



Vanadium Health Research Programme: Recent Published Literature

July 2019 – September 2019

Report to Vanitec
IEH Consulting Ltd. | September 2019

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

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17th September 2019

Introduction

This report presents the bibliographic details of the 34 papers identified as being published during the period July 2019 to September 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

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.

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 Pahl; 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.

Pedro, E.M., da Rosa Franchi Santos, L.F., Scavuzzi, B.M., et al. (2019) Trace Elements Associated with Systemic Lupus Erythematosus and Insulin Resistance. *Biological Trace Element Research*, 191(1): 34-44.

Keywords: Glucose homeostasis; Heavy metals; Insulin resistance; SLE disease activity index (SLEDAI); Trace elements

Abstract:

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

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

Zhou, Y., Zhu, Q., Ma, W., et al. (2019) Prenatal vanadium exposure, cytokine expression, and fetal growth: A gender-specific analysis in Shanghai MCPC study. *Science of the Total Environment*, 685: 1152-1159.

Keywords: Vanadium; Gender; Cytokines; Intrauterine growth

Abstract:

Increasing evidence supports that maternal exposure to vanadium (V) is associated with adverse birth outcomes including preterm birth and low birth weight. However, the effect of V exposure on intrauterine fetal growth and the underlying biological mechanism are still unclear. The present study includes 227 mother-infant pairs from the Shanghai Maternal-Child Pairs Cohort to assess the gender-specific effect of intrauterine V exposure on fetal growth and related cytokines. Maternal blood samples were collected to measure V concentration and biomarkers of growth. We used multiple linear regression to evaluate the gender-specific effect of prenatal V exposure on birth parameter and growth-related cytokines. Mixed-effect models were applied to assess the non-linear association between gestational V exposure and intrauterine fetal growth. Covariates adjusted in the regression models as potential confounders including maternal age, pre-pregnancy body mass index, gestational weeks,

parity, socio-demographic status, etc. Results showed that prenatal V exposure was negatively associated with birth weight ($\beta = -64.73$) in female newborns and body length ($\beta = -0.10$) in male. During the fetal period, maternal V exposure was associated with decreased biparietal diameter ($\beta = -0.91$), head circumference ($\beta = -2.96$), femur length ($\beta = -0.72$) and humerus length ($\beta = -0.64$) in male. Trimester-specific analyses showed that serum V concentration in the second trimester was associated with significant reductions in intrauterine growth parameters. Besides, prenatal V exposure could down-regulate the expression of growth hormone (GH) in both maternal blood ($\beta = -0.23$) and umbilical cord blood ($\beta = -1.66$) in male fetuses, and the expression of brain derived neurotrophic factor (BDNF) in cord blood in females ($\beta = -0.52$). Our results suggest that prenatal V exposure has a gender-specific effect on fetal growth and the second trimester may be a sensitive window. The disruption of growth-related cytokines may potentially be the biological mechanism of these effects.

2. HEALTH EFFECTS

Jardine, T.D., Doig, L.E., Jones, P.D., et al. (2019) Vanadium and thallium exhibit biodilution in a northern river food web. *Chemosphere*, 233: 381-386.

Keywords: Fishes; Invertebrates; Periphyton; Slave river; Trace elements; Trophic transfer

Abstract:

Trophic transfer of contaminants dictates concentrations and potential toxic effects in top predators, yet biomagnification behaviour of many trace elements is poorly understood. We examined concentrations of vanadium and thallium, two globally-distributed and anthropogenically-enriched elements, in a food web of the Slave River, Northwest Territories, Canada. We found that tissue concentrations of both elements declined with increasing trophic position as measured by $\delta(15)N$. Slopes of \log [element] versus $\delta(15)N$ regressions were both negative, with a steeper slope for V (-0.369) compared with Tl (-0.099). These slopes correspond to declines of 94% with each step in the food chain for V and 54% with each step in the food chain for Tl. This biodilution behaviour for both elements meant that concentrations in fish were well below values considered to be of concern for the health of fish-eating consumers. Further study of these elements in food webs is needed to allow a fuller understanding of biomagnification patterns across a range of species and systems.

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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.

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 intraperitoneal 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.

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3. BIOLOGICAL MECHANISMS

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 $\mu\text{g/l}$, pH 8.3) and S2 (vanadium 20-25 $\mu\text{g/l}$, 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.

Go, Y., Smith, M., Fernandes, J., *et al.* (2019) Cadmium at Human Dietary Levels Disturbed Homeostasis of Nutritional Metals in Lung (P24-055-19). *Current Developments in Nutrition*, 3(Suppl 1).

Raffel, N., Klemm, K., Dittrich, R., *et al.* (2019) The effect of bpV(HOpic) on in vitro activation of primordial follicles in cultured swine ovarian cortical strips. *Reproduction in Domestic Animals*, 54(8): 1057-1063.

Keywords: bpV (HOpic); fertiprotekt; follicle activation follicle reserve; in vitro culture; ovarian cortical tissue; Early Antral Follicles; Porcine Oocytes; Developmental Ability; Growth; Maturation; Fertilization; Preservation; Improves; Model; Agriculture; Reproductive Biology; Veterinary Sciences

Abstract:

The vanadate-derivative dipotassium bisperoxo (5-hydroxy-pyridine-2-carboxylic) oxovanadate (V) (bpV(HOpic)), a pharmacological inhibitor of phosphatase and tensin homolog (PTEN), has been used in ovarian follicle culture systems for activation of follicular growth in vitro and suggested to be responsible for primordial follicle survival through indirect Akt activation. For pig ovarian tissue, it is still not clear which culture medium needs to be used, as well as which factors and hormones could influence follicular development; this also applies to bpV(HOpic) exposure. Therefore, ovarian cortical strips from pigs were cultured in 1 μ M bpV(HOpic) (N = 24) or control medium (N = 24) for 48 hr. Media were then replaced with control medium and all tissue pieces incubated for additional 4 days. The strips were embedded in paraffin for histological determination of follicle proportions at the end of the culture period and compared to histological sections from tissue pieces without cultivation, which had been embedded right after preparation; comparison of healthy follicles for each developmental stage was performed to quantify follicle survival and activation. After 6-day culture, follicle activation occurred in tissue samples from both cultured groups but significantly more follicles showed progression of follicular development in the presence of 1 μ M bpV(HOpic). The amount of non-vital follicles was not significantly increased during cultivation. BpV(HOpic) affects pig ovarian follicle development by promoting the initiation of follicle growth and development, similar as in rodent species and humans.

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.

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

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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 intraperitoneal 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.

4. USES OF VANADIUM

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 culture media 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.

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.

Keywords: Glycemic 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. 3T3-L1 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.

Go, Y., Smith, M., Fernandes, J., et al. (2019) Cadmium at Human Dietary Levels Disturbed Homeostasis of Nutritional Metals in Lung (P24-055-19). *Current Developments in Nutrition*, 3(Suppl 1).

Kokulnathan, T., Karthik, R., Chen, S.M., et al. (2019) A cerium vanadate interconnected with a carbon nanofiber heterostructure for electrochemical determination of the prostate cancer drug nilutamide. *Mikrochimica Acta*, 186(8): 579-019-3665-5.

Keywords: Anti-cancer drug; Binary metal oxides; Electrochemical sensor; Real time determination

Abstract:

Cerium vanadate resembling the shape of a hedgehog were interconnected with carbon nanofibers to give a heterostructure (referred to as CeV/CNF) that exhibits efficient catalytic activity for the electrochemical detection of the drug nilutamide (NLT). The heterostructure material and its modification were characterized by XRD, Raman spectra, XPS, FESEM, TEM, SAED, and EDX. A glassy carbon electrode was modified with the CeV/CNF nanocomposite. Best operated at -0.52 V (vs. Ag/AgCl), it exhibits a very low detection limit (2.0 nM), wide linear range (0.01-540 µM), high sensitivity (1.36 µA µM⁻¹ cm⁻²) and rapid response towards NLT. It was applied to the determination of NLT in spiked human urine. Graphical abstract Schematic presentation of cerium vanadate interconnected with carbon nanofiber heterostructure for electrochemical determination of prostate cancer drug nilutamide in biological samples.

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-phenanthroline)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 μ M).

Qiao, J., Lv, M., Qu, Z., et al. (2019) Preparation of a novel Z-scheme KTaO₃/FeVO₄/Bi₂O₃ nanocomposite for efficient sonocatalytic degradation of ceftriaxone sodium. *Science of the Total Environment*, 689: 178-192.

Keywords: Z-scheme laaO₃/FeVO₄/812O₃ sonocatalyst; FeVO₄ conductive channel; Electron transfer driving force; Sonocatalytic degradation; Ceftriaxone sodium; Light Photocatalytic Activity; Visible-Light; Hydrothermal Synthesis; Composite; Construction; Performance; Heterojunction; Heterostructure; Nanostructure; Norfloxacin; Environmental Sciences & Ecology

Abstract:

In this k, a novel Z-scheme sonocatalyst, KTaO₃/FeVO₄/Bi₂O₃, is prepared via ultrasonic-assisted isoelectric point method. The prepared samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy. The catalytic activity of Z-scheme ICTaO₃/FeVO₄/Bi₂O₃ sonocatalyst is studied in degradation of ceftriaxone sodium under ultrasonic irradiation. In addition, the influences of ultrasonic irradiation time, scavengers and sonocatalyst used times on sonocatalytic degradation of ceftriaxone sodium are examined. Under the experimental conditions of 150 min ultrasonic irradiation time, 1.00 g/L ICTaO₃/FeVO₄/Bi₂O₃ addition amount and 10.00 mg/L ceftriaxone sodium concentration, the sonocatalytic degradation ratio of ceftriaxone sodium achieves 81.30%. Finally, the possible sonocatalytic degradation mechanism of ceftriaxone sodium caused by Z-scheme KTaO₃/FeVO₄/Bi₂O₃ sonocatalyst is proposed. The enhanced sonocatalytic activity may be attributed to the fact that the FeVO₄ as a special conductive channel provides a strong driving force to transfer electrons through valence state changes of iron and vanadium, which accelerates electron transfer from conduction band (CB) of Bi₂O₃ to valence band (VB) of KTaO₃. Perhaps, the KTaO₃/FeVO₄/Bi₂O₃ composite is an excellent Z scheme sonocatalyst which can be used to effectively degrade the organic pollutants in wastewater under ultrasonic irradiation. © 2019 Elsevier B.V. All rights reserved.

Raffel, N., Klemm, K., Dittrich, R., et al. (2019) The effect of bpV(HOPic) on in vitro activation of primordial follicles in cultured swine ovarian cortical strips. *Reproduction in Domestic Animals*, 54(8): 1057-1063.

Keywords: bpV (HOPic); fertiprotekt; follicle activation follicle reserve; in vitro culture; ovarian cortical tissue; Early Antral Follicles; Porcine Oocytes; Developmental Ability; Growth;

Maturation; Fertilization; Preservation; Improves; Model; Agriculture; Reproductive Biology; Veterinary Sciences

Abstract:

The vanadate-derivative dipotassium bisperoxo (5-hydroxy-pyridine-2-carboxylic) oxovanadate (V) (bpV(HOpic)), a pharmacological inhibitor of phosphatase and tensin homolog (PTEN), has been used in ovarian follicle culture systems for activation of follicular growth in vitro and suggested to be responsible for primordial follicle survival through indirect Akt activation. For pig ovarian tissue, it is still not clear which culture medium needs to be used, as well as which factors and hormones could influence follicular development; this also applies to bpV(HOpic) exposure. Therefore, ovarian cortical strips from pigs were cultured in 1 μ M bpV(HOpic) (N = 24) or control medium (N = 24) for 48 hr. Media were then replaced with control medium and all tissue pieces incubated for additional 4 days. The strips were embedded in paraffin for histological determination of follicle proportions at the end of the culture period and compared to histological sections from tissue pieces without cultivation, which had been embedded right after preparation; comparison of healthy follicles for each developmental stage was performed to quantify follicle survival and activation. After 6-day culture, follicle activation occurred in tissue samples from both cultured groups but significantly more follicles showed progression of follicular development in the presence of 1 μ M bpV(HOpic). The amount of non-vital follicles was not significantly increased during cultivation. BpV(HOpic) affects pig ovarian follicle development by promoting the initiation of follicle growth and development, similar as in rodent species and humans.

Scalese, G., Machado, I., Fontana, C., et al. (2018) New heteroleptic oxidovanadium(V) complexes: synthesis, characterization and biological evaluation as potential agents against Trypanosoma cruzi. *Journal of Biological Inorganic Chemistry : JBIC : A Publication of the Society of Biological Inorganic Chemistry*, 23(8): 1265-1281.

Keywords: Animals; Apoptosis/drug effects; Cercopithecus aethiops; Coordination Complexes/chemical synthesis/chemistry/pharmacology/toxicity; Hydrophobic and Hydrophilic Interactions; Molecular Structure; Parasitic Sensitivity Tests; Trypanocidal Agents/chemical synthesis/chemistry/pharmacology/toxicity; Trypanosoma cruzi/drug effects; Vanadium/chemistry; Vero Cells; Zebrafish; 8-Hydroxyquinoline; Metallomics; Semicarbazones; Trypanosoma cruzi; Vanadium

Abstract:

Searching for prospective vanadium-based agents against Trypanosoma cruzi, the parasite causing Chagas disease, four new [V(V)O(8HQ-H)(L-2H)] compounds, where 8HQ is 8-hydroxyquinoline and L are tridentate salicylaldehyde semicarbazone derivatives L1-L4, were synthesized and characterized in the solid state and in solution. The compounds were evaluated on T. cruzi epimastigotes (CL Brener) as well as on VERO cells, as mammalian cell model. Compounds showed activity against T. cruzi (IC₅₀ 6.2-10.5 μ M) of the same order than Nifurtimox and 8HQ, and a four- to sevenfold activity increase with respect to the free semicarbazones. For comparison, [V(V)O₂(L-H)] series was prepared and the new [V(V)O₂(L3-H)] was fully characterized. They showed negligible activity and low selectivity towards the parasite. The inclusion of 8HQ as ligand in [V(V)O(8HQ-H)(L-2H)] compounds led to good activities and increased selectivity towards the parasite with respect to 8HQ. (51)V NMR experiments, performed to get insight into the nature of the active species, suggested partial decomposition of the compounds in solution to [V(V)O₂(L-H)] and 8HQ. Depending on the dose, the compounds act as trypanocide or trypanostatic. A high uptake of vanadium in the parasites (58.51-88.9% depending on dose) and a preferential accumulation in the soluble protein fraction of the parasite was determined. Treated parasites do not seem to show a late

apoptotic/necrotic phenotype suggesting a different cell death mechanism. In vivo toxicity study on zebrafish model showed no toxicity up to a 25 microM concentration of [V(V)O(8HQ-H)(L1-2H)]. These compounds could be considered prospective anti-T. cruzi agents that deserve further research.

Xu, Y.H., Brandl, H., Osterwalder, S., et al. (2019) Vanadium-basidiomycete fungi interaction and its impact on vanadium biogeochemistry. *Environment International*, 130: 104891.

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018329416/pdf?md5=ddbe239218c751500a8d90e1266f2e0c&pid=1-s2.0-S0160412018329416-main.pdf>

Keywords: Bioaccumulation; Bioremediation; Fungi; Immobilisation; Solubilisation; Vanadium

Abstract:

Fungi are well known to strongly interact with metals, thereby influencing metal biogeochemistry in the terrestrial environment. To assess and quantify potential fungi-vanadium (V) interactions, *Amanita muscaria*, *Armillaria cepistipes*, *Xerocomus badius* and *Bjerkandera adusta* were cultured in media containing soluble V (VOSO₄ or NaVO₃) or solid-phase V of different chemical forms and oxidation state (V₂O₃, VO₂, V₂O₅, or V-Ti magnetite slag). All fungi underwent physiological and structural changes, as revealed by alterations in FT-IR peak positions and intensities relative to the control, and morphological changes of mycelia, as observed by scanning electron microscopy. The diametric growth size generally decreased with decreasing oxidation state of V and with increasing concentrations of VOSO₄ and NaVO₃, implying that V toxicity is dependent on V speciation. The tolerance index, the ratio of treated and control mycelium (dry weight), shows different tendencies, suggesting additional factors influencing fungi weight, such as the formation of extrahyphal crystals. Vanadium accumulation from VOSO₄ and NaVO₃ medium in all fungi (up to 51.3mgg⁻¹) shows the potential of fungi to immobilise soluble V, thereby reducing its impacts on environmental and human health. Uptake and accumulation of V in slag was insignificant, reflecting the association of slag V with insoluble crystalline materials. The fungal accumulation of V in medium amended with V-oxides demonstrates the ability of fungi to solubilise solid-phase V compounds, thereby introducing previously immobile V into the V biogeochemical cycle and into the food chain where it may impact ecological and human health. *A. muscaria* lowered the pH of the medium substantially during cultivation, indicating acidolysis and complexolysis via excretion of organic acids (e.g. oxalic acid). Oxidation of VOSO₄ was observed by a colour change of the medium to yellow during *B. adusta* cultivation, revealing the role of fungally-mediated redox transformation in V (im)mobilisation. The calculated removal efficiencies of soluble V were 40-90% for *A. cepistipes* and *X. badius*, but a much lower recovery (0-20%) was observed from V oxides and slag (0-20%) by all fungi. This suggests the probable application of fungi for bio-remediation of mobile/soluble V in contaminated soils but not of V incorporated in the lattice of soil minerals.

5. ENVIRONMENTAL EFFECTS in PLANTS and SOIL

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.

Guo, D., Ren, C., Ali, A., et al. (2019) *Streptomyces pactum* combined with manure compost alters soil fertility and enzymatic activities, enhancing phytoextraction of potentially toxic metals (PTMs) in a smelter-contaminated soil. *Ecotoxicology and Environmental Safety*, 181: 312-320.

Keywords: *Streptomyces pactum*; Compost; Soil fertility; Enzymatic activities; Phytoextraction; Heavy-Metals; Organic-Matter; Assisted Phytoextraction; Plant-Growth; Phytoremediation; Biochar; Remediation; Bioavailability; Vanadium; Cd; Environmental Sciences & Ecology; Toxicology

Abstract:

The effect of manure compost alone and combined with *Streptomyces pactum* (Act12) applied in the smelter contaminated soil was investigated. The soil fertility, enzymatic activities, potentially toxic metals (PTMs) solubility, and phytoremediation efficiency of potherb mustard (*Brassica jwwea*, Coss.) were assessed. Results showed that the application of compost reduced the soil pH, while significantly increased the soil electrical conductivity (EC) (7.0 folds), available phosphorus (AP) (10.8 folds), available potassium (AK) (2.81 folds), dissolved organic carbon (DOC) (5.22 folds), organic matter (OM) (4.93 folds), together with soil enzymatic activities viz. urease (UR) (4.39 folds), dehydrogenase (DEH) (45.0 folds) and alkaline phosphatase (ALP) (123.9 folds) in comparison with control. The inoculation of Act12 increased AP, AK, DOC, OM and UR values, but reduced EC, DEH and ALP values compared to corresponding lone compost amendment. Additionally, Act12 solubilized PTMs (Cd and Zn) in the soil, and accordingly enhanced the PTMs uptake in the plant. The phytoextraction indices viz. biological concentration factor (BCE), translocation factor (TF) and metal extraction amount (MEA) indicated that compost and Act12 had a synergistic role in enhancing the phytoremediation efficiency, among which MEA values of Cd and Zn maximally increased by

9.64 and 11.4 folds, respectively, compared to control. Redundancy analysis (RDA) indicated that phytoextraction indices correlated well with soil parameters. Our results suggested that manure compost associated with Act12 is a potential strengthening strategy in phytoremediation of PTMs contaminated soil.

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.

Nahlik, A.M., Blocksom, K.A., Herlihy, A.T., et al. (2019) Use of national-scale data to examine human-mediated additions of heavy metals to wetland soils of the US. *Environmental Monitoring and Assessment*, 191(Suppl 1): 336.

Available at: <https://link.springer.com/content/pdf/10.1007%2Fs10661-019-7315-5.pdf>

Keywords: Anthropogenic disturbance; Background concentrations; Heavy Metal Index (HMI); Lead (Pb); National Wetland Condition Assessment (NWCA); Trace elements

Abstract:

Soil concentrations of 12 heavy metals that have been linked to various anthropogenic activities were measured in samples collected from the uppermost horizon in approximately 1000 wetlands across the conterminous US as part of the 2011 National Wetland Condition Assessment (NWCA). The heavy metals were silver (Ag), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), vanadium (V), tungsten (W), and zinc (Zn). Using thresholds to distinguish natural background concentrations from human-mediated additions, we evaluated wetland soil heavy metal concentrations in the conterminous US and four regions using a Heavy Metal Index (HMI) that reflects human-mediated heavy metal loads based on the number of elements above expected background concentration. We also examined the individual elements to detect concentrations of heavy

metals above expected background that frequently occur in wetland soils. Our data show that wetland soils of the conterminous US typically have low heavy metal loads, and that most of the measured elements occur nationally in concentrations below thresholds that relate to anthropogenic activities. However, we found that soil lead is more common in wetland soils than other measured elements, occurring nationally in 11.3% of the wetland area in concentrations above expected natural background (> 35 ppm). Our data show positive relationships between soil lead concentration and four individual landscape metrics: road density, percent impervious surface, housing unit density, and population density in a 1-km radius buffer area surrounding a site. These relationships, while evident on a national level, are strongest in the eastern US, where the highest road densities and greatest population densities occur. Because lead can be strongly bound to wetland soils in particular, maintenance of the good condition of our nation's wetlands is likely to minimize risk of lead mobilization.

Xu, Y.H., Brandl, H., Osterwalder, S., et al. (2019) Vanadium-basidiomycete fungi interaction and its impact on vanadium biogeochemistry. *Environment International*, 130: 104891.

Available at:

<https://www.sciencedirect.com/science/article/pii/S0160412018329416/pdf?md5=ddbe239218c751500a8d90e1266f2e0c&pid=1-s2.0-S0160412018329416-main.pdf>

Keywords: Bioaccumulation; Bioremediation; Fungi; Immobilisation; Solubilisation; Vanadium

Abstract:

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6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

No titles were identified.

7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS

Baniamam, M., Moradi, A.M., Bakhtiari, A.R., *et al.* (2019) Distribution and pollution level of nickel and vanadium in sediments from south part of the Caspian Sea, Iran. *Indian Journal of Geo-Marine Sciences*, 48(5): 765-771.

Available at:

<http://nopr.niscair.res.in/bitstream/123456789/47412/1/IJMS%2048%285%29%20765-771.pdf>

Abstract:

Distribution and pollution level of nickel and vanadium in sediment from south part of the Caspian Sea, north of Iran, were studied. Sediment samples obtained by Van Veen Grab from four stations, including, Turkaman, Amirabad, Fereydunkenar and Noushahr along the south part of the Caspian Sea, during fall of 2015 and april, summer and winter of 2016. The concentrations of metal were ranged from 21.63 µg/g to 55.45 µg/g for nickel and from 58.23 µg/g to 146.27 µg/g for vanadium in sediments samples collected from all stations. There was significant difference in metals concentration between different stations along the Caspian Sea ($P < 0.05$), and the highest mean concentration of metals was absorbed in Fereydunkenar estuary, followed by Amirabad, Turkaman and Noushahr, respectively. The results showed that there were significant differences between metals pollution during four seasons ($P < 0.05$), and the highest concentration of metals were absorbed in dry season (summer) and the lowest concentration in wet season (winter). There was a positive correlation between nickel and vanadium concentration in sediment samples, and the Pearson correlation was ($r = 0.67$) between nickel and vanadium in sediment samples. The positive correlation between heavy metals can be related to same source of both metals in the environment. Based on our results, anthropogenic activities such as oil industry and agriculture activities are the main sources of pollution in the coasts along south part of Caspian Sea.

Bouchoucha, M., Chekri, R., Leufroy, A., *et al.* (2019) Trace element contamination in fish impacted by bauxite red mud disposal in the Cassidaigne canyon (NW French Mediterranean). *The Science of the Total Environment*, 690: 16-26.

Keywords: Arsenic speciation; Bioaccumulation; Fish; ICP-MS; Industrial discharge; Trace element

Abstract:

From 1966 to 2015, the Gardanne alumina refinery discharged some 20 million tons of bauxite residue (called red mud) into the Cassidaigne Canyon (northwest French Mediterranean) with impacts on local ecosystem functioning. Although these red muds contained high levels of trace elements (TE), in particular titanium (Ti), vanadium (V), aluminum (Al) and arsenic (As), surprisingly, their impacts on fish contamination levels and the risk related to fish consumption have been little studied until now. Here, 11 trace elements (Al, As, Cd, Cr, Co, Cr, Mn, Ni, Pb, Ti and V) were analyzed in muscle and, when possible, liver, from 1308 fish of 26 species from an impacted zone in the vicinity of the Cassidaigne Canyon and a reference zone, unaffected by red mud disposals. Moreover, 66 arsenic speciation analyses were performed. Although the impact of human activities on the levels of fish contamination by

trace elements is generally not easy to assess in situ because it is blurred by interaction with biological effects, we highlighted significant contamination of the fish species collected from the Cassidaigne Canyon, especially by the main trace elements attributable to the discharges of the Gardanne alumina refinery, namely Al, V and Ti. Moreover, inorganic toxic As concentrations were higher in the impacted zone. The results of this baseline research also confirmed the concern previously raised regarding Hg in Mediterranean organisms and that trace element contamination levels in fish are generally negatively related to fish length for all TE except Hg.

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: 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.

Jardine, T.D., Doig, L.E., Jones, P.D., et al. (2019) Vanadium and thallium exhibit biodilution in a northern river food web. *Chemosphere*, 233: 381-386.

Keywords: Fishes; Invertebrates; Periphyton; Slave river; Trace elements; Trophic transfer

Abstract:

Trophic transfer of contaminants dictates concentrations and potential toxic effects in top predators, yet biomagnification behaviour of many trace elements is poorly understood. We examined concentrations of vanadium and thallium, two globally-distributed and anthropogenically-enriched elements, in a food web of the Slave River, Northwest Territories, Canada. We found that tissue concentrations of both elements declined with increasing trophic position as measured by $\delta(15)N$. Slopes of \log [element] versus $\delta(15)N$ regressions were both negative, with a steeper slope for V (-0.369) compared with Tl (-0.099). These slopes correspond to declines of 94% with each step in the food chain for V and 54% with each step in the food chain for Tl. This biodilution behaviour for both elements meant that concentrations in fish were well below values considered to be of concern for the health of fish-eating consumers. Further study of these elements in food webs is needed to allow a fuller understanding of biomagnification patterns across a range of species and systems.

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

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

Abstract:

In China, the wastewater produced after vanadate precipitation (AVP wastewater) from industrial vanadium extraction contains toxic V(V) and carcinogenic Cr(VI). When considering environmental protection and wastewater use, V(V) and Cr(VI) must be extracted and separated from the hazardous AVP wastewater. However, separating V(V) and Cr(VI) is difficult because of their highly similar physicochemical properties. Herein, we propose a novel anion exchange method based on the in situ selectively reductive desorption of Cr(VI) to separate and extract V(V) and Cr(VI) using a weak organic reductant (ethanol) to selectively reduce Cr(VI) anions and transform them into Cr³⁺ cations, while maintaining V(V) in a H₂V₁₀O₂₈⁴⁻ anion form. We indicate that the efficient separation of Cr(VI) from V(V) can be attributed to selective Cr(VI) anion reduction via ethanol. We applied this anion exchange method to separate and recover Cr(VI) and V(V) in AVP wastewater with a Cr(VI) recovery of 95.59% and a V(V) recovery of 94.54%. The final Cr₂O₃ and V₂O₅ products had a purity of 98.03% and 96.82%, respectively. This study provides novel insights into the simultaneous separation and extraction of analog transition metals and a comprehensive method to use hazardous wastewater. © 2019 Elsevier B.V.

Roche, K., Kuta, J., Sedlacek, I., et al. (2019) Concentrations of Thirteen Trace Metals in Scales of Three Nototheniid Fishes from Antarctica (James Ross Island, Antarctic Peninsula). *Biological Trace Element Research*, 191(1): 214-223.

Keywords: Antarctic peninsula; Bioaccumulation; Czech Antarctic Station; Notothenioidei; Trace metal contaminants; Shallow coastal waters; King-George Island; Uranium Bioaccumulation; Climate-Change; Heavy-Metals; Elements; Tissue; Variability; Ecosystem; Mercury; Habits; Biochemistry & Molecular Biology; Endocrinology & Metabolism

Abstract:

In this study, we assessed concentrations of 13 trace metals in the scales of *Notothenia coriiceps*, *Trematomus bernacchii* and *Gobionotothen gibberifrons* caught off the coast of James Ross Island (Antarctic Peninsula). Overall, our results for scales broadly match those of previous studies using different fish and different organs, with most metals found at trace levels and manganese, aluminium, iron and zinc occurring at high levels in all species. This suggests that scales can serve as a useful, non-invasive bioindicator of long-term contamination in Antarctic fishes. High accumulation of manganese, aluminium, iron and zinc is largely due to high levels in sediments associated with nearby active volcanic sites. Manganese, vanadium and aluminium showed significant positive bioaccumulation in *T. bernacchii* (along with non-significant positive accumulation of iron, zinc, cobalt and chromium), most likely due to greater dietary specialisation on sediment feeding benthic prey and higher trophic species. Levels of significance in bioaccumulation regressions were strongly affected by large-scale variation in the data, driven largely by individual differences in diet

and/or changes in habitat use and sex differences associated with life stage and reproductive status. Increased levels of both airborne deposition and precipitation and meltwater runoff associated with climate change may be further adding to the already high levels of manganese, aluminium, iron and zinc in Antarctic Peninsula sediments. Further long-term studies are encouraged to elucidate mechanisms of uptake (especially for aluminium and iron) and possible intra- and interspecific impacts of climate change on the delicate Antarctic food web.

Shirinpur-Valadi, A., Hatamzadeh, A. & Sedaghatthoor, 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.

Ueki T and Adi TK (2019) Mechanism of vanadium accumulation and possible function of vanadium in underwater adhesion in ascidians. In: Anonymous AIP Conference Proceedings.: AIP Publishing, 020001

Abstract:

Ascidians are marine animals that belong to the same phylogenetic group (Phylum Chordata) as human beings do. One of the three suborders in ascidians can accumulate a high level of vanadium ions in blood cells. *Ascidia gemmata* has been reported to accumulate the highest levels of vanadium at 350 mM, which is 10^7 -fold higher than the vanadium concentration in seawater. In the last two decades, many genes and proteins related to vanadium accumulation and reduction have been revealed by molecular biological and biochemical methods. Modern omics approach enhanced the comprehensive identification of factors related to this phenomenon. In this review article, first, we would like to summarize the history of studies on vanadium accumulation in ascidians briefly. Then, we would like to overview recent advances by omics studies. How ascidians selectively accumulate vanadium is discussed from biochemical properties of proteins responsible for each step, and why ascidians accumulate vanadium is discussed in relation to the underwater adhesion.

Zhang, B., Cheng, Y., Shi, J., *et al.* (2019) Insights into interactions between vanadium (V) bio-reduction and pentachlorophenol dechlorination in synthetic groundwater. *Chemical Engineering Journal*, 375: 121965.

Keywords: Vanadium (V); Pentachlorophenol; Microbial reduction; Groundwater

Abstract:

Aquifer co-contamination by vanadium (V) and pentachlorophenol (PCP) involves complicated biogeochemical processes that remain poorly understood, particularly from the perspective of microbial metabolism. Batch experiment results demonstrated that V(V) and PCP could be competitively bio-reduced, with $96.0 \pm 1.8\%$ of V(V) and $43.4 \pm 4.6\%$ of PCP removed during 7 d operation. V(V) was bio-transformed to vanadium (IV), which could precipitate naturally under circumneutral conditions, facilitating the removal of up to $78.2 \pm 3.1\%$ dissolved total V. The PCP reductive dechlorination products were mainly 2,4,6-trichlorophenol and 4-monochlorophenol with lower toxicity. High-throughput 16S rRNA gene sequencing indicated that *Pseudomonas*, *Soehngenia*, and *Anaerolinea* might be responsible for the two bio-transformations, with detected functional genes of *nirS* and *cprA*. Extracellular reduction by cytochrome c and intracellular conversion by nicotinamide adenine dinucleotide (NADH) occurred for both V(V) and PCP. Extracellular proteins in microbial-secreted extracellular polymeric substances (EPS) might also be involved in these enzymatic bioprocesses. EPS could protect microbial cells through V(V) binding by the chemically reactive carboxyl (COO⁻), and hydroxyl (-OH) groups. These findings elucidate the metabolic processes during anaerobic V(V) and PCP biotransformation, advance understanding of their biogeochemical fates, and provide a foundation on which to develop novel strategies for remediation of co-contaminated aquifers.

8. MISCELLANEOUS

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.

Velenturf, A.P.M., Archer, S.A., Gomes, H.I., et al. (2019) Circular economy and the matter of integrated resources. *Science of the Total Environment*, 689: 963-969.

Keywords: Resource efficiency; Waste management; Whole system design; Resource recovery technology; Circular business models; Governance; Steel Slag; Recovery; Metals; Leachates; Vanadium; Waste; Sustainability; Efficiency; Catalysts; Removal; Environmental Sciences & Ecology

Abstract:

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

Wen, J., Jiang, T., Gao, H., et al. (2019) An efficient utilization of chromium-containing vanadium tailings: Extraction of chromium by soda roasting-water leaching and preparation of chromium oxide. *Journal of Environmental Management*, 244: 119-126.

Keywords: Chromium-containing vanadium tailings; Soda roasting-water leaching; Chromium extraction; Chromium oxide; Ore Processing Residue; Hexavalent Chromium; Selective Extraction; Reaction-Mechanism; Aqueous-Solution; Remove Chromium; Solid-Waste; Cr(VI); Immobilization; Detoxification; Environmental Sciences & Ecology

Abstract:

Chromium-containing vanadium tailings (CCVT), an industrial waste, were utilized to extract chromium efficiently by soda roasting-water leaching process and for the preparation of highly pure chromium oxide. The effect of extraction of chromium under different roasting and leaching conditions were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The maximum chromium extraction rate of 91.51% was obtained when soda (Na_2CO_3) and CCVT were mixed in a molar ratio ($n(\text{Na}_2\text{CO}_3)/n(\text{Cr}_2\text{O}_3)$) of 8, roasted at

900 degrees C and maintained for 120 min. Then, the roasted product was leached in water at 60 degrees C for 60 min with a liquid-solid mass ratio (L/S) of 10. During soda roasting, the chromium-containing phase $(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$ combines with Na_2CO_3 to form Na_2CrO_4 , which was then transferred into the leaching liquid, post water leaching. The by-products such as NaFeTiO_4 , $\text{Na}_2\text{CaSiO}_4$, and $\text{Na}_6\text{Fe}_{0.68}\text{Si}_{0.32}\text{O}_2$ were left in the leaching residue which was called chromium tailings (CT). 87.40% chromium oxide was recovered from the unpurified leaching liquid after reduction and precipitation by adding Na_2S , followed by roasting the deposit. This process not only relieved the potential threat of the industrial waste CCVT to the environment but also realized the recovery of the valuable element chromium.