulation of four major essential elements and five trace essential elements was detected, and the root length and stem height were measured. The results showed that vanadium in soil solution enhanced the accumulation of all major essential elements in shoot. Vanadium concentrations lower than 47.4mg/L showed an obvious positive ($p<0.05$) effect on P accumulation and translocation. In the case of trace essential elements, there were threshold values for solution vanadium stimulation of element uptake. The threshold values for Cu and Zn, Fe, and Mo uptake were 4.3, 16.3, and 40.6mg/L, respectively. When vanadium levels surpassed these values, accumulation was suppressed and the solution vanadium concentrations attenuated the solution-to-shoot translocation of most of the essential elements. Among the trace essential elements, translocation of Fe was obviously enhanced ($p<0.05$) by vanadium. Solution vanadium also enhanced plant growth at lower concentrations and inhibited it at higher levels. The threshold values for stem height and root length were 36.8 and 16.3mg/L, respectively. Concentrations of 40 and 55.8mg/L vanadium in soil solution caused a 50% decrease in root length and stem height, respectively, showing that root length of Setaria viridis is more susceptible to vanadium toxicity than stem growth.

**Almalki, A.M., Ajarem, J., Altoom, N.*, et al.* (2019) Effects of Mining Activities on Gerbillus nanus in Saudi Arabia: A Biochemical and Histological Study. *Animals : An Open Access Journal from MDPI,* 9(9): 10.3390/ani9090664.**
Available at: https://www.mdpi.com/2076-2615/9/9/664/pdf
Keywords: Balochistan gerbil; heavy metals; kidney damage; liver injury; mining.

**Abstract:**
Mining can impact the environment, biodiversity, and human health through direct and indirect practices. This study investigated the effects of gold mining on Gerbillus nanus, in relation to organ dysfunction and redox imbalance. Soil samples, Lycium shawii, and G. nanus were collected from a site near a mining plant, and a control site. Soil and L. shawii samples from the mining site showed significantly higher cadmium (Cd), copper (Cu), mercury (Hg), arsenic (As), zinc (Zn), lead (Pb), and vanadium (V) levels. Hepatic, renal, and pulmonary Cd, Pb, Hg, Zn, Cu, Fe, As, and V concentrations were significantly higher in G. nanus from the mining site. Markers of liver and kidney function were elevated in serum, and several

histological manifestations were observed in the liver, kidney, and lung of G. nanus from the mining site. Malondialdehyde and nitric oxide levels increased, and glutathione and antioxidant enzymes decreased in the liver and kidney of G. nanus. In conclusion, mining practices trigger tissue damage and oxidative stress in G. nanus that live close to the mining site. These findings can represent a scientific basis for evaluating the environmental and health impacts of mining on nearby communities.

**Cheng, Y., Nathanail, C.P. & Ja'afaru, S.W. (2019) Generic assessment criteria for human health risk management of agricultural land scenario in Jiangsu Province, China. *Science of the Total Environment,* 697**.
Keywords: Agricultural land; China; CLEA model; Generic Assessment Criteria; Jiangsu Province

**Abstract:**
The widespread of agricultural soil pollution in China is posing great risks to food safety and human health. Lack of human health-based generic assessment criteria (GAC) for Chinese agricultural land makes it impossible to efficiently screen and assess the risks unless site-specific risk assessments being carried out, which are both time-consuming and costly. This paper has thus derived the first set human health-based generic assessment criteria (GAC) for 13 substances of concern (including isomers) using the CLEA model for agricultural land scenario in Jiangsu province of China. As there is no authoritative human health risk assessment model in China yet, this paper has determined and demonstrated the applicability of the CLEA model to Chinese agricultural land exposure scenarios. The derived GAC are generally less stringent than the current two Chinese standards (i.e. GB 15618-2018, GB36600-2018) for most substances except for five substances (including cadmium, nickel, alpha-HCH, beta-HCH and gamma-HCH) for which the oral background intake accounts for 50% of the Total Daily Intake. This indicates that the two Chinese soil quality standards maybe over conservative, and oral background intake (i.e. MDIoral) can be a critical parameter when deriving regional GAC for Chinese agricultural land scenarios. Since there is a notable regional difference in MDIoral for some of the substances of concern, as well as in the vegetable consumption rates and vegetable varieties consumed, it is considered necessary to derive GAC for other provinces of China for agricultural land scenario, to further examine the sensitivity of MDIoral on GAC. In addition, the 13 substances of concern in this paper are some of the most prevalent contaminants in agricultural soils in China, but GAC for some emerging new contaminants, such as thallium, vanadium, should also be derived in further research. © 2019 Elsevier B.V.

**Conversa, G., Miedico, O., Chiaravalle, A.E.*, et al.* (2019) Heavy metal contents in green spears of asparagus (Asparagus officinalis L.) grown in Southern Italy: Variability among farms, genotypes and effect of soil mycorrhizal inoculation. *Scientia Horticulturae,* 256: 108559.**
Keywords: Arbuscular mycorrhizal fungi; Genotypic effect; Essential trace elements; Non-essential trace elements; Organic soil amendment; trace-elements; tomato crop; antioxidant; cadmium; fungi; accumulation; selenium; vegetables; lead; ZN; Agriculture.

**Abstract:**
The concentration of sixteen different heavy metals (HMs) [arsenicum (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), tin (Sn), uranium (U), vanadium (V) and zinc (Zn)] were determined in green asparagus spears produced in an intensively cultivated area of Southern Italy. The level of the HMs was analysed in the most common

cultivar in the area ('Grande'), along with the variability in HM contents on four different farms within this area. The effect on HM levels of soil inoculation with arbuscular mycorrhizal fungi (AMF) and of three different genotypes ('Atlas', 'Italo' and 'Purple passion') was also evaluated. Asparagus spears had greater amounts of Fe (29.3 mg kg(-1) fresh weight - fw), Zn (3.1 mg kg(-1) fw) and Mn (2.0 mg kg(-1) fw) than the other micronutrients. As a whole the observed values were within the range reported in the literature and in food composition databases for asparagus and other vegetables, being even richer in iron and lower in As, Cd, Hg and Pb. The principal component analysis underlined a larger HM concentration in both plant essential (Fe, Mn), beneficial (Co, Se and V) and non-essential (As, Cr, Pb) elements in the product obtained from two out of the four farms investigated, likely to be due to the larger application of organic amendments. Between the less intensively fertilized farms, a lower content of Cu and Ni and an improved Mo level further seems to result from the non-application of mineral phosphorus and of guano-based fertilizers. The product from AMF inoculated soil was distinctively richer in almost all the elements, particularly in non-essential ones, but also in several important micronutrients for humans health (e.g.: Cu, Fe, Mn). Compared with the standard cultivar ('Grande'), 'Atlas' and 'Italo' had a greater concentration of As, whereas no changes or lower levels were detected for the other HMs. The violet type ('Purple passion') stood out for the highest Se content along with a generally lower level of other HMs.

**Demarco, C.F., Afonso, T.F., Pieniz, S.*, et al.* (2019) Phytoremediation of heavy metals and nutrients by the Sagittaria montevidensis into an anthropogenic contaminated site at Southern of Brazil. *International Journal of Phytoremediation,* 21(11): 1145-1152.**
Keywords: Environmental contamination; eutrophication; heavy metals; Santa Bárbara stream.

**Abstract:**
The evaluation of plants occurring naturally at contaminated environments are essential for applying this species in remediation techniques. In this context, the Sagittaria montevidensis with potential for phytoremediation was studied at an anthropogenic polluted stream in southern Brazil. The nutrients and heavy metal content were determined in the phytomass. The phytoremediation indexes were evaluated such as bioconcentration factor (BCF), translocation factor (TF), plant effective number (PEN), and potential phytoremoval (mg m−2). The S. montevidensis was then detected as presenting natural phytoextraction ability for potassium and calcium elements and also demonstrated rhizofiltration potential for phosphorus, manganese, aluminum, vanadium, sulfur, iron, arsenic, copper, magnesium, zinc, sodium, lead, cadmium, nickel, chromium, considering its ability of bioaccumulating these contaminants and retain high levels in the roots. The highest potential for bioremoval (mg m−2) of the S. montevidensis was detected for potassium and calcium (recommending thus the use for phytoextraction) and for aluminum, phosphorus, iron, magnesium, sulfur, and sodium, along with heavy metals (recommended for rhizofiltration). The S. montevidensis decontamination ability, along with its biomass production and its adaptability represents a great advance in order to the recovery of this degraded area and possible application in other contaminated watercourses in Brazil. © 2019, © 2019 Taylor & Francis Group, LLC.

**Elbehiry, F., Elbasiouny, H., El-Ramady, H.*, et al.* (2019) Mobility, distribution, and potential risk assessment of selected trace elements in soils of the Nile Delta, Egypt. *Environmental Monitoring and Assessment,* 191(12): 713-019-7892-3.**
Keywords: Kafrelsheikh; Nile Delta; Risk assessment; Spatial distribution; Trace elements.

**Abstract:**

Environmental pollution has received considerable attention over the last 50 years. Recently, there has been an increasing interest in pollution of the Nile Delta, Egypt, which is one of the longest settled deltaic systems in the world. Pollution in the delta is increasingly recognized as a serious health concern that requires proper management of ecosystems. Therefore, this project aimed to study the distribution and assess the risk associated with selected trace elements (TEs) in different soils (i.e., marine, fluvial, and lacustrine parent materials) in the northern Nile Delta. Mehlich-3 extraction was used to determine the availability of antimony, vanadium, strontium, and molybdenum in agro-ecosystems in this area and their spatial distributions were investigated. Five indices were used to assess ecological risk. Results showed that TEs were higher in the southern part of the study area because it is affected by multiple pollution sources. The available concentrations of TEs were Sr < V < Sb < Mo. The bioavailability of Sr was highest among the studied TEs. The studied indices suggested the study area was moderately polluted by Sr and Sb. Furthermore, the results showed that marine soils had higher TE levels then lacustrine and fluvial soils. The ecological risk assessment indicated that V and Mo were of natural origin, while Sr and Sb were anthropogenically linked. Therefore, the situation calls for planning to reduce pollution sources, especially in the protected north Nile Delta, so these productive soils do not threaten human and ecological health.

**Gcasamba, S.P., Ramasenya, K., Ekolu, S.*, et al.* (2019) A laboratory investigation on the performance of South African acid producing gold mine tailings and its possible use in mine reclamation. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering,* 54(13): 1293-1301.**
Keywords: backfilling; geochemical characterization and geotechnical characterization; Gold mine tailings (GMT).

**Abstract:**
This paper presents the results of laboratory investigations conducted on gold mine tailings (GMT) to assess their chemical, mineralogical and geotechnical characteristics in view of assessing its suitability as an alternative backfilling solution in mine reclamation. Chemical characterization revealed that GMT is dominated by Si, Al, and Fe with notable amounts of Cr, Zr, Zn, Pb, Ce, As, Ba, Ni, V, Sr, Nd, Cu, U, and Co. Mineralogical characterization revealed a composition of silicate minerals with secondary minerals such as jarosite, goethite and hematite. GMT composites showed improved strength characteristics. The particle sizes of the tailings are capable of producing a good paste fill that will require lower water–cement ratio. Moreover, the plasticity of the tailings provide for a likelihood for shear resistance to sliding in fluvial conditions. Curing and addition of cement showed positive effects on the compressive strength and shear strength of the tailings. However, the effect of curing and cement addition on the compaction characteristics and permeability of the tailings were negligible. GMT showed favorable characteristics for use in mine backfilling; it would be interesting to evaluate higher cement ratios to improve the characteristics of the tailings. 

**Gonçalves, F., Correa, C.Z., Lopes, D.D.*, et al.* (2019) Monitoring of the process of waste landfill leachate diffusion in clay and sandy soil. *Environmental Monitoring and Assessment,* 191(9)**.
Keywords: Landfill waterproofing barrier; Leak detection techniques; Principal component analysis (PCA); Soil contamination; Temporal analysis.
**Abstract:**
The objective of this research was to evaluate the interaction of landfill leachate of urban solid waste in clayey (CL) and sandy soils (SL) in order to determine physical and chemical

parameters that can be used as indicators of soil contamination when there are faults in the landfill waterproofing. In the diffusion tests, compacted soil samples were placed in contact with leachate (methanogenic phase). The temporal analysis (200 days) considered the parameters pH, electrical conductivity (EC), alkalinity, nitrogen series, chemical oxygen demand (COD), solids and color for the leachate and pH, ΔpH, EC, total nitrogen (TN), chemical elements, and cation exchange capacity (CEC) for the soils. Correlation analysis and principal component analysis (PCA) were performed to results. It was observed that the studied soils have potential to attenuate chemicals present in the leachate; this indicates the possibility of using them as base in landfills. Correlation analysis and PCA carried out to CL showed that in a process of CL monitoring the pH would be the key parameter to indicate contamination of this soil, due to the high correlation of this parameter with the others analyzed. For the SL, the parameters pH, alkalinity, apparent color, and COD (total and filtered) could be used as indicators of contamination. In both soils, monitoring of concentrations of Ca, Mg, K, SB, V, and CTC can be used to indicate possible faults in the waterproofing system of the landfill. 

**Iriel, A., Cordon, G., Fernandez Cirelli, A.*, et al.* (2019) Non-destructive methodologies applied to track the occurrence of natural micropollutants in watering: Glycine max as a biomonitor. *Ecotoxicology and Environmental Safety,* 182: UNSP 109368.**

Keywords: Arsenic; Fluoride; Vanadium; Boron; Chlorophyll fluorescence; Reflectance; chlorophyll fluorescence-spectra; reflectance spectra; optical-properties; supported dyes; red edge; leaves; light; photosynthesis; groundwater; stress; Environmental Sciences & Ecology; Toxicology.

**Abstract:**
Groundwater is habitually used for watering purposes in rural areas where the rainfall is not enough to adequately cover the crop requirements. However, groundwater sources could be naturally contaminated with trace micropollutants like As and associated elements (B, V and F) adversely affecting the plant health. In this work, non-destructive methodologies based on reflectance and chlorophyll emission processes were applied to assess the presence of micropollutants in watering by using a widespread crop (soybean plant). One of the most substantial results is that the co-occurrence of As, V, B and F in the watering solution clearly produced a synergistic effect in the plants. In fact, both reflectance and fluorescence techniques were proved in this work to be effective in detecting non-destructively stress by multielement treatment. Particularly, for reflectance measurements the most sensitive parameters were the derivative peak area between 480 and 560 nm and the chlorophyll content. Furthermore, it was demonstrated that it is possible to successfully use a portable hyperspectral spectroradiometer instead of a conventional spectrophotometer as the determinations performed with both instruments were positively correlated. Concerning fluorescence, variable emission of chlorophyll-a was more sensitive to stress than steady-state emission. The parameter F-v/F-0 was a valuable indicator of stress but the quantum yields of PSII and NPQ stood out as the most sensitive indices with variations of around 60 and 100% respectively.

**Landis, M.S., Berryman, S.D., White, E.M.*, et al.* (2019) Use of an epiphytic lichen and a novel geostatistical approach to evaluate spatial and temporal changes in atmospheric deposition in the Athabasca Oil Sands Region, Alberta, Canada. *The Science of the Total Environment,* 692: 1005-1021.**
Available at:

https://www.sciencedirect.com/science/article/pii/S0048969719331249/pdfft?md5=b7860a2687e399212f69168d4452fdf7&pid=1-s2.0-S0048969719331249-main.pdf
Keywords: Air Pollutants/analysis; Alberta; Atmosphere; Dust/analysis; Environmental Monitoring/methods; Lichens/chemistry; Oil and Gas Fields; Atmospheric deposition; Cokriging; Hypogymnia physodes; Lichen biomonitoring; Time series analysis; Wood Buffalo Environmental Association.

**Abstract:**
Temporal and spatial atmospheric deposition trends of elements to the boreal forest surrounding bitumen production operations in the Athabasca Oil Sands Region (AOSR), Alberta, Canada were investigated as part of a long-term lichen bioindicator study. The study focused on eight elements (sulfur, nitrogen, aluminum, calcium, iron, nickel, strontium, vanadium) that were previously identified as tracers for the major oil sand production sources. Samples of the in situ epiphytic lichen Hypogymnia physodes were collected in 2002, 2004, 2008, 2011, 2014, and 2017 within a ~150km radius from the center of surface oil sand production operations in the AOSR. Site-specific time series analysis conducted at eight jack pine upland sites that were repeatedly sampled generally showed significant trends of increasing lichen concentrations for fugitive dust linked elements, particularly at near-field (<25km from a major oil sands production operation) sample locations. Multiple regional scale geostatistical models were developed and evaluated to characterize broad-scale changes in atmospheric deposition based on changes in H. physodes elemental concentrations between 2008 and 2014. Empirical Bayesian kriging and cokriging lichen element concentrations with oil sands mining, bitumen upgrading, coke materials handling, and limestone quarry/crushing influence variables produced spatial interpolation estimates with the lowest validation errors. Gridded zonal mean lichen element concentrations were calculated for the two comprehensive sampling years (2008, 2014) and evaluated for spatial and temporal change. Lichen sulfur concentrations significantly increased in every grid cell within the domain with the largest increases (44-88%) in the central valley in close proximity to the major surface oil sand production operations, while a minor nitrogen concentration decrease (-20%) in a single grid cell was observed. The areal extent of fugitive dust element deposition generally increased with significantly higher deposition to lichens restricted to the outer grids of the enhanced deposition field, reflecting new and expanding surface mining activity.

**Ma, L., Abuduwaili, J. & Liu, W. (2019) Spatial Distribution and Health Risk Assessment of Potentially Toxic Elements in Surface Soils of Bosten Lake Basin, Central Asia. *International Journal of Environmental Research and Public Health,* 16(19): 10.3390/ijerph16193741.**
Available at: https://www.mdpi.com/1660-4601/16/19/3741/pdf
Keywords: arid land; classical linear model; geographically weighted regression; influencing factors; soil geochemistry.

**Abstract:**
A geographically weighted regression and classical linear model were applied to quantitatively reveal the factors influencing the spatial distribution of potentially toxic elements of forty-eight surface soils from Bosten Lake basin in Central Asia. At the basin scale, the spatial distribution of the majority of potentially toxic elements, including: cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), thallium (Tl), vanadium (V), and zinc (Zn), had been significantly influenced by the geochemical characteristics of the soil parent material. However, the arsenic (As), cadmium (Cd), antimony (Sb), and mercury (Hg) have been influenced by the total organic matter in soils. Compared with the results of the classical linear model, the geographically weighted regression can significantly increase the level of simulation at the basin spatial scale. The fitting coefficients of the predicted values and the

actual measured values significantly increased from the classical linear model (Hg: r(2) = 0.31; Sb: r(2) = 0.64; Cd: r(2) = 0.81; and As: r(2) = 0.68) to the geographically weighted regression (Hg: r(2) = 0.56; Sb: r(2) = 0.74; Cd: r(2) = 0.89; and As: r(2) = 0.85). Based on the results of the geographically weighted regression, the average values of the total organic matter for As (28.7%), Cd (39.2%), Hg (46.5%), and Sb (26.6%) were higher than those for the other potentially toxic elements: Cr (0.1%), Co (4.0%), Ni (5.3%), V (0.7%), Cu (18.0%), Pb (7.8%), Tl (14.4%), and Zn (21.4%). There were no significant non-carcinogenic risks to human health, however, the results suggested that the spatial distribution of potentially toxic elements had significant differences.

**McNaughton, C.S., Vandenberg, J. & Thiede, P. (2019) Reanalysis of aerial deposition of metals and polycyclic aromatic compounds to snow in the Athabasca Oil Sands Region of Alberta Canada. *Science of the Total Environment,* 682: 692-708.**
Keywords: Athabasca oil sands; Atmospheric deposition; Metals; Polycyclic aromatic compounds; Snow.

**Abstract:**
Oil sands mining and bitumen upgrading activities in the Athabasca Oil Sands Region (AOSR)have been identified as sources of metals and polycyclic aromatic compounds (PAC)being deposited to the regional snowpack. We performed an independent reanalysis of publicly available AOSR snow pack data to: replicate previous results; to provide new insights into the spatial and temporal patterns of metal and PAC deposition; and, to determine whether certain metals or PACs were associated with specific oil sands mining or upgrading activities. Using PAC ratios, we use a K-means clustering approach to classify snowpack data into two combustion-dominated classes, and three classes associated with oil sands mining and bitumen upgrading. Snow samples dominated by “oil sands mine” emissions are consistent with a petrogenic source and exhibited low UNS ratios and high DBT ratios. Snow samples dominated by “petroleum coke” emissions had the highest BaP ratios, high DBT ratios, and were collected nearest the upgrader complexes. Metals data indicate snow samples dominated by oil sands mine emissions are consistent with an Athabasca Sands type composition. Those dominated by emissions from petroleum coke show enrichment of biophile metals V, Ni, and M. We conclude that previous studies have over-estimated environmental loadings of PACs, their spatial extent, and direction of their trend over time. These differences are attributed to the use of arithmetic rather than geometric spatial averaging, use of an arbitrary location (AR6)to determine the extent of metals and PAC deposition, and because previous studies neglected to account for metals and PACs being deposited from non-oil sands sources. Oil sands operators continue to reduce their emissions intensity, however there is an emerging consensus that mitigating fugitive emissions from petroleum coke stockpiles may represent the greatest opportunity to reduce environmental loadings of PACs in the AOSR. © 2019 Elsevier B.V.

**Muñoz, A.A., Klock-Barría, K., Sheppard, P.R., *et al.* (2019) Multidecadal environmental pollution in a mega-industrial area in central Chile registered by tree rings. *Science of the Total Environment,* 696: 133915.**
Available at:
https://www.researchgate.net/profile/Alvaro_Gonzalez_Reyes/publication/335213413_Multidecadal_environmental_pollution_in_a_mega-industrial_area_in_central_Chile_registered_by_tree-rings/links/5d62b68aa6fdccc32cd19e16/Multidecadal-environmental-pollution-in-a-mega-industrial-area-in-central-Chile-registered-by-tree-rings.pdf

Keywords: Baseline; Cupressus macrocarpa; Dendrochemistry; Industrial pollution; Trace metals.

**Abstract:**
One of the most polluted areas in Chile is the Ventanas Industrial Area (VIA; 32.74°S / 71.48°W), which started in 1958 and today comprises around 16 industries in an area of ca. 4 km2. A lack of consistent long-term instrumental records precludes assessing the history of contamination in the area and also limits the evaluation of mitigation actions taken since the late 1980s. Here, we use dendrochemistry as an environmental proxy to analyze environmental changes over several decades at the VIA. We present chemical measurements of tree rings from planted, exotic Cupressus macrocarpa growing near the VIA with 4-year resolution over a period of 52 years (1960–2011). These data provide unprecedented information on regional anthropogenic pollution and are compared with a tree-ring elemental record of 48 years (1964–2011) from the Isla Negra (INE) control site not exposed to VIA emissions. For the 48 years of overlap between both sites, higher concentrations of Zn, V, Co, Cd, Ag, Fe, Cr, and Al were especially registered after the year 2000 at VIA compared to INE for the periods under study. Concentrations of Pb, Cu, As, Fe, Mo, Cr, and Zn increased through time, particularly over the period 1980–1990. Decontamination plans activated in 1992 appear to have had a positive effect on the amount of some elements, but the chemical concentration in the tree rings suggest continued accumulation of pollutants in the environment. Only after several years of implementation of the mitigation measures have some elements tended to decrease in concentration, especially at the end of the evaluated period. Dendrochemistry is a useful tool to provide a long-term perspective of the dynamics of trace metal pollution and represents a powerful approach to monitor air quality variability to extend the instrumental records back in time. © 2019 Elsevier B.V.

**Nkinahamira, F., Suanon, F., Chi, Q.*, et al.* (2019) Occurrence, geochemical fractionation, and environmental risk assessment of major and trace elements in sewage sludge. *Journal of Environmental Management,* 249.**
Keywords: Co-occurrence; Geochemical fractions; Risk assessment; Sewage sludge; Temporal and spatial variations.

**Abstract:**
Industrialization and accelerated population growth have created a huge amount of sewage sludge. Many studies have reported the sewage sludge as a sink of major and trace elements, but less is known about their geochemical fractionations. In order to assess the mobility, the distribution, bioavailability, and toxicity of those elements in sludge, we collected the sewage sludge samples from all the seven wastewater treatment plants in Xiamen City, China. Results revealed a strong spatial variation and the occurrence of 48 elements with concentrations ranging from 1.00×10-2 mg kg−1 (Re) to 9.03×101 g kg−1 (Fe) on the basis of dry sludge weight. Sequential extraction procedure showed that residual and oxidizable fractions were the main geochemical fractions of most studied elements. However, Ca, Mn, Sr, and Ni were mainly bound to acid-exchangeable fractions, while Fe, Zn, Cd, Cr, Co, and V were mainly distributed in the reducible fractions. The contamination factor and risk assessment code indicated that Ni, Cu, Zn, Cd, Cr, Co, Sr, Ca, Mn, Mo, Re, and W were highly mobile with less retention time and exerted high environmental risks through sludge land application. The sludge disposal strategy should consider not only the total concentrations of a broad range of elements but also their bioavailability. © 2019 Elsevier Ltd.

**Shirinpur-Valadi, A., Hatamzadeh, A. & Sedaghathoor, S. (2019) Study of the accumulation of contaminants by Cyperus alternifolius, Lemna minor, Eichhornia crassipes, and Canna x**

**generalis in some contaminated aquatic environments. *Environmental Science and Pollution Research,* 26(21): 21340-21350.**
Keywords: Canna; Duckweed; Heavy elements; Hyacinth; Pollution; waste-water; heavy-metals; chromium; phytoremediation; removal; L.; toxicity; soil; Environmental Sciences & Ecology.

**Abstract:**
Today, environmental pollution, especially heavy metal pollution, is known as a new and possibly more dangerous pollutant than other environmental ones. For this purpose, the uptake of four aquatic plants in different environments was chosen. In this experiment, four macrophytes, i.e., umbrella palm (Cyperus alternifolius), duckweed (Lemna minor), water hyacinth (Eichhornia crassipes), and canna (Canna x generalis), were studied in five contaminated aquatic environments, i.e., Gohar Rood river, Zarjoob river, Eynak lagoon, Anzali lagoon, and control solution (containing Cd, Cr, Pb, and Zn). The results showed that the highest uptake rates of cadmium, cobalt, vanadium, chromium, zinc, nickel, and lead were observed for duckweed fronds. The highest bioconcentration factor (BCF) of nickel was related to duckweed stem and water hyacinth root, and the highest BCF of cadmium belonged to duckweed fronds and canna root. The highest rate of uptake of cadmium, chromium, zinc, and lead was related to control. The least amount of uptake of several metals by plants was obtained from the water of Gohar Rood and Zarjoob. Generally, based on the results of this study, it can be stated that duckweed is suitable for the uptake of most heavy metals.

**Starostina I, Vasilenko T, Simonov M and Pendurin E (2019) Evaluating Toxicological Properties of Claydite Gravel, Containing Ferrovanadium Production Sludge, by Method of Biotesting with the of Higher Plants. In: Anonymous *E3S Web of Conferences*: EDP Sciences, 00068**

**Abstract:**
Recycling of sludge wastes, generated at industrial wastewater treatment and containing heavy metals, is a relevant and long-term task in building materials production. At that, the possibility of toxicants emission to the environment should be taken into account. This paper presents the findings of evaluating toxicological properties of artificial porous aggregates (claydite gravel), containing ferrovanadium production sludge, by means of using higher plants (Avena Sativa and Allium cepa) as test objects. It is demonstrated that adding sludge to the raw charge in amount up to 15% in the process of baking intensifies the melt formation with clay minerals, which contributes to the safe binding of heavy metals, reducing their diffusion to water media. Water extracts of the obtained claydite have no phytotoxic effect on higher plants.

**Wang, L., Lin, H., Dong, Y.*, et al.* (2019) Effects of endophytes inoculation on rhizosphere and endosphere microecology of Indian mustard (Brassica juncea) grown in vanadium-contaminated soil and its enhancement on phytoremediation. *Chemosphere,* 240: 124891.**
Keywords: Bacterial community; Endophyte-assisted phytoremediation; Heavy metal speciation; Microbial inoculants; Vanadium.

**Abstract:**
We investigated the effects of endophytes inoculation on ecological factors such as root morphology, rhizosphere soil properties, heavy metal speciation, and rhizosphere and endophytic bacterial communities and their role on phytoremediation. Indian mustards were grown for two months in V-contaminated soil with three treatments (control, inoculation with Serratia PRE01 or Arthrobacter PRE05). Inoculation with PRE01 and PRE05 increased organic

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

**Weissmannová, H.D., Mihočová, S., Chovanec, P.*, et al.* (2019) Potential ecological risk and human health risk assessment of heavy metal pollution in industrial affected soils by coal mining and metallurgy in Ostrava, Czech Republic. *International Journal of Environmental Research and Public Health,* 16(22).**
Available at: https://www.mdpi.com/1660-4601/16/22/4495/pdf
Keywords: Ecological risk; Heavy metals; Human health risk; Pollution assessment; Soils

**Abstract:**
The heavy metal pollution of soils has become serious environmental problem, mainly in localities with high industrialization and rapid growth. The purpose of this detailed research was to determine the actual status of heavy metal pollution of soils and an assessment of heavy metal pollution in a highly industrialized city, Ostrava, with a history of long-term impacts from the metallurgy industry and mining. The ecological risks to the area was subsequently also assessed. The heavy metals Cd, Hg, Cu, Mn, Pb, V, Zn, Cr and Fe were determined in top-soils (0–20 cm) using atomic absorption spectrometry (F AAS, GF AAS) from three areas with different anthropogenic loads. The obtained data expressed as mean metal concentrations were very varied among the sampled soils and values of all analyzed metal concentrations were higher than its background levels. To identify the ecological risk and assessment of soil pollution, various pollution indices were calculated, such as single pollution indices (Igeo, CF, EF, PI) and total complex indices (IPI, PLI, PINemerow, Cdeg, mCdeg, Er and PERI). The identification of pollution sources was assessed using Pearson's correlation analysis and multivariate methods (HCA, PCA/FA). The obtained results confirmed three major groups of metals (Fe–Cr, Pb–Cu and Mn–V). A human health risk was identified in the case of Pb, Cd and Cr, and the HI value of V for children also exceeded 1. © 2019 by the authors. Licensee MDPI, Basel, Switzerland.

**Xu, D., Gao, B., Chen, S.*, et al.* (2019) Release risk assessment of trace metals in urban soils using in-situ DGT and DIFS model. *Science of the Total Environment,* 694.**
Keywords: Diffusive gradients in thin-films (DGT); DIFS model; Megacity; Release risk; Trace metals; Urban soils.

**Abstract:**
Urbanization and urban construction lead to entensive environmental deterioration. Trace metals in urban soils pose a threat to urban water bodies and local populations. However, the release ability of labile metals and their release risk in urban soils remains unclear. Here, soils were collected from different functional zones in the Pingshan District (PSD) of Shenzhen. Based on results of soil properties, total contents of trace metals, geochemical index (Igeo), and risk assessment code (RAC), diffusive gradients in thin films (DGT) and DGT-induced fluxes

in soil (DIFS) model were further used to assess the release risk of trace metals in urban soils. The results showed that the average total concentrations of trace metals (As, Cr, Cu, Pb, and V) were higher than the local soil background values, implying that trace metals accumulated in urban soils. However, the distributions of labile metals determined by DGT were not similar to those of total metal concentrations. Except for As, urban soils from PSD sites exhibited "uncontaminated to moderately contaminated" levels based on the average values of Igeo. Moreover, the pollution and migration of Cu in urban soils are problematic as evidenced by the Igeo and RAC assessments. Release ability of Cu was assessed using parameters of DIFS model (i.e., bioavailability concentrations (CE), resupply ability (R), response time (Tc), desorption rate (k−1), and sorption rate (k1)). Residential areas showed high CE values for Cu, while the resupply ability was low. Furthermore, considering the influences of R, Tc, k−1, and k1, membership function value was used to re-calculate the order of CE in urban soils. The final results suggested that the agricultural zone exhibited the highest release risk among soils from various functional zones. Therefore, DGT and DIFS model should be effective tools to assess the release risk of trace metals in urban soils. © 2019 Elsevier B.V.

**Zádrapová, D., Titěra, A., Száková, J.*, et al.* (2019) Mobility and bioaccessibility of risk elements in the area affected by the long-term opencast coal mining. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering,* 54(12): 1159-1169.**
Keywords: arsenic; Cadmium; in vitro tests; plant and animal uptake; soil contamination.

**Abstract:**
The potential environmental hazards of risk elements in the area affected by the opencast coal mine and/or coal combustion for plants and animals was assessed by using a suite of laboratory bioaccessibility tests. The chosen sampling area was in the vicinity of the largest coal mine spoil in the Sokolov coal basin (Czech Republic). For an estimation of the oral bioaccessibility of the risk elements in soils, the physiologically based extraction tests were applied. Among the available methods for estimating the pulmonary bioaccessibility of elements, the Gamble's and Hatch's tests were chosen. The results showed elevated pseudo-total soil contents of As, Be, Cd, Cu, Pb, V, and Zn. Among these elements, only Cd showed substantial bioaccessibility for plants, as documented by the high Risk Assessment Code, reaching up to 47%, and the highest plant-availability, where the maximum Bioaccumulation Factor in plants reached up to 4.5. The simulated body fluids showed the highest bioaccessibility of Cd, but also substantial bioaccessible pools of As and Be, the elements frequently found at the brown coal mining and processing areas. For better understanding of the risk element bioaccessibility under the specific conditions, the released element pools should be related to the particular soil physicochemical parameters. © 2019, © 2019 Taylor & Francis Group, LLC.

**Zou, Q., Xiang, H., Jiang, J.*, et al.* (2019) Vanadium and chromium-contaminated soil remediation using VFAs derived from food waste as soil washing agents: A case study. *Journal of Environmental Management,* 232: 895-901.**
Keywords: Chromium; Environmental Restoration and Remediation; Fatty Acids, Volatile; Humans; Soil; Soil Pollutants; Vanadium; Food waste; Reusability; Soil washing; Volatile fatty acids

**Abstract:**
Food waste (FW) is environmentally unfriendly and decays easily under ambient conditions. Vanadium (V) and chromium (Cr) contamination in soils has become an increasing concern due to risks to human health and environmental conservation. Volatile fatty acids (VFAs)

derived from FW was applied as soil washing agent to treat V and Cr-contaminated soil collected from a former V smelter site in this work. The Community Bureau of Reference (BCR) three-step sequential extraction procedure was used to identify geochemical fractions of V and Cr influencing their mobility and biological toxicity. Optimal parameters of a single washing procedure were determined to be a 4h contact time, liquid-solid ratio of 10:1, VFAs concentration of 30g/L, and reaction temperature of 25 degrees C, considering for typical soil remediation projects and complete anaerobic fermentation of FW. Under the optimal conditions, butyric acid fermentation VFAs attained removal rates of 57.09 and 23.55% for extractable fractions of V and Cr, respectively. Simultaneously, a multi-washing process under a constant liquid-solid ratio using fresh and recycled VFAs was conducted, which led to an improvement on the total removal efficiency of toxic metals. The washing procedure could reach the pollution thresholds for several plants, such as of S. viridis, K. scoparia, M. sativa, and E. indica. This strategy enhances the utilization of VFAs derived from food waste, has a positive effect on V and Cr-contaminated soil remediation, wastewater control of soil washing and FW disposal.

# 6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

**Almalki, A.M., Ajarem, J., Altoom, N.*, et al.* (2019) Effects of Mining Activities on Gerbillus nanus in Saudi Arabia: A Biochemical and Histological Study. *Animals : An Open Access Journal from MDPI,* 9(9): 10.3390/ani9090664.**
Available at: https://www.mdpi.com/2076-2615/9/9/664/pdf
Keywords: Balochistan gerbil; heavy metals; kidney damage; liver injury; mining.

**Abstract:**
Mining can impact the environment, biodiversity, and human health through direct and indirect practices. This study investigated the effects of gold mining on Gerbillus nanus, in relation to organ dysfunction and redox imbalance. Soil samples, Lycium shawii, and G. nanus were collected from a site near a mining plant, and a control site. Soil and L. shawii samples from the mining site showed significantly higher cadmium (Cd), copper (Cu), mercury (Hg), arsenic (As), zinc (Zn), lead (Pb), and vanadium (V) levels. Hepatic, renal, and pulmonary Cd, Pb, Hg, Zn, Cu, Fe, As, and V concentrations were significantly higher in G. nanus from the mining site. Markers of liver and kidney function were elevated in serum, and several histological manifestations were observed in the liver, kidney, and lung of G. nanus from the mining site. Malondialdehyde and nitric oxide levels increased, and glutathione and antioxidant enzymes decreased in the liver and kidney of G. nanus. In conclusion, mining practices trigger tissue damage and oxidative stress in G. nanus that live close to the mining site. These findings can represent a scientific basis for evaluating the environmental and health impacts of mining on nearby communities.

# 7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS

Dahms-Verster, S., Nel, A., van Vuren, J.H.J.*, et al.* (2020) Biochemical responses revealed in an amphibian species after exposure to a forgotten contaminant: An integrated biomarker assessment. *Environmental Toxicology and Pharmacology,* 73: 103272.
Available at:
https://www.sciencedirect.com/science/article/pii/S1382668919301462/pdfft?md5=b1cc64fe07fc8e851abb895668b11db2&pid=1-s2.0-S1382668919301462-main.pdf
Keywords: Amphibians; Biomarkers; Integrated biomarker response v2; Metal toxicity; Reactive oxygen species; Vanadium pentoxide.

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

**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.** Available at:
https://jpoll.ut.ac.ir/article_68940_e1571c4817109b169a491825064b51a5.pdf
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 g/L), copper (1-20 mu g/L), manganese (1-313 mu g/L) and zinc (1.2-57 mu 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 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.

**Embaby, A. & Redwan, M. (2019) Sources and behavior of trace elements in groundwater in the South Eastern Desert, Egypt. *Environmental Monitoring and Assessment,* 191(11).** Keywords: Geochemistry; Groundwater aquifers; Multivariate analyses; South Eastern Desert, Egypt; Trace element; Treatment.

**Abstract:**
Due to water scarcity, the groundwater will represent an essential source of water in many communities worldwide. This study was carried out to investigate the main hydrogeochemical characteristic of trace elements composition, their sources, and its vulnerability in groundwater to the human population. Fifteen groundwater samples were collected from boreholes and hand dug wells from the South Eastern Desert, Egypt, and analyzed for Al, As, B, Fe, Mn, Cd, Co, Cr, Cu, Hg, Ni, Pb, Rb, Sb, Sr, Th, U, V, and Zn using inductively coupled plasma mass spectrometry. Multivariate analyses were applied to identify the distribution and potential source of trace elements. The groundwater is tapped from the Miocene and the fractured basement rock aquifers. The mean concentrations of trace elements exceed the guideline values of all organizations, except in some wells for Zn, Cu, and Co. Cationic trace elements declined in the order of Mn > Fe > Zn > Al > V > Ni > Rb > Sr > U > Cu > Cr > Co > Cd > Pb > Th > Sb > Hg. Oxyanions As (mean 15.48 mg/L) and B (mean 1.24 mg/L) showed very high concentrations and higher than the average WHO concentrations in water suggesting potential adverse toxicity to all aquatic organisms. Five factor analyses indicated that different geochemical contributions are involved in the chemical characteristics of groundwater in the study area. Water–rock interaction and dissolution processes in bed rocks from different coastal Miocene deposits, meta-volcanics, basic-ultrabasic rocks, granitic and meta-sediments, seawater intrusion, residential wastes, and mining activities, in addition to the pH/Eh conditions, adsorption, and surface complexation during the chemical weathering are the main factors influence the trace elements distribution in groundwater. Results from this study for the six different groundwater aquifers are a unique insight into the sources and mobility of the observed trace elements in the groundwater and can be used in the assessment of contamination for drinking water wells. The association of trace elements from different aquifers might be useful in tracers studies of water-rock interaction. Due to the enrichment of trace elements in nearshore and crystalline groundwater aquifers in the study area and in similar areas worldwide, treatment technologies, and sustainable water management processes should be applied to prevent severe risks to the communities. © 2019, Springer Nature Switzerland AG.

**Fang, X., Peng, B., Wang, X.*, et al.* (2019) Distribution, contamination and source identification of heavy metals in bed sediments from the lower reaches of the Xiangjiang River in Hunan province, China. *Science of the Total Environment,* 689: 557-570.** Keywords: Distribution pattern; Heavy metal contamination; Natural and anthropogenic contamination; Spatial contamination variation; Xiangjiang River.

**Abstract:**
Concentrations of heavy metals Ba, Sc, V, Cr, Mn, Co, Ni, Th, U, Cu, Pb, Zn, and Cd in sediments from the lower reaches of the Xiangjiang River were analyzed using inductively coupled plasma mass spectrometry. The results suggest that there are two metal distribution patterns in these sediments: (1) Ba, Sc, V, Cr, Mn, Th, and U are relatively homogeneously distributed and (2) Cd, Pb, Zn Cu, Co and Ni are heterogeneously distributed. The heterogeneously distributed metals are significantly enriched in these sediments and, thereby, contribute to contamination. Assessments of heavy metal contamination using the Geoaccumulation index, Pollution load index, and potential ecological risk index suggest that the levels of contamination from Cd and Mn are extremely high and moderately high, respectively, in all

the sediments from the lower river. In comparison, the levels of contamination by Cu, Zn, and Pb varied spatially, decreasing progressively downriver. The level of contamination by Pb, Zn, and Cu in sediments from the Zhuzhou reach is extremely high, and is moderate to significant high for the Xiangtan, Changsha, and Xiangyin reaches. The ecological potential risks posed heavy metals are ranked, in descending order, as Cd > Pb > Cu > Zn > Cr > Ni > Co > Mn for sediments from the Zhuzhou reach and Cd > Pb > Cu > Ni > Cr > Co > Zn > Mn for sediments from the Xiangtan, Changsha, and Xiangyin reaches. Principal component analysis and enrichment factor calculations suggest that Ba, Sc, V, Cr, Th, and U mostly originate from natural processes. While, Cd, Pb, Zn, Cu, Co, Ni, and Mn are derived from both natural processes and anthropogenic activities. Therefore, strategies for environmental protection in this watershed should focus on contamination by Cd, Pb, Zn, and Cu, with Cd requiring particular attention. © 2019 Elsevier B.V.

**Fazio, F., Saoca, C., Sanfilippo, M.*, et al.* (2019) Response of vanadium bioaccumulation in tissues of Mugil cephalus (Linnaeus 1758). *The Science of the Total Environment,* 689: 774-780.**

Keywords: Animals; Hematologic Tests/veterinary; Sicily; Smegmamorpha/blood/metabolism; Tissue Distribution; Vanadium/metabolism; Water Pollutants, Chemical/metabolism; Aquatic pollution; Biomarkers; Fish blood parameters; Mugil cephalus; Tissues; Vanadium.

**Abstract:**
Vanadium accumulation levels in different tissues (muscle and organs) of the striped mullet Mugil cephalus (Linnaeus, 1758) and possible relationships with blood parameters were evaluated in a Natural Protected Area (Lake Faro, Sicily, Italy), during the winter of 2017. Hematological parameters (red blood cell, RBC; white blood cell, WBC; hemoglobin concentration, Hb; hematocrit, Hct; mean corpuscular volume, MCV; mean corpuscular hemoglobin, MCH; mean corpuscular hemoglobin concentration, MCHC; thrombocytes, TC), biometric indices (weight, total and fork length), and vanadium levels in muscles and organs (gills, liver, stomach and intestine) were determined. Statistical analyses showed significant differences in concentrations of vanadium of the analyzed tissue of M. cephalus and a positive relationship between vanadium concentration in the liver and some hematological parameters (RBC, Hb and Hct) and biometric indices. Our results underline the importance of fish blood parameters as sensitive indicators of toxic impact of environmental factors such as metals. This study, focusing on an ongoing topic, represents a valuable contribution to research concerning the monitoring and prevention of vanadium pollution in aquatic organisms and environments.

**Galon-Negru, A.G., Olariu, R.I. & Arsene, C. (2019) Size-resolved measurements of PM2.5 water-soluble elements in Iasi, north-eastern Romania: Seasonality, source apportionment and potential implications for human health. *Science of the Total Environment,* 695.**

Available at:
https://www.sciencedirect.com/science/article/pii/S0048969719337866/pdfft?md5=8406f3ebb8ab38c9ff5e0098346a1364&pid=1-s2.0-S0048969719337866-main.pdf

Keywords: Emission sources; Fine particle; Health risks; Positive matrix factorization; Water-soluble metals

**Abstract:**
The present paper reports the first size-resolved element measurements in the PM2.5 fraction collected throughout 2016 in the Iasi urban area in north-eastern Romania. Concentrations of water-soluble elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cu, Cr, Fe, Ga, Mg, Mn, Mo, Ni, Pb,

Rb, Se, Sr, Te, Ti, U, V, Zn) were determined using inductively coupled plasma mass spectrometry. Several water-soluble heavy metals (Al, Fe, Zn, As, Cr, Pb) exhibit clear seasonal patterns with maxima over the cold season and minima over the warm season. Elements as Al, Fe, Mg, Zn, Ni, Mn, and Cu present the highest levels in the PM2.5 fraction, indicating significant contributions from soil-dust resuspension or brake lining and tires. Clear fine mode size-dependent distributions were observed for anthropogenic source-origin elements (Pb, Zn, Cd, V, etc.) due to an acidity-driven metals dissolution process. Positive matrix factorization, concentration weighted trajectory and bivariate polar plot analyses were applied to the entire PM2.5 database. Based on relative concentrations of various elements, five factors associated with specific sources were identified. The most important contributions to the total PM2.5 mass concentration (during the total period) come from secondary formation of the ammonium sulfate form (~44%) and from nitrate (~37%). Resuspended dust accounts for a contribution of about 16%, while biomass burning mixed with NaCl salt/sea-salt sources contribute as much as ~3%. Traffic and industrial sources seem to yield little contribution (<0.05%). An assessment investigation of non-carcinogenic and carcinogenic health risks revealed water-soluble arsenic and chromium (VI) as elements with the largest incremental carcinogenic risks. Both metals have traffic and industrial related sources and therefore it is believed that in the future, at the local/regional level, these sources should receive attention by implementing appropriate emission control measures. 

**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: Oil sands; OSPW; Vanadium; 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 (LC 50 )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 3 )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 LC 50 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 (LC 50 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. © 2019 Elsevier Inc.

**Gurbuz, F., Akpinar, S., Ozcan, S.*, et al.* (2019) Reducing arsenic and groundwater contaminants down to safe level for drinking purposes via Fe(3+)-attached hybrid column. *Environmental Monitoring and Assessment,* 191(12): 722-019-7862-9.**
Keywords: Arsenic reduction; Groundwater; Hybrid column; Regeneration; Subsurface chemicals.

**Abstract:**
Monitoring of groundwater is fundamentally important due to it has emerged as a major source of drinking water and also used for irrigation purposes in many places in the world. Arsenic contamination in surface water and groundwater resources is a major concern due to its presence at high concentration and associated adverse health effects. Thus, the remediation of As in water resources, alongside other chemical species including fluoride, lithium, vanadium aluminium and nitrate is necessary. We have designed a hybrid [polyethyleneimine (PEI)-supported Fe(3+)-attached poly-(HEMA-co-GMA)] column for the reduction of arsenic (III and V) and other groundwater chemicals from natural groundwater as a potential contribution to water resource management. Swelling behaviour and scanning electron microscopy (SEM) were performed for the characterization of hybrid material. For the optimization of experimental conditions, the effects of pH and initial arsenic concentrations on adsorption were studied using arsenic solutions. Maximum adsorption capacity in equilibrium was 11.44 and 5.79 mg/g polymer for As(III) and As(V), respectively at pH 7. The reduction of metalloids and other subsurface chemicals were carried out with natural groundwater samples obtained from local sources. The mean concentrations of arsenic were recorded between 44.96 and 219.04 mug/L and of which 71.3-95.4 % (0.32-1.22 mg/g) were removed. The average removals were determined as F(-1) 50-86%, Li(+) 43.2-99.7%, Al(+3) 83.8-91.4%, NO3(-) 48.4-72.2% and V 91.3-95.7. Chemical-loaded hybrid columns were regenerated successfully 15 times with only a loss of 5% in adsorption capacity by 0.01 M NaCl(-) treatment for potential adaptation into water industry. No pre-oxidation of As species was performed for the treatment of ground water samples prior to the hybrid column testing.

**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 & Technology,* 53(8): 4088-4098.**
Available at: https://pubs.acs.org/doi/pdf/10.1021/acs.est.8b06391
Keywords: British Columbia; Minerals; Rivers; Vanadium; Water Pollutants, Chemical

**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(3+) substituted into magnetite and V(3+) and V(4+) 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 E1/2 positions and pre-edge features consistent with the presence of V(5+) species, suggesting sorption of this species on these secondary phases. PHREEQC modeling suggests that the stream waters mostly contain V(5+) and the inflow and pore waters contain a mixture of V(3+) and V(5+). 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) oxhydroxides, and V-bearing Al(OH)3 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)3, 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.

**Kakareka, S., Kukharchyk, T. & Kurman, P. (2019) Major and trace elements content in freshwater lakes of Vecherny Oasis, Enderby Land, East Antarctica. *Environmental Pollution,* 255.**
Keywords: Antarctic lakes; Enderby land; Heavy metals; Human activity; Trace elements.

**Abstract:**
In the article the results of major and trace elements investigation in freshwater lakes of Vecherny Oasis (Enderby Land, East Antarctica) are considered. Water sampling was carried out during seasonal Belarusian Antarctic expeditions in 2011–2017. Totally 22 water samples from four lakes, three temporal ponds and one water course were collected for major and trace elements determination. The total concentrations of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Na, Mg, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, V, W, Zn in all samples as well as more than 40 additional trace elements in 3 samples from lakes were determined using ICP-MS method. It is shown that increase of heavy metals concentration (Cd, Pb, Zn, Sb, Co, Ni, Se, Mn) and As in the lakes compared to temporary ponds can be explained by anthropogenic impact including previous human activity in the oasis in late 1970th – early 1990th. The maximum concentrations of a number of technophilic elements (Pb, Mo, Mn, V, Sb, Zn) in Lake Nizhneye are possibly connected with the its lowest hypsometric location in catchment and the drainage of the territory impacted by past and present human activity. © 2019 Elsevier Ltd.

**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 CaCO3) 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.

**Montoya-Mendoza, J., Alarcon-Reyes, E., Castaneda-Chavez, M.D.R.*, et al.* (2019) Heavy Metals in Muscle Tissue of Pterois volitans from the Veracruz Reef System National Park, Mexico. *International Journal of Environmental Research and Public Health,* 16(23): 10.3390/ijerph16234611.**
Available at: https://www.mdpi.com/1660-4601/16/23/4611/pdf
Keywords: lionfish; reef; trace metals.

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

**Olszewska, J.P., Heal, K.V., Edwards, R.*, et al.* (2019) Assessing the legacy of red mud pollution in a shallow freshwater lake: long-term chemical recovery in the water column. *Inland Waters,* 9(4): 453-463.**
Keywords: aluminium; arsenic; lake; phosphorus; recovery; vanadium.

**Abstract:**
Little is known about chemical and ecological recovery following red mud leachate pollution in fresh waters. This deficiency is confounded by a lack of knowledge on the chemical composition of red mud leachate and the changes in composition that occur as a result of interactions with sediments and freshwater organisms during transport through aquatic ecosystems. We used over 30 years of data from a shallow lake (Kinghorn Loch, Fife, Scotland) with a well-documented history of several decades of red mud leachate pollution to characterise the chemical loads (during a pollution period from 1981 to 1983), resultant impacts on surface water chemistry (comparison between 1983 and 2009), and recovery trajectories following leachate diversion (1983–2010) of constituents that pose a risk to the environment. Between 1981 and 1983, the input of leachate resulted in loads of total aluminium (Al), total arsenic (As), total vanadium (V), and phosphate (PO4-P) to the lake of 107, 2.3, 3.3, and 2.3 g m−2 (lake surface area) yr−1, respectively. During the same period, the lake acted as a sink of Al, As, V, and PO4-P, retaining 63.6, 0.6, 0.8, and 1.6 g m−2 yr−1, respectively. We used generalised additive modelling to assess the response trajectories and recovery end points of these constituents. Our results demonstrate the complexity of sediment–pollutant interactions during pollutant transport through the aquatic environment and provide insight into likely recovery trajectories in other aquatic ecosystems following red mud contamination. The PO4-P, total As, and total V surface water concentration recovery times, defined statistically as the point on the time series beyond which no further significant decrease in concentrations was observed, ranged from 18 to 26 years. Total Al concentrations continued to decrease significantly following the end of the monitoring period in 2010. In Kinghorn Loch, the legacy of red mud pollution continues to represent an environmental risk,

demonstrating the importance of long-term monitoring and management strategies following similar pollution events. © 2019, © 2019 International Society of Limnology (SIL).

**Pan, F., Liu, H., Guo, Z.*, et al.* (2019) Metal/metalloid and phosphorus characteristics in porewater associated with manganese geochemistry: A case study in the Jiulong River Estuary, China. *Environmental Pollution,* 255.**
Keywords: Exchange flux; Heavy metal; Metalloids; Mn cycling; Peeper; Phosphorus.

**Abstract:**
Sediment porewater can be an important source of contaminants in the overlying water, but the mechanisms of metal(loid) and phosphorus (P) remobilization remain to be investigated. In this study, high-resolution dialysis (HR-Peeper) and diffusive gradients in thin films (DGT) samplers were used to determine the porewater dissolved iron (Fe), manganese (Mn), cobalt (Co), chromium (Cr), vanadium (V), selenium (Se), arsenic (As), P and DGT-Labile S in coastal sediments in the Jiulong River Estuary (JRE), China. The results showed that high concentrations of dissolved Mn, Se and P were present in the overlying water, indicating potential water pollution with excessive amounts of Mn, Se and P. The dissolved Mn concentrations in the porewater were higher than the dissolved Fe concentrations, especially at submerged sites, demonstrating that Mn(III/IV) reduction is the dominant diagenetic pathway for organic carbon (OC) degradation, which directly affects Fe cycling by the competitive inhibition of Fe(III) reduction and Fe(II) reoxidation. Dissolved Co, Cr, V, Se, As and P show significant positive correlations with Mn but nearly no correlations with Fe, suggesting that the mobility of these metal(loid)s and P is associated with Mn but not Fe cycling in this region. In addition, the coelevated concentrations of the metal(loid)s, P and Mn at the submerged sites are attributed to the strengthened Mn reduction coupled with OC degradation fueled by hypoxia. The higher positive diffusion fluxes of Mn, Se and P were consistent with the excess Mn, Se and P concentrations in the overlying water, together with the approximately positive fluxes of the other metal(loid)s, indicating that sediment Mn(III/IV) reduction and concomitant metal(loid) and P remobilization might be vital pathways for metal(loid) and P migration to the overlying water. © 2019 Elsevier Ltd The retention and remobilization of metal(loid)s and P are controlled by Mn cycling and the liberation of metal(loid)s and P fueled by hypoxia is a major source for the overlying water. © 2019 Elsevier Ltd.

**Pérez-del-Olmo, A., Nachev, M., Zimmermann, S.*, et al.* (2019) Medium-term dynamics of element concentrations in a sparid fish and its isopod parasite after the Prestige oil-spill: Shifting baselines? *Science of the Total Environment,* 686: 648-656.**
Keywords: Bioindication; Boops boops; Ceratothoa oestroides; Multivariate analysis; North East Atlantic; Trace elements.

**Abstract:**
Historically, the European Atlantic is probably the most important oil-spill hotspot worldwide. One of the most recent accidents occurred in 2002 when the oil-tanker Prestige sank over the Galician Bank causing two major oil-spills followed by several small leaks until March 2003. This resulted in contamination of virtually all types of marine habitat. Considering that parasites have proved to be good effect and accumulation bioindicators, the present study addresses the medium-term changes in trace element content after the Prestige oil-spill in a model host-parasite system, the bogue, Boops boops (Sparidae) and the isopod Ceratothoa oestroides. To our knowledge, this study is the first to address trace element concentrations in natural fish and parasite populations associated with the effects of an oil-spill. We observed that both test organisms examined, the host and the parasite, indicate a detectable change in

the relative composition of trace element concentrations before and after the Prestige oil-spill. Multivariate analyses also indicated a differential response of the different tissues to the temporal sampling sequence. However, analyses of both host and parasite tissues supported the pattern of a gradual temporal transition to a state of relative trace element content distinctly departing from the pre-spill situation. Moreover, the parasite-host element accumulation ratios better depicted this temporal pattern. Additionally, changes in V concentrations in fish liver tissues and Ni concentrations in the parasite tissues suggest that this host-parasite system may be a useful tool to assess these two element contaminations linked to heavy fuel oil-spill. 

**Xiong, X., Qian, Z., Mei, Z.*, et al.* (2019) Trace elements accumulation in the Yangtze finless porpoise (Neophocaena asiaeorientalis asiaeorientalis) – A threat to the endangered freshwater cetacean. *Science of the Total Environment,* 686: 797-804.**
Keywords: Bioaccumulation; Cetacean; Trace element; Yangtze finless porpoise.

**Abstract:**
As a freshwater cetacean with a population of only approximately 1000 individuals, the Yangtze finless porpoise (Neophocaena asiaeorientalis asiaeorientalis) is threatened by water pollution. However, studies of contaminants accumulated in the Yangtze finless porpoise remain limited. In this study, concentrations of 11 trace elements in different tissues sampled from 38 Yangtze finless porpoise individuals were determined. The elements V, Ni, Zn, and Pb were mostly accumulated in the epidermis, Cr, Mn, Cu, Se, and Hg were mostly accumulated in the liver, while As and Cd were mostly accumulated in the blubber and kidney, respectively. The results show that trace elements concentrations in the epidermis do not reliably indicate concentrations in internal tissues of the Yangtze finless porpoises. Positive correlations between different trace elements concentrations in tissues with the highest concentrations suggested the similar mechanism of metabolism or uptake pathway of those elements. Concentrations of As, Se, Cd, Hg, and Pb in the tissues with the highest concentrations were significantly positively correlated with the body length. Furthermore, significantly higher trace elements concentrations were measured in the reproductive organs of females (ovaries) than males (testis). However, no significant difference of trace elements concentrations between habitats was found. In consideration of higher Hg and Cd level in Yangtze finless porpoises compared to other small cetaceans, the potential risk of Hg (in particular) and Cd toxicity to Yangtze finless porpoises needs further attention. 

# 8. MISCELLANEOUS

**Canepari, S., Astolfi, M.L., Catrambone, M.*, et al.* (2019) A combined chemical/size fractionation approach to study winter/summer variations, ageing and source strength of atmospheric particles. *Environmental Pollution,* 253: 19-28.**
Keywords: Biomass burning; Elemental composition; MOUDI impactor; Size distribution; Source tracers.

**Abstract:**
We studied the size distribution of ions (Cl−, NO3−, SO4=, Na+, NH4+, K+, Mg++, Ca++) and elements (As, Ba, Cd, Co, Cs, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn) during the winter and summer seasons of seven consecutive years (2008–2014) in an area of the Po Valley (Northern Italy) characterised by industrial, agricultural and urban settings. The study included the collection and analysis of 41 series of size-segregated samples (MOUDI sampler, 10 stages, cut sizes from 0.18 to 18 μm). Ions were analysed by ion chromatography; elemental analysis was carried out by ICP-MS, by applying a chemical fractionation method able to increase the selectivity of PM source tracers. Our results indicate that important

winter/summer variations occurred in both the concentration and size distribution of most PM components. These variations were explained in terms of variations in the strength of the prevailing sources of each component. The contribution of biomass burning for domestic heating was highlighted by the well-known tracer K+ but also by the soluble fraction of Rb, Cs and Li. Biomass burning contribution to atmospheric PM was mostly contained in the fine fraction, with a broad size-distribution from 0.18 to 1.8 µm. This source also appreciably increased the concentration of other elements in fine PM (As, Cd, Co, Mn, Pb, Sb, Sn). A few PM components (tracers of sea-spray, brake lining and some industries) did not show marked seasonal variations in concentration and size distribution. However, during winter, for brake lining and industry tracers we observed an upward shift in the dimension of fine particles and a downward shift in the dimension of coarse particles, due to the ageing of the air masses. © 2019 Elsevier Ltd.

**Karginov, A.V., Fokina, A.V., Kang, H.A.*, et al.* (2018) Dissection of differential vanadate sensitivity in two Ogataea species links protein glycosylation and phosphate transport regulation. *Scientific Reports,* 8(1): 16428-018-34888-5.**
Available at: https://www.nature.com/articles/s41598-018-34888-5.pdf
Keywords: Drug Resistance, Fungal; Glycosylation; Phosphate Transport Proteins/metabolism; Phosphates/metabolism; Saccharomyces cerevisiae/drug effects/metabolism/physiology; Saccharomyces cerevisiae Proteins/metabolism; Vanadates/pharmacology.

**Abstract:**
The closely related yeasts Ogataea polymorpha and O. parapolymorpha differ drastically from each other by sensitivity to the toxic phosphate analog vanadate. Search for genes underlying this difference revealed two genes, one designated as ABV1 (Alcian Blue staining, Vanadate resistance), which encodes a homologue of Saccharomyces cerevisiae Mnn4 responsible for attachment of mannosylphosphate to glycoside chains of secretory proteins, and the other designated as its S. cerevisiae homologue PHO87, encoding the plasma membrane low affinity phosphate sensor/transporter. The effect of Pho87 on vanadate resistance was bidirectional, since it decreased the resistance on phosphate-depleted medium, but was required for pronounced protection against vanadate by external phosphate. This highlights the dual function of this protein as a low affinity phosphate transporter and an external phosphate sensor. Involvement of Pho87 in phosphate sensing was confirmed by its effects on regulation of the promoter of the PHO84 gene, encoding a high affinity phosphate transporter. The effect of Abv1 was also complex, since it influenced Pho87 level and enhanced repression of the PHO84 promoter via a Pho87-independent pathway. Role of the identified genes in the difference in vanadate resistance between O. polymorpha and O. parapolymorpha is discussed.

**Kumar, V., AlMomin, S., Al-Shatti, A.*, et al.* (2019) Enhancement of heavy metal tolerance and accumulation efficiency by expressing Arabidopsis ATP sulfurylase gene in alfalfa. *International Journal of Phytoremediation,* 21(11): 1112-1121.**
Available at:
https://www.researchgate.net/profile/Vinod_Kumar55/publication/332827433_Enhancement_of_heavy_metal_tolerance_and_accumulation_efficiency_by_expressing_Arabidopsis_ATP_sulfurylase_gene_in_alfalfa/links/5cda805a92851c4eab9d8994/Enhancement-of-heavy-metal-tolerance-and-accumulation-efficiency-by-expressing-Arabidopsis-ATP-sulfurylase-gene-in-alfalfa.pdf
Keywords: Arabidopsis; ATP sulfurylase; genetic engineering; phytoremediation; agrobacterium-mediated transformation; oil-contaminated soil; INDIAN; mustard plants;

somatic embryogenesis; transgenic plants; mesophyll; protoplasts; sulfate transporter; degraded soils; remediation; Environmental Sciences & Ecology.

**Abstract:**
Transgenic alfalfa (Medicago sativa L.) plants overexpressing the Arabidopsis ATP sulfurylase gene were generated using Agrobacterium-mediated genetic transformation to enhance their heavy metal accumulation efficiency. The ATP sulfurylase gene was cloned from Arabidopsis, following exposure to vanadium (V) and lead (Pb), and transferred into an Agrobacterium tumefaciens binary vector. This was co-cultivated with leaf explants of the alfalfa genotype Regen SY. Co-cultivated leaf explants were cultured on callus and somatic embryo induction medium, followed by regeneration medium for regenerating complete transgenic plants. The transgenic nature of the plants was confirmed using PCR and southern hybridization. The expression of Arabidopsis ATP sulfurylase gene in the transgenic plants was evaluated through RT-PCR. The selected transgenic lines showed increased tolerance to a mixture of five heavy metals and also demonstrated enhanced metal uptake ability under controlled conditions. The transgenic lines were fertile and did not exhibit any apparent morphological abnormality. The results of this study indicated an effective approach to improve the heavy metal accumulation ability of alfalfa plants which can then be used for the remediation of contaminated soil in arid regions.

**Muller, A.A., Moldoveanu, A., Asavei, V.*, et al.* (2019) 3D Smith charts scattering parameters frequency-dependent orientation analysis and complex-scalar multi-parameter characterization applied to Peano reconfigurable vanadium dioxide inductors. *Scientific Reports,* 9(1).**
Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6892935/pdf/41598_2019_Article_54600.pdf

**Abstract:**
Recently, the field of Metal-Insulator-Transition (MIT) materials has emerged as an unconventional solution for novel energy efficient electronic functions, such as steep slope subthermionic switches, neuromorphic hardware, reconfigurable radiofrequency functions, new types of sensors, terahertz and optoelectronic devices. Employing radiofrequency (RF) electronic circuits with a MIT material like vanadium Dioxide, VO2, requires appropriate characterization tools and fabrication processes. In this work, we develop and use 3D Smith charts for devices and circuits having complex frequency dependences, like the ones resulting using MIT materials. The novel foundation of a 3D Smith chart involves here the geometrical fundamental notions of oriented curvature and variable homothety in order to clarify first theoretical inconsistencies in Foster and Non Foster circuits, where the driving point impedances exhibit mixed clockwise and counter-clockwise frequency dependent (oriented) paths on the Smith chart as frequency increases. We show here the unique visualization capability of a 3D Smith chart, which allows to quantify orientation over variable frequency. The new 3D Smith chart is applied as a joint complex-scalar 3D multi-parameter modelling and characterization environment for reconfigurable RF design exploiting Metal-Insulator-Transition (MIT) materials. We report fabricated inductors with record quality factors using VO2 phase transition to program multiple tuning states, operating in the range 4 GHz to 10 GHz. © 2019, The Author(s).

**Pedrinelli, V., Zafalon, R.V.A., Rodrigues, R.B.A.*, et al.* (2019) Concentrations of macronutrients, minerals and heavy metals in home-prepared diets for adult dogs and cats. *Scientific Reports,* 9(1).**
Available at:

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6736975/pdf/41598_2019_Article_49087.pdf

**Abstract:**
Pet owners often don't acknowledge the need for home-prepared diet formulation by a trained professional and may use recipes from sources such as the internet. Macronutrient and mineral composition of home-prepared diets were analyzed and compared to NRC and FEDIAF recommendations, and heavy metal concentrations were analyzed and compared to FDA maximum tolerable levels (MTL) for dogs and cats. Recipes of home-prepared diets for adult dogs (n = 75) and cats (n = 25) were evaluated. Analyses of protein, fat, and fiber were performed according to AOAC, and mineral and heavy metal analyses were performed using inductively coupled plasma optical emission spectrometry (ICP-OES). None of the diets supplied recommended levels of all nutrients evaluated, and more than 84.0% of diets presented three or more nutrients below recommendations. Nutrients with most levels below recommendations were calcium and potassium in recipes for dogs and iron and zinc in recipes for cats. As for heavy metals, levels of lead, cobalt, mercury, uranium, and vanadium were above MTLs. Results suggest that home-prepared diets may be a health risk to dogs and cats if not properly formulated. Furthermore, the chronic heavy metal intake must be better elucidated in order to understand the full impact of results. © 2019, The Author(s).

**Roje, V. & Galinec, F. (2019) Water as a mild extractant of metals and metalloids from the samples of the selected certified reference materials and subsequent multi-elemental quantification by ICP-AES. *Environmental Monitoring and Assessment,* 191(9).**
Keywords: Certified reference materials; Heavy metals; ICP-AES; Soil; Trace elements; Water extraction.

**Abstract:**
An assessment of mobility and bioavailability of trace elements present in the soil requires the determination of these elements in soil samples by an appropriate methodology. In such a context, the use of mild extraction reagents—such as water—is considered to be appropriate. On the other hand, performing an analysis of a reference material together with real samples is recommended in order to control the quality of analytical procedure. The quantification of 27 analytes in aqueous extracts of the soil CRMs samples is described. The methodology consisted of single-step extraction of analytes by deionized water (m/v = 1/10) with their subsequent direct determination by inductively coupled plasma–atomic emission spectrometry (ICP-OES). Three certified reference materials (CRM) for soils have been selected as model samples: NCS DC 77302 (alias GBW 07410), Metranal-31, and Metranal-33. Although the recoveries of the selected elements obtained by water extractions are very low (i.e., the values usually do not exceed 1%), the results obtained in this study reveal the elements that by means of ICP-OES can be quantified in the water extracts of unpolluted soils are as follows: Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, S, Sr, Ti, and V. However, ICP-OES is not sensitive enough to quantify the elements As, Be, Cd, Co, Pb, Sb, Se, Tl, and Zn that are present in the water extracts of clean soil samples in too low mass fractions. The results obtained in this paper are useful for future uses of the three tested CRMs, in the cases of the extraction of the analytes by deionized water at room temperature. © 2019, Springer Nature Switzerland AG.

**Trinh, D.T.T., Khanitchaidecha, W., Channei, D.*, et al.* (2019) Synthesis, characterization and environmental applications of bismuth vanadate. *Research on Chemical Intermediates,* 45(10): 5217-5259.**
Keywords: Bismuth vanadate; Photocatalysis; Visible light; Water treatment; Pollutant degradation.

**Abstract:**
Pollution and the scarcity of water resources are considered major issues of concern in recent years. Treatment technology is important for reuse of water and wastewater, especially industrial wastewater. The photocatalytic process using semiconductors has emerged as a promising method in removing aqueous pollutants. Among the semiconductor photocatalysts, bismuth vanadate ($BiVO_4$) is an effective visible light driven photocatalyst with various excellent properties such as narrow bandgap, resistance to corrosion, and low toxicity. In the past, much research was focused on synthesizing $BiVO_4$ and enhancing its photocatalytic activity. A comprehensive discussion on synthesis and characterization (including morphology and structure) are presented in this review. Furthermore, the application of $BiVO_4$ photocatalytic activity in water treatment is also discussed; the degradation of dye molecules and actual organic pollutants in the photocatalytic system under visible light irradiation is explained. This review is beneficial for further related research such as material development and pollution prevention.