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Vanadium Health Research Programme: Recent Published Literature

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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 81 papers identified as being published during the period January 2019 to March 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

Barbosa, I.D.S., Brito, G.B., dos Santos, G.L.*, et al.* (2019) Multivariate data analysis of trace elements in bivalve molluscs: Characterization and food safety evaluation. *Food Chemistry,* 273: 64-70.

Keywords: Bivalve molluscs; Hierarchical cluster analysis; Microwave-assisted digestion; Principal component analysis; Trace elements

Abstract

Four species of bivalve molluscs (Anomalocardia brasiliana, Iphigenia brasiliana, Lucina pectinata and Trachycardium muricatum) were collected in the Todos os Santos Bay (TSB), Bahia, Brazil, in order to evaluate As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Se, V and Zn levels and, consequently, the risk of bivalve mollusc consumption in humans. The samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) after closed-vessel microwave digestion. The accuracy was confirmed using the certified reference materials of oyster tissue (NIST 1566b) and mussel tissue (NIST 2977), and the results were statistically equivalent to the certified values. Application of principal component analysis (PCA) and hierarchical cluster analysis (HCA) showed a tendency to form two groups between samples of Lucina pectinata and Trachycardium muricatum. All species showed As and Cr concentrations higher than the maximum tolerable limit specified in Brazilian legislation. © 2018 Elsevier Ltd.

Baur, X., Sanyal, S. & Abraham, J.L. (2019) Mixed-dust pneumoconiosis: Review of diagnostic and classification problems with presentation of a work-related case. *Science of the Total Environment,* 652: 413-421.

Keywords: Diagnostics; Energy dispersive x-ray spectroscopy; Environmental exposure; Health risks; Inorganic particulates; Pathology; Pneumoconiosis; Scanning electron microscopy

Abstract

Environmental aerosolized particulates pose a potential risk to human health worldwide. Among others, high amounts of contaminants are generated especially in newly industrializing countries in the vicinity of industrial manufacturing, mining operations, but also during agricultural and natural processes. As an example of the needed multi-disciplinary diagnostic and differential diagnostic approach, we report a case of a 59-year old industrial worker who has suffered from chronic bronchitis and progressive dyspnea on exertion for 8 years. He showed severe lung function impairment, a cavity in his right upper lung lobe, nodular and irregular opacities, fibrotic pleural changes and emphysema. According to the occupational history and the industrial hygiene report, he had been engaged in the production of various refractory materials and been exposed to very high levels of inorganic dust, especially to silica, silicon carbide and aluminum compounds, but also to carbon and other dusty materials for 28 years. Histopathology of the two resected lung segments showed focally infarcted granulomas and chronic inflammation. Stains for organisms were negative. The lung tissue away from the granulomas showed significant dust deposition including dust macules. In spite of the inorganic dust deposits, with adjacent tissue lesions evident from the radiological findings (which were interpreted as atypical for pneumoconiosis) and the presence of granulomas in lung tissue, a diagnosis of necrotizing sarcoid granulomatosis was made, which was later changed to mixed-dust pneumoconiosis on further detailed examination. Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy (SEM/EDS) analysis of individual particles showed predominantly Si (silica or silicon carbide [SiC]) and Al particles (consistent with aluminum metal and/or oxide), as well as numerous Al silicates, Ti, and occasional Zr, Nb, V, steel, including Si fibers (consistent with SiC). We present the controversy about the

pathogenesis of the lung disorder and whether it represents an occupational disease - which is more or less representative for many such cases. © 2018 Elsevier B.V.

Bittencourt, T., Santos, A., Silva, M.*, et al.* (2018) Toxic effects of vanadium compounds on biological parameters of embryos and adults of zebrafish (Danio rerio). *Arquivo Brasileiro De Medicina Veterinária e Zootecnia,* 70(6): 1877-1886.
Keywords: toxicity test; teratogenic effects; animal behavior

Abstract:
The toxic effects of sodium metavanadate (MV), vanadium pentoxide (PV) and oxovanadium sulfate (SV), potential antidiabetic drug, on embryos and adults of zebrafish (Danio rerio) were evaluated. Embryos were exposed to concentrations of 10-1000μg/mL for evaluation of 96-h LC_{50} and their teratogenic effects. Adults were exposed to 10 and 20μg/mL of the same compounds to evaluate behavioral changes related to chemical exposure and mortality. The 96-h LC_{50} were 22.48, 53.62, and 74.14μg/mL for MV, SV, and PV, respectively. Mortality of 100% was observed at the concentrations of 400-1000μg/mL of the three compounds. The teratogenic effects most observed ($P<0.05$) were pericardial and yolk sac edemas. Adult animals exposed to the vanadium compounds had higher opercular beats and congestion in the gill arches. The exhibition of behaviors Floating and Resting in the exposed adults was significant ($P<0.05$), as well as the Air breathing behavior. Chemical exposure to vanadium compounds caused toxic effects in embryos and adults of zebrafish with high mortality. In conclusion, its use as a potential antidiabetic drug should be better studied due to the toxic effect.

Chen, C-F., Chio, C-P., Yuan, T-H.*, et al.* (2018) Increased cancer incidence of Changhua residents living in Taisi Village north to the No. 6 Naphtha Cracking Complex. *Journal of the Formosan Medical Association,* 117(12): 1101-1107.
Available at:
https://www.sciencedirect.com/science/article/pii/S0929664617307313/pdfft?md5=583ef7986d7aae0b3177005d0e759dda&pid=1-s2.0-S0929664617307313-main.pdf
Keywords: Cancer; Changhua; Petrochemical complex

Abstract
Background/Purpose: Cancer risks of residents living north to the No. 6 Naphtha Cracking Complex has not been studied before. Methods: Our study subjects were recruited in 2014–16 from three zones north to the No. 6 Naphtha Cracking Complex, which included 229 participants from the Taisi Village (average 5.5 km from the complex), 1333 participants from the other 14 villages in Dacheng Township (9.2 km), and 372 participants from the Zhutang Township (19.9 km). Their occurrence of cancer in years-post-complex-operation (YPO) was defined by having a new cancer recorded (ICD-9: 140–208) in National Health Insurance Research Database since 1999. Poisson regression was conducted to compare incidence rate ratio among three zones in 10–16 YPO. Results: We found that all-cause cancer incidence of 10–16 YPO (per 1,000 person-years) in Taisi Village (8.44) was higher than that in Dacheng (3.42) and Zhutang (2.72). Taisi residents had significantly higher concentrations of V, Cr, Mn, Ni, Cu, As, Cd, and Tl than Dacheng and Zhutang residents. The all-cause cancer incidence rate ratio between 10–16 and 0–9 YPO was 8.44 for Taisi residents. All-cause cancer incidence rate of Taisi residents was 2.55 times higher than Dacheng residents (95% CI: 1.89–3.45) and 2.43 times higher than Zhutang residents (95% CI: 1.54–3.84) in 10–16 YPO. Conclusion: We conclude that all-cause cancer risk was significantly increased for Taisi residents living near the No. 6 Naphtha Cracking Complex for 10–16 years after the complex began operating. © 2018.

Costa, B.C., Tokuhara, C.K., Rocha, L.A.*, et al.* (2019) Vanadium ionic species from degradation of Ti-6Al-4V metallic implants: In vitro cytotoxicity and speciation evaluation. *Materials Science & Engineering.C, Materials for Biological Applications,* 96: 730-739.
Keywords: Cytotoxicity; Ionic speciation; Oxidovanadium(IV); Ti-6Al-4V; Tribocorrosion; Vanadate(V)

Abstract
Among the metallic materials used in biomedical industry, the most common choice for orthopedics and dental implants is titanium (Ti) and its alloys, mainly due to their superior corrosion and tribocorrosion resistance and biocompatibility. Under different conditions in vivo, such as different pH levels, composition of body fluid and mechanical loads, metallic materials may suffer from degradation, resulting in the release of undesired wear particles and ions. In particular, the Ti-6Al-4V system represents almost half of the production of Ti as a biomaterial and many concerns have been raised about titanium, aluminum and vanadium ions releasing. This work evaluates the cytotoxic effects of vanadium ionic species generated from Ti-6Al-4V surfaces regarding mouse pre-osteoblasts and fibroblasts. In our cell viability tests, we noticed a significant decrease in the fibroblasts' cell viability with vanadium concentrations (23muM) close to those previously reported to be observed in vivo in patients with poor functioning of their medical devices based on Ti-6Al-4V (30muM). Speciation modelling was carried-out, for the first time, to this system. Results of the modelling reveal that vanadates(V), namely H2VO4(-) and HVO4(2-), are the main species present in cell culture media. Otherwise, in synovial fluids of individuals with poorly functioning implants, wherein the concentration of vanadium may go up to ca. 30muM, the tentative theoretical speciation data indicates a high occurrence probability for V(V)- and V(IV)-species bound to albumin and hyaluronic acid. In conclusion, even though relatively low concentrations of vanadium may be released from Ti-6Al-4V implants in vivo, the continuous contact with peri-implant cells for long periods of time may represent a potentially hazardous situation.

Domingo-Relloso, A., Grau-Perez, M., Galan-Chilet, I.*, et al.* (2019) Urinary metals and metal mixtures and oxidative stress biomarkers in an adult population from Spain: The Hortega Study. *Environment International,*123: 171-180.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018312947/pdfft?md5=59346fc87b7c17341a269ec52bc3118c&pid=1-s2.0-S0160412018312947-main.pdf
Keywords: Metal mixtures; Oxidative stress; Population-based; Urine metals

Abstract
Introduction: Few studies have investigated the role of exposure to metals and metal mixtures on oxidative stress in the general population. Objectives: We evaluated the cross-sectional association of urinary metal and metal mixtures with urinary oxidative stress biomarkers, including oxidized to reduced glutathione ratio (GSSG/GSH), malondialdehyde (MDA), and 8-oxo-7,8-dihydroguanine (8-oxo-dG), in a representative sample of a general population from Spain (Hortega Study). Methods: Urine antimony (Sb), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), vanadium (V) and zinc (Zn) were measured by ICPMS in 1440 Hortega Study participants. Results: The geometric mean ratios (GMRs) of GSSG/GSH comparing the 80th to the 20th percentiles of metal distributions were 1.15 (95% confidence intervals [95% CI]: 1.03–1.27) for Mo, 1.17 (1.05–1.31) for Ba, 1.23 (1.04–1.46) for Cr and 1.18 (1.00–1.40) for V. For MDA, the corresponding GMRs (95% CI) were 1.13 (1.03–1.24) for Zn and 1.12 (1.02–1.23) for Cd. In 8-oxo-dG models, the corresponding GMR (95% CI) were 1.12 (1.01–1.23) for Zn and 1.09 (0.99–1.20) for Cd. Cr for GSSG/GSH and

Zn for MDA and 8-oxo-dG drove most of the observed associations. Principal component (PC) 1 (largely reflecting non-essential metals) was positively associated with GSSG/GSH. The association of PC2 (largely reflecting essential metals) was positive for GSSG/GSH but inverse for MDA. Conclusions: Urine Ba, Cd, Cr, Mo, V and Zn were positively associated with oxidative stress measures at metal exposure levels relevant for the general population. The potential health consequences of environmental, including nutritional, exposure to these metals warrants further investigation. © 2018 The Authors. (Note: This was also in December update but with the wrong year, it should be 2019 not 2018.)

Jin, Y., O'Connor, D., Ok, Y.S.*, et al.* (2019) Assessment of sources of heavy metals in soil and dust at children's playgrounds in Beijing using GIS and multivariate statistical analysis. *Environment International,* 124: 320-328.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018328757/pdfft?md5=d4c9da959d56c8ced8534ff69e7f45d4&pid=1-s2.0-S0160412018328757-main.pdf
Keywords: Air pollution; Atmospheric deposition; GIS; Heavy metals; Soil contamination

Abstract
Potentially toxic elements such as heavy metals are ubiquitous in the environment. Risk-based environmental management relies upon identifying pollution sources, pathways, and the exposed population. In a Chinese urban setting, many residents live in high-rise buildings without private gardens. Therefore, the main residential risk of exposure to contaminated soils and dusts may be associated with public open spaces. As children are the most vulnerable receptor, playgrounds represent an important yet often overlooked exposure point. The present study assessed plausible sources of heavy metals at children's playgrounds in a representative metropolitan environment. Soil and equipment dust samples were collected from 71 playgrounds across Beijing, which were analyzed for 11 different heavy metals. Principal component analysis (PCA) was used to identify the latent constructs which control heavy metal variability and reflect potential sources. Cluster analysis (CA) was conducted to group sampled locations, which provided further insights on plausible sources. The main factors extracted from the PCA were then subject to geostatistical analysis. The systematic combination of GIS with multivariate statistical analysis proved valuable for elucidating anthropogenic and natural sources. Elevated Be, V, Cr, Mn, Co, Ni, As in playground soils were found to derive mainly from the natural background (spatial autocorrelation = 2 km), while elevated Cu and Pb was attributed to traffic activities (spatial autocorrelation = 17 km), especially along the routes of Beijing's inner ring-roads, the major roads toward the northwest and northeast, and the international airport. These results suggest that heavy metals in playground equipment dust may derive mainly from atmospheric deposition of air pollution of both natural and anthropogenic origin (spatial autocorrelation = 11–13 km). Among them, Be, V, Mn, Co, Cu, As, Pb were attributed to atmospheric pollution deriving from the north of Beijing, brought by the prevailing northern wind in the winter season; whereas, Cr and Ni may possibly be brought from the southeast by the summer season winds. Knowledge of anthropogenic vs. natural origins of heavy metals in playgrounds is critical in assessing health impact and designing policy instruments for metropolitan areas. © 2019 The Authors.

Lewicka, I., Kocyłowski, R., Grzesiak, M.*, et al.* (2019) Relationship between pre-pregnancy body mass index and mineral concentrations in serum and amniotic fluid in pregnant women during labor. *Journal of Trace Elements in Medicine and Biology,* 52: 136-142.
Keywords: Amniotic fluid; Body mass index; Pregnancy; Pregnancy outcomes; Trace elements

Abstract
The aim of the study was to determine the correlations between body mass index (BMI) values before pregnancy and the concentrations of selected elements (Mg, Co, Cu, Zn, Sr, Cd, Ba, Pb, U, Ca, Cr, Al, Mn, V, Fe) in blood serum and amniotic fluid (AF) in pregnant women. Elemental analysis of serum and amniotic fluid in 225 Polish women (Caucasian/white) showed a relationship between the concentration of minerals in the above-mentioned samples and the pre-pregnancy BMI. Analysis of blood serum was performed by using ICP-MS and it demonstrated that iron concentration was significantly lower in overweight and obese women. Being underweight in pregnant women was associated with a significantly lower concentration of magnesium and cobalt in the blood serum. Both underweight and overweight women were associated with significantly lower concentrations of calcium and strontium in the blood serum. The concentration of cobalt was significantly higher in underweight women. The concentration of lead in the blood serum of overweight and obese women was significantly higher than in other groups. Analysis of the AF showed that the concentration of copper was significantly lower in overweight and obese women, and the concentration of manganese and vanadium significantly higher than in other groups of women. A deficiency in essential minerals and an excess of heavy metals in women may be associated with abnormal body weight and this is important in the etiopathogenesis of pregnancy and fetal development disorders. © 2018 Elsevier GmbH.

Liang, C.M., Wu, X.Y., Huang, K.*, et al.* (2019) Trace element profiles in pregnant women's sera and umbilical cord sera and influencing factors: Repeated measurements. *Chemosphere,* 218: 869-878.
Keywords: Birth cohort; China; Pregnant women; Repeated measurements; Trace elements

Abstract
In utero exposure to toxic heavy metals and deficient or excessive essential trace elements during pregnancy may have adverse effects on pregnant women and their offsprings, which are of great concern. The objective of the present study was to characterize serum concentrations of multiple trace elements at multiple time points during pregnancy in Chinese women. Three thousand four hundred and sixteen pregnant women in total were included from MABC (Ma'anshan Birth Cohort) study. Fasting sera in the morning and questionnaires were obtained at three separate follow-up visits. Nineteen trace elements from serum samples were analyzed, including aluminum (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), barium (Ba), thallium (Tl), lead (Pb), calcium (Ca), magnesium (Mg), mercury (Hg) and molybdenum (Mo). The total detection rates for most elements were 100% rather than Ni (99.98%), As (99.97%), Cd (99.6%), Ba (99.9%), Pb (99.8%), Hg (99.8%). The concentration distributions of 19 elements varied vastly. Median concentrations for all trace elements ranged from 38.5 ng/L to 102.9 mg/L. The moderate interclass correlation coefficients (ICCs) were observed for Co, Cu, Se and Hg, ranging from 0.40 to 0.62; the lower ICCs, ranging from 0.13 to 0.32 were for Fe, Zn, Cd, Ba, Tl, Mg and Mo. The intraclass correlation effects were not observed for the remaining elements, such as Al, V, Cr, Mn, Ni, As and Pb. The concentrations of each element between three time points were significantly different; significant differences were also found between any two time points except for Ni, Cd and Mo. Many factors could affect the levels of trace elements, and a very important factor of them was season. Consequently, a single measurement of elements in sera seems not enough to describe exposure levels throughout pregnancy; additionally, season affected exposure levels of trace elements with moderate ICCs showed certain regularity. Future analyses should take sampling seasons into consideration carefully.

Liu, L., Urch, B., Szyszkowicz, M.*, et al.* (2018) Metals and oxidative potential in urban particulate matter influence systemic inflammatory and neural biomarkers: A controlled exposure study. *Environment International,* 121: 1331-1340.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018320014/pdfft?md5=5f7964304a63a141b04ae2c52a1c1eef&pid=1-s2.0-S0160412018320014-main.pdf

Abstract
Background: Oxidative stress and inflammation are considered to be important pathways leading to particulate matter (PM)-associated disease. In this exploratory study, we examined the effects of metals and oxidative potential (OP) in urban PM on biomarkers of systemic inflammation, oxidative stress and neural function. Methods: Fifty-three healthy non-smoking volunteers (mean age 28 years, twenty-eight females) were exposed to coarse (2.5–10 μm, mean 213 μg/m 3), fine (0.15–2.5 μm, 238 μg/m 3), and/or ultrafine concentrated ambient PM (<0.3 μm, 136 μg/m 3). Exposures lasted 130 min, separated by ≥2 weeks. Metal concentrations and OP (measured by ascorbate and glutathione depletion in synthetic airway fluid) in PM were analyzed. Blood and urine samples were collected pre-exposure, and 1-h and 21-h post exposure for assessment of biomarkers. We used mixed-regression models to analyze associations adjusting for PM size and mass concentration. Results: Results for metals were expressed as change (%) from daily pre-exposure biomarker levels after exposure to a metal at a level equivalent to the mean concentration. Exposure to various metals (silver, aluminum, barium, copper, iron, potassium, lithium, nickel, tin, and/or vanadium) was significantly associated with increased levels of various blood or urinary biomarkers. For example, the blood inflammatory marker vascular endothelia growth factor (VEGF) increased 5.3% (95% confidence interval: 0.3%, 10.2%) 1-h post exposure to nickel; the traumatic brain injury marker ubiquitin C-terminal hydrolase L1 (UCHL1) increased 11% (1.2%, 21%) and 14% (0.3%, 29%) 1-h and 21-h post exposure to barium, respectively; and the systemic stress marker cortisol increased 1.5% (0%, 2.9%) and 1.5% (0.5%, 2.8%) 1-h and 21-h post exposure to silver, respectively. Urinary DNA oxidation marker 8-hydroxy-deoxy-guanosine increased 14% (6.4%, 21%) 1-h post exposure to copper; urinary neural marker vanillylmandelic acid increased 29% (3%, 54%) 1-h post exposure to aluminum; and urinary cortisol increased 88% (0.9%, 176%) 1-h post exposure to vanadium. Results for OP were expressed as change (%) from daily pre-exposure biomarker levels after exposure to ascorbate-related OP at a level equivalent to the mean concentration, or for exposure to glutathione-related OP at a level above the limit of detection. Exposure to ascorbate- or glutathione-related OP was significantly associated with increased inflammatory and neural biomarkers including interleukin-6, VEGF, UCHL1, and S100 calcium-binding protein B in blood, and malondialdehyde and 8-hydroxy-deoxy-guanosine in urine. For example, UCHL1 increased 9.4% (1.8%, 17%) in blood 21-h post exposure to ascorbate-related OP, while urinary malondialdehyde increased 19% (3.6%, 35%) and 8-hydroxy-deoxy-guanosine increased 24% (2.9%, 48%) 21-h post exposure to ascorbate- and glutathione-related OP, respectively. Conclusion: Our results from this exploratory study suggest that metal constituents and OP in ambient PM may influence biomarker levels associated with systemic inflammation, oxidative stress, perturbations of neural function, and systemic physiological stress. © 2018.

Mikelson, C.K., Troisi, J., LaLonde, A.*, et al.* (2019) Placental concentrations of essential, toxic, and understudied metals and relationships with birth outcomes in Chattanooga, TN. *Environmental Research,* 168: 118-129.
Keywords: Birth weight; Lead; Manganese; Metals; Placenta; Rhodium

Abstract

Background: Comprehensive examinations of placental metal concentrations and correlations with infant parameters are under-investigated. Chattanooga, Tennessee's consistently high incidence of low birth weight and potential for metal exposure provides an ideal opportunity to investigate potential correlations. Objectives: To investigate the associations between a wide variety of metals in placental tissue and multiple infant parameters. Methods: A total of 31 elements were screened via ICP-MS in 374 individual placental samples. Of those, 14 were quantifiable in > 86% of the samples. We examined correlations between metal concentrations and infant parameters (birth weight, gestational age, birth weight centile, placental weight, birth length and head circumference). We fit multivariable regression models to estimate the covariate-adjusted associations of birth weight with ln-transformed concentrations of each of the 14 metals and used generalized additive models to examine nonlinear relationships. Results: Some of the strongest relationships with infant parameters came from several lesser-studied metals. Placental rhodium concentrations were negatively correlated with almost all infant parameters. In the fully adjusted regression model, birth weight was significantly associated with several metals. On an IQR (25th to the 75th percentile) basis, estimated changes in birthweight were: for cobalt (82.5 g, IQR=6.05 μg/kg, p = 0.006), iron (−51.5 g, IQR = 171800 μg/kg, p = 0.030), manganese (−27.2 g, IQR=152.1 μg/kg, p = 0.017), lead (−72.7 g, IQR=16.55 μg/kg, p = 0.004) and rhodium (−1365.5 g, IQR = 0.33 μg/kg, p < 0.001). Finally, a generalized additive model showed significant nonlinear relationships between birth weight and concentrations of Co and Rh. Conclusions: Our comprehensive examination of placental metals illustrate many strong associations between lesser-studied metals and infant parameters. These data, in combination with our correlations of well-studied metals, illustrate a need to consider in utero exposure to a broad array of metals when considering fetal development.

O'Brien, K.M., White, A.J., Sandler, D.P.*, et al.* (2019) Do Post-breast Cancer Diagnosis Toenail Trace Element Concentrations Reflect Prediagnostic Concentrations? *Epidemiology (Cambridge, Mass.),* 30(1): 112-119.

Abstract

BACKGROUND: Exposure to trace elements may affect health, including breast cancer risk. Trace element levels in toenails are potentially useful biomarkers of exposure, but their reliability is not established. We assessed the reproducibility of toenail element concentrations over time and whether concentrations change following a breast cancer diagnosis. METHODS: We assessed trace element levels in toenails collected at two time points from 221 women (111 with and 110 without an intervening breast cancer diagnosis). We measured levels of arsenic, cadmium, chromium, cobalt, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, selenium, tin, vanadium, and zinc using inductively coupled plasma mass spectrometry in samples collected at baseline and 4-10 years later. We compared trace element concentrations over time using Spearman's rank correlation coefficient (R). We used linear models to examine the magnitude and direction of changes and the influence of a breast cancer diagnosis. RESULTS: Overall, we observed positive correlations (R = 0.18-0.71) between paired samples for all trace elements. However, nickel (R = -0.02) and antimony (R = 0.12) were not correlated among cases. We observed decreases in cadmium, chromium, mercury, manganese, molybdenum, nickel, and lead between baseline and follow-up, but case status was unrelated to these changes. The declines are consistent with decreases over calendar time rather than age time. CONCLUSIONS: Toenail trace element concentrations were correlated over time, but many elements showed systematic decreases by calendar year. Aside from nickel and antimony, postdiagnostic toenail levels correlated with prediagnostic levels, providing support for using postdiagnostic toenail samples in retrospective studies.

Saarikoski, S., Reyes, F., Vázquez, Y.*, et al.* (2019) Characterization of submicron aerosol chemical composition and sources in the coastal area of Central Chile. *Atmospheric Environment,* 199: 391-401.

Keywords: Aerosol Mass Spectrometer; Chemical composition; Source apportionment; South America; Submicron particles

Abstract

Chemical characteristics and the sources of submicron particles (<1 μm in diameter) were investigated in Valle Alegre, the coastal area of Central Chile. The chemical composition of particles was studied by using a Soot particle Aerosol Mass Spectrometer and Multi-Angle Absorption Photometer. Submicron particles were dominated by organics (42% of mass) and sulfate (39% of mass) while the mass fractions of ammonium, nitrate and black carbon were much smaller (13, 2 and 4% of mass, respectively). Additionally, several metals (V, Zn, Fe, Cd, Cu, K, Na and Mg) were detected in submicron particles and also some of their inorganic salts (e.g. NaCl+, MgCl2 +, CaCl2 +, KCl+ and KNO3 +). The sources of particles were examined by using Positive Matrix Factorization (PMF). Organic aerosol (OA) was divided into five factors by using PMF; hydrocarbon-like OA (HOA), biomass burning OA (BBOA), low-volatility oxygenated OA (LV-OOA), semi-volatile OA (SV-OOA) and marine oxygenated OOA (MOOA). Oxygenated factors (LV-OOA; SV-OOA and MOOA) comprised 75% of total OA with LV-OOA being the dominant factor (38% of OA). Sulfate had two major sources in Valle Alegre; ∼70% of sulfate was related to anthropogenic sources through the oxidation of gas phase SO2 whereas ∼24% of sulfate was associated with biogenic origin related to the oxidation of dimethyl sulfide in the marine environment. Regarding total submicron particle mass (campaign-average 9.5 μg m−3), the contribution of anthropogenic sources was at least as large as that of biogenic origin. © 2018 The Authors.

Skalny, A.V., Simashkova, N.V., Skalnaya, A.A.*, et al.* (2018) Trace element levels are associated with neuroinflammatory markers in children with autistic spectrum disorder. *Journal of Trace Elements in Medicine and Biology,* 50: 622-628.

Keywords: Autism spectrum disorders; Cadmium; Magnesium; Manganese; Neuroinflammation

Abstract

The objective of the present study was to estimate the association between brain inflammatory markers and serum trace element levels as assessed by inductively coupled plasma mass spectrometry at NexION 300D. Leukocyte elastase (LE), α1-proteinase inhibitor (α1-PI) activity, anti-nerve growth factor-antibodies (anti-NGF-Ab), and anti-myelin basic protein-antibodies (anti-MBP-Ab) levels were assessed as inflammatory markers. The obtained data demonstrate that the increase in LE and α1-PI activity is associated with higher serum Cr and Cu levels, respectively. The increase in Anti-NGF-Ab levels was associated with a nearly significant 16% increase in serum Mn levels. Autistic children with high MBP-Ab levels were characterized by 28% higher serum Mn and lower Mg concentration. The results of correlation analysis were generally in agreement with the outcome of group comparisons. Regression analysis demonstrated that serum Mg was significantly negatively associated with LE activity, whereas both serum Fe and V concentrations were characterized by a positive influence on the parameter. In turn, serum Cu was a significant predictor of α1-PI, as well as Cr levels. At the same time, the serum concentrations of Cd and Fe were found to be inversely associated with α1-PI levels. Serum Cd and Mn levels were significant positive predictors of anti-MBP-Ab levels, whereas Mg levels had a negative impact on anti-MBP-Ab values. Generally, the obtained data demonstrate the interrelationship between trace element

homeostasis and neuroinflammation in autism. Hypothetically, modulation of trace element status may be used for reduction of neuroinflammatory response, although further studies are required to reveal the underlying mechanisms of the observed associations. © 2018 Elsevier GmbH.

Sobhanardakani, S. (2019) Ecological and Human Health Risk Assessment of Heavy Metal Content of Atmospheric Dry Deposition, a Case Study: Kermanshah, Iran. *Biological Trace Element Research,* 187(2): 602-610.
Keywords: Atmospheric dry deposition; Health risk assessment; Heavy metals; Iran; Potential ecological risk

Abstract
The present study was intended to investigate the ecological and human health risk of cobalt, nickel, and vanadium in the atmospheric dry deposition of the Kermanshah city, Iran, in 2015. Totally 54 samples of atmospheric dry deposition were collected from the three regions of the city with different traffic intensity, and after acid digestion of the samples with ultrapure concentrated HNO3, the total contents of the metals were determined using inductively coupled plasma optical emission spectrometer (ICP-OES). Also, all statistical analyses were performed using the SPSS statistical package. The atmospheric dry deposition element contents increase according to the following descending order for both autumn seasons: Ni > Co > V. The results of potential ecological risk analysis demonstrated that metals in the samples are in low ecological risk levels, whereas the results of human health risk assessment showed that ingestion is the main exposure pathway of heavy metals in the dust to the local residents compared with inhalation and dermal pathways. Also, the upper limit of the 95% confidence interval (95% UCL) of hazard indices for non-carcinogenic risks of all analyzed metals in the dust samples was within the safe level for both children and adults. On the other hand, the carcinogenic risk levels of Co and Ni were all lower than the acceptable range (10(-6)-10(-4)) to local citizens. Consequently, the results advocate the necessity of understanding the heavy metal content of atmospheric dry deposition and regular monitoring of air pollution.

Tinkov, A.A., Skalnaya, M.G., Simashkova, N.V.*, et al.* (2019) Association between catatonia and levels of hair and serum trace elements and minerals in autism spectrum disorder. *Biomedicine and Pharmacotherapy,* 109: 174-180.
Available at:
https://www.sciencedirect.com/science/article/pii/S0753332218360529/pdfft?md5=b073affbe2041c69b36187ce13628166&pid=1-s2.0-S0753332218360529-main.pdf
Keywords: Autism spectrum disorder; Catatonia; Children; Mercury; Neurotoxicity

Abstract
The objective of the study was to investigate the association between catatonia in autism spectrum disorder (ASD) and the levels of hair and serum trace elements and minerals in children with ASD. The levels of hair and serum trace elements and minerals of boys suffering from ASD with (n = 30) and without (n = 30) catatonia, as well as 30 age- and sex-matched neurotypical controls were assessed using ICP-MS. Hair calcium (Ca) and selenium (Se) levels were lower in ASD patients as compared to the controls. Hair mercury (Hg) levels in ASD patients were more than 3-fold and 2-fold higher as compared to the controls and children with catatonia in ASD. Hair iodine (I) and manganese (Mn) were the lowest and the highest in ASD + Catatonia, respectively. Serum aluminium (Al) and cadmium (Cd) levels in healthy controls were significantly higher in comparison to the patients of both groups. Serum chromium (Cr), copper (Cu) levels were significantly increased in patients with ASD and

catatonia, whereas vanadium (V) levels were elevated in patients both with and without catatonia. Multiple regression analysis demonstrated that hair Hg and serum Al and Cd levels were negatively associated with catatonia in ASD in crude and adjusted models. Although the etiology of catatonia in ASD is unclear, the obtained data demonstrate that catatonic symptoms in ASD may be at least partially mediated by altered trace element levels. Further studies are required to elucidate the role of trace elements in the potential signaling mechanisms of catatonia. © 2018 Elsevier Masson SAS.

Ubaid Ali, M., Liu, G., Yousaf, B.*, et al.* (2019) Evaluation of floor-wise pollution status and deposition behavior of potentially toxic elements and nanoparticles in air conditioner dust during urbanistic development. *Journal of Hazardous Materials,* 365: 186-195.
Keywords: Air conditioner dust; nanoparticles; potential toxic elements; urban areas

Abstract
The study was undertaken to investigate deposition behaviors of various size-segregated particles and indoor air quality using dust accumulated on the air conditioner filter acting as a sink for PTEs and nanoparticles that can pose a significant health risk. However, the particulate matter size and chemical composition in AC dust and its relationship with PTEs remains uncertain. Current study aims to investigate the PTEs and nanoparticles composition of AC dust using different analytical approaches including ICP-MS, XRD, XPS, SEM/TEM along with EDS and Laser Diffraction particle size analyzer. The mean concentration of PTEs like Al, As, Cd, Cu, Li, Pb, Sb, Se, Sn, Ti, V and Zn exceeded the corresponding background value. Pb, As, Sn, Sb, Cd were categorizing under geo-accumulation index class IV. Most of the particles were found to be > 100 µm and it decreased significantly with increase in floor altitude. A significantly negative correlation was found between particles size and PTEs concentration showing a significant increase in PTEs content with decrease in particles size. The XPS results showed dominant peaks for TiO 2 , Ti-O-N, As 2 O 3 , Fe +3 , Fe +2 , Al-OH and Al 2 0 3 . Additionally, As, Pb, Si and Fe were dominant metallic nanoparticles identified using SEM/TEM along with EDS. © 2018 Elsevier B.V.

Vanska, M., Diab, S.Y., Perko, K.*, et al.* (2019) Toxic Environment of war: Maternal prenatal heavy metal load predicts infant emotional development. *Infant Behavior & Development,* 55: 1-9.
Keywords: Child development; Emotional development; Heavy metals; PTSD; War trauma

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

uranium, adversely predicted children's early emotional development, indicated by decreased positive affectivity, increased negative emotionality, and problems in early orientation and regulation. Mother's PTSD did not moderate the impact of heavy metal contamination on children's emotional development. CONCLUSIONS: Adverse impact of war is not limited to those who experience it directly, but is passed on to future generations through multiple mechanisms. International organizations are obliged to protect parents and infants from the modern weaponry in wars.

Wan, Z.Z., Chen, H.G., Lu, W.Q.*, et al.* (2019) Metal/metalloid levels in urine and seminal plasma in relation to computer-aided sperm analysis motion parameters. *Chemosphere,* 214: 791-800.
Keywords: Dimenhydrinate/chemistry; Humans; Male; Metalloids/urine; Semen/chemistry; Semen Analysis/methods; Spermatozoa/physiology; CASA motion parameters; epidemiology; metals; seminal plasma; urine

Abstract
BACKGROUND: Exposure to high levels of metals/metalloids may impair semen quality. Computer-aided sperm analysis (CASA) can be used for kinematic analysis of spermatozoa, which provides additional insights into sperm motion characteristics. OBJECTIVE: To explore the associations of urinary and seminal plasma metal/metalloid concentrations with CASA motion parameters and assess the degree of correspondence between the two sample types. METHODS: Eighteen metals/metalloids in seminal plasma and repeated urine samples were determined among 746 men recruited from a reproductive center. We assessed their associations with 6 CASA motion parameters [i.e., straight-line velocity (VSL), curvilinear velocity (VCL), average path velocity (VAP), linearity (LIN), straightness (STR) and amplitude head displacement (ALH)] using multivariable linear regression models. RESULTS: We found significantly inverse dose-dependent relationships between seminal plasma arsenic (As) and VSL, VCL and VAP, between seminal plasma selenium (Se) and VSL and VAP, between seminal plasma zinc (Zn) and STR and LIN, and between seminal plasma manganese (Mn) and LIN in single-metal models [all false discovery rate (FDR) adjusted P for trend<0.05]. These dose-response relationships remained statistically significant based on multiple-metal models and restricted cubic spline functions. Metal/metalloid concentrations in urine poorly predicted the same-day seminal plasma concentrations [coefficient of determination (R(2))<0.15]. We didn't find any significant associations between urinary metal/metalloid concentrations and the CASA motion parameters. CONCLUSION: Exposure to high levels of As, Se, Mn and Zn may impair sperm motion capacity. Concentrations of metals/metalloids in spot urine samples cannot accurately predict same-day seminal plasma exposure levels.

Wang, S., Cai, L-M., Wen, H-H.*, et al.* (2019) Spatial distribution and source apportionment of heavy metals in soil from a typical county-level city of Guangdong Province, China. *Science of the Total Environment,* 655: 92-101.
Keywords: Positive matrix factorization; Soil heavy metals; Source apportionment; Spatial distribution

Abstract
The contents of ten heavy metals (Cr, Hg, As, Pb, Ni, Cd, Ti, Cu, Zn and V) in 413 topsoil samples from Puning City, Guangdong Province, China were investigated. Obvious enrichment of Hg, As, Pb, Cd and Zn were presented, and the contents of Hg and As in 5.8% and 3.4% samples respectively were higher than the guideline values recommended by the Chinese Environmental Quality Standard for Soils. Chromium and V were presented no enrichment and no pollution. According to one-way analysis of variance, the mean contents of Hg, Pb, Cu

and Zn in land for construction were significantly higher than farmland and natural vegetation, but the land use had no obvious effect on other heavy metals. Furthermore, the potential sources of ten heavy metals were identified and apportioned in combination with geostatistics, correlation analysis and positive matrix factorization model. The results were following as: a) Pb, Zn and Cu mainly origin from vehicle emission and atmosphere deposition, and the hotspots approximately distributed in the areas of intensive traffic and near main roads; b) Hg and Cd were derived to industrial activities related to pharmaceutical industries, the textile and dyeing industries and e-waste recycling industries, and high-value areas were mainly concentrated in the northeast of the urban area where the industrial parks have been distributed; c) Soil parent material (Jurassic shale) was the main source of Cr, Ni, V and Ti; d) As mainly came from agricultural inputs such as pesticides or herbicides, livestock and fertilizers. Meanwhile, the contributions of four sources were 33.08%, 24.04%, 27.11% and 15.77% of the total contribution, respectively.

Wang, Y-X., Chen, H-G., Li, X-D.*, et al.* (2018) Concentrations of vanadium in urine and seminal plasma in relation to semen quality parameters, spermatozoa DNA damage and serum hormone levels. *Science of the Total Environment,* 645: 441-448.
Keywords: DNA damage; Reproductive hormone; Semen quality; Vanadium

Abstract
Widespread human exposure to vanadium has been well documented. Vanadium exposure was reported to induce male reproductive toxicity in toxicological studies, yet human epidemiologic studies are lacking. Here we determined the associations between environmental exposure to vanadium and semen quality, spermatozoa DNA damage and serum reproductive hormones. Concentrations of vanadium in seminal plasma and repeated urine samples were determined among 764 men recruited from a reproductive medicine centre. Associations of vanadium concentrations with semen quality parameters (n = 764), DNA integrity measures (n = 404) and serum reproductive hormones (n = 381) were assessed by logistic or linear regression models with adjustment for potential confounders. Significant positive dose–response relationships were observed between vanadium concentrations in seminal plasma and tail length and serum estradiol, as well as odds ratios for a below-reference-value sperm concentration; whereas inverse relationships between seminal plasma vanadium with total testosterone (T) and free T (all p values for trends <0.05) were observed. These relationships were maintained after adjusting for seminal plasma concentrations of other elements (i.e., arsenic, cadmium, copper, selenium, or tin). No significant associations was revealed between urinary vanadium concentrations and semen quality, spermatozoa DNA integrity and reproductive hormones. Our findings suggested that elevated vanadium exposure may be adversely associated with male reproductive health, and that seminal plasma vanadium may be a more direct exposure biomarker for the male reproductive system than urinary vanadium. © 2018 Elsevier B.V.

Yang, Y., Ruan, Z., Wang, X.*, et al.* (2018) Short-term and long-term exposures to fine particulate matter constituents and health: A systematic review and meta-analysis. *Environmental Pollution (Barking, Essex : 1987),* 247: 874-882.
Keywords: Air pollution; Constituents of fine particulate matter; Morbidity; Mortality; PM(2.5)

Abstract
BACKGROUND: Fine particulate matter (Particulate matter with diameter</=2.5mum) is associated with multiple health outcomes, with varying effects across seasons and locations. It remains largely unknown that which components of PM2.5 are most harmful to human health. METHODS: We systematically searched all the relevent studies published before

August 1, 2018, on the associations of fine particulate matter constituents with mortality and morbidity, using Web of Science, MEDLINE, PubMed and EMBASE. Studies were included if they explored the associations between short term or long term exposure of fine particulate matter constituents and natural, cardiovascular or respiratory health endpoints. The criteria for the risk of bias was adapted from OHAT and New Castle Ottawa. We applied a random-effects model to derive the risk estimates for each constituent. We performed main analyses restricted to studies which adjusted the PM2.5 mass in their models. RESULTS: Significant associations were observed between several PM2.5 constituents and different health endpoints. Among them, black carbon and organic carbon were most robustly and consistently associated with all natural, cardiovascular mortality and morbidity. Other potential toxic constituents including nitrate, sulfate, Zinc, silicon, iron, nickel, vanadium, and potassium were associated with adverse cardiovascular health, while nitrate, sulfate and vanadium were relevant for adverse respiratory health outcomes. CONCLUSIONS: Our analysis suggests that black carbon and organic carbon are important detrimental components of PM2.5, while other constituents are probably hazardous to human health. However, more studies are needed to further confirm our results.

Yu, Y-Q. & Yang, J-Y. (2019) Oral bioaccessibility and health risk assessment of vanadium(IV) and vanadium(V) in a vanadium titanomagnetite mining region by a whole digestive system in-vitro method (WDSM). *Chemosphere,* 215: 294-304.
Keywords: Oral bioaccessibility; Oral ingestion; Vanadium(IV); Vanadium(V); Whole digestive system in-vitro method (WDSM)

Abstract
Oral bioaccessibility of vanadium(IV) and vanadium(V) in soil, dust and concentrate fines from a vanadium titanomagnetite mining region was assessed by a whole digestive system in-vitro scheme. The scheme including the addition of sweat and the large intestinal digestion was used to estimate the oral bioaccessibility of vanadium(IV) and vanadium(V) in the whole digestive system for the first time. Higher oral bioaccessibility of vanadium(IV) and vanadium(V) was determined in gastric and small intestinal phases demonstrating that their major roles for vanadium digestion and absorption. The decreasing order of the oral bioaccessibility of vanadium(IV) and vanadium(V) in each digestive phase was stomach, small intestine, large intestine and mouth. Higher oral bioaccessibility of vanadium(V) in the whole digestion indicated its higher risk potential for human than vanadium(IV). Lower oral bioaccessibility of vanadium(IV) and vanadium(V) determined in bionic digestion illustrated detoxicity potential of human body for ingested vanadium. Compared with soil and dust, higher digestion rate of vanadium in vanadium titanomagnetite concentrate fines indicated its higher risk for human, especially for mining workers. Based on vanadium oral bioaccessibility, hazard quotients of the vanadium were much less than the critical level suggested for no non-carcinogenic risks to the populations surrounding the sampling sites. Indeed, compared with the estimations based on total vanadium content, the incorporation of oral vanadium bioaccessibility into risk assessments could give more realistic information.

2. HEALTH EFFECTS

Adebiyi, O.E., Olayemi, F.O., Olopade, J.O*., et al.* (2019) Beta-sitosterol enhances motor coordination, attenuates memory loss and demyelination in a vanadium-induced model of experimental neurotoxicity. *Pathophysiology,* 26(1): 21-29.
Available at:
https://www.sciencedirect.com/science/article/pii/S0928468018300543/pdfft?md5=a7e1e89ba22b8c5110355616a8d68ccf&pid=1-s2.0-S0928468018300543-main.pdf

Keywords: Sodium metavanadate; Beta-sitosterol; Neurotoxicity; Oxidative stress; Antioxidant enzymes

Abstract
Environmental discharge of vanadium causes cognitive and behavioral impairments in humans and animals via production of reactive oxygen species leading to lipid peroxidation and alteration in antioxidant defence system. The current study was carried out to investigate the cognitive-enhancing ability of β-sitosterol in vanadium-induced neurotoxicity. Forty eight mice were randomly assigned into 4 groups (A–D) with the following treatments: group A; distilled water, B; α-tocopherol + sodium metavanadate (NaO3V), C; β-sitosterol + NaO3V and D; only NaO3V. NaO3V was administered intraperitoneally while other treatments were administered through gavage for 7 consecutive days. Neurobehavioral parameters measuring cognition, locomotion, anxiety and grip strength were evaluated at day 8. Following sacrifice, brain levels of catalase, superoxide dismutase, glutathione, malonaldehyde (MDA) and hydrogen peroxide (H2O2) were measured. Immunohistochemical expression of Myelin Basic Protein (MBP) in the brain was also investigated. The results showed that deficits in spatial learning, locomotor efficiency, and motor coordination, induced by acute vanadium neurotoxicity were mitigated by beta-sitosterol. Significantly ($\alpha \leq 0.05$) decreased in vivo antioxidant enzyme activities, increased brain levels of MDA and H2O2, structural damage to myelin sheaths and decreased expression of MBP were also observed in the NaO3V group (D), however, co-administration of β-sitosterol reduced these pathologic features. It is concluded that β-sitosterol alleviates vanadium-induced neurotoxicity by enhancing cognition and improving motor co-ordination via its antioxidant and myelo-protective activities.

Baur, X., Sanyal, S. & Abraham, J.L. (2019) Mixed-dust pneumoconiosis: Review of diagnostic and classification problems with presentation of a work-related case. *Science of the Total Environment,* 652: 413-421.

Keywords: Diagnostics; Energy dispersive x-ray spectroscopy; Environmental exposure; Health risks; Inorganic particulates; Pathology; Pneumoconiosis; Scanning electron microscopy

Abstract
Environmental aerosolized particulates pose a potential risk to human health worldwide. Among others, high amounts of contaminants are generated especially in newly industrializing countries in the vicinity of industrial manufacturing, mining operations, but also during agricultural and natural processes. As an example of the needed multi-disciplinary diagnostic and differential diagnostic approach, we report a case of a 59-year old industrial worker who has suffered from chronic bronchitis and progressive dyspnea on exertion for 8 years. He showed severe lung function impairment, a cavity in his right upper lung lobe, nodular and irregular opacities, fibrotic pleural changes and emphysema. According to the occupational history and the industrial hygiene report, he had been engaged in the production of various refractory materials and been exposed to very high levels of inorganic dust, especially to silica, silicon carbide and aluminum compounds, but also to carbon and other dusty materials for 28 years. Histopathology of the two resected lung segments showed focally infarcted granulomas and chronic inflammation. Stains for organisms were negative. The lung tissue away from the granulomas showed significant dust deposition including dust macules. In spite of the inorganic dust deposits, with adjacent tissue lesions evident from the radiological findings (which were interpreted as atypical for pneumoconiosis) and the presence of granulomas in lung tissue, a diagnosis of necrotizing sarcoid granulomatosis was made, which was later changed to mixed-dust pneumoconiosis on further detailed examination. Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy (SEM/EDS) analysis of individual particles showed predominantly Si (silica or silicon carbide [SiC]) and Al particles (consistent with

aluminum metal and/or oxide), as well as numerous Al silicates, Ti, and occasional Zr, Nb, V, steel, including Si fibers (consistent with SiC). We present the controversy about the pathogenesis of the lung disorder and whether it represents an occupational disease - which is more or less representative for many such cases. © 2018 Elsevier B.V.

Chen, C-F., Chio, C-P., Yuan, T-H.*, et al.* (2018) Increased cancer incidence of Changhua residents living in Taisi Village north to the No. 6 Naphtha Cracking Complex. *Journal of the Formosan Medical Association,* 117(12): 1101-1107.
Available at:
https://www.sciencedirect.com/science/article/pii/S0929664617307313/pdfft?md5=583ef7986d7aae0b3177005d0e759dda&pid=1-s2.0-S0929664617307313-main.pdf
Keywords: Cancer; Changhua; Petrochemical complex

Abstract
Background/Purpose: Cancer risks of residents living north to the No. 6 Naphtha Cracking Complex has not been studied before. Methods: Our study subjects were recruited in 2014–16 from three zones north to the No. 6 Naphtha Cracking Complex, which included 229 participants from the Taisi Village (average 5.5 km from the complex), 1333 participants from the other 14 villages in Dacheng Township (9.2 km), and 372 participants from the Zhutang Township (19.9 km). Their occurrence of cancer in years-post-complex-operation (YPO) was defined by having a new cancer recorded (ICD-9: 140–208) in National Health Insurance Research Database since 1999. Poisson regression was conducted to compare incidence rate ratio among three zones in 10–16 YPO. Results: We found that all-cause cancer incidence of 10–16 YPO (per 1,000 person-years) in Taisi Village (8.44) was higher than that in Dacheng (3.42) and Zhutang (2.72). Taisi residents had significantly higher concentrations of V, Cr, Mn, Ni, Cu, As, Cd, and Tl than Dacheng and Zhutang residents. The all-cause cancer incidence rate ratio between 10–16 and 0–9 YPO was 8.44 for Taisi residents. All-cause cancer incidence rate of Taisi residents was 2.55 times higher than Dacheng residents (95% CI: 1.89–3.45) and 2.43 times higher than Zhutang residents (95% CI: 1.54–3.84) in 10–16 YPO. Conclusion: We conclude that all-cause cancer risk was significantly increased for Taisi residents living near the No. 6 Naphtha Cracking Complex for 10–16 years after the complex began operating. © 2018.

Cheng, Y., Sun, T., Yin, C.*, et al.* (2019) Downregulation of PTEN by sodium orthovanadate protects the myocardium against ischemia/reperfusion injury after chronic atorvastatin treatment. *Journal of Cellular Biochemistry,* 120(3): 3709-3715.
Keywords: Akt signaling; atorvastatin; ischemia/reperfusion injury; PTEN; sodium orthovanadate

Abstract
Acute statin treatment has been reported to be critical in protecting the cardiac cells against ischemia/reperfusion injury by activating PI3K/Akt signal pathway. In vitro rat myocardial ischemia/reperfusion model, chronic statin treatment led to upregulation of phosphatase and tensin homolog (PTEN). This has been potentially indicated the correlation in PTEN and protective effect of statin on myocardium. In this current study, we evaluated the role of sodium orthovanadate a nonspecific inhibitor to PTEN and its correlation with atorvastatin on protecting myocardium against ischemia/reperfusion injury. We found a long-term statin treatment could increase the PTEN level, and this process was counteracted in the presence of sodium orthovanadate. However, the phosphotyrosine level was not affected by this statin. Besides, this process was mediated by Akt signaling since phosphorylated Akt level was altered by statin and sodium orthovanadate treatment. In a conclusion, this study showed a

potential mechanism underlying PTEN-induced attenuation in long-term statin's therapeutic effect, which provided the new insight into the synergic role of PTEN and atorvastatin in protecting cardiac cells against ischemia/reperfusion injury. © 2018 Wiley Periodicals, Inc.

Costa, B.C., Tokuhara, C.K., Rocha, L.A.*, et al.* (2019) Vanadium ionic species from degradation of Ti-6Al-4V metallic implants: In vitro cytotoxicity and speciation evaluation. *Materials Science & Engineering.C, Materials for Biological Applications,* 96: 730-739.
Keywords: Cytotoxicity; Ionic speciation; Oxidovanadium(IV); Ti-6Al-4V; Tribocorrosion; Vanadate(V)

Abstract
Among the metallic materials used in biomedical industry, the most common choice for orthopedics and dental implants is titanium (Ti) and its alloys, mainly due to their superior corrosion and tribocorrosion resistance and biocompatibility. Under different conditions in vivo, such as different pH levels, composition of body fluid and mechanical loads, metallic materials may suffer from degradation, resulting in the release of undesired wear particles and ions. In particular, the Ti-6Al-4V system represents almost half of the production of Ti as a biomaterial and many concerns have been raised about titanium, aluminum and vanadium ions releasing. This work evaluates the cytotoxic effects of vanadium ionic species generated from Ti-6Al-4V surfaces regarding mouse pre-osteoblasts and fibroblasts. In our cell viability tests, we noticed a significant decrease in the fibroblasts' cell viability with vanadium concentrations (23muM) close to those previously reported to be observed in vivo in patients with poor functioning of their medical devices based on Ti-6Al-4V (30muM). Speciation modelling was carried-out, for the first time, to this system. Results of the modelling reveal that vanadates(V), namely H2VO4(-) and HVO4(2-), are the main species present in cell culture media. Otherwise, in synovial fluids of individuals with poorly functioning implants, wherein the concentration of vanadium may go up to ca. 30muM, the tentative theoretical speciation data indicates a high occurrence probability for V(V)- and V(IV)-species bound to albumin and hyaluronic acid. In conclusion, even though relatively low concentrations of vanadium may be released from Ti-6Al-4V implants in vivo, the continuous contact with peri-implant cells for long periods of time may represent a potentially hazardous situation.

Fatola, O.I., Olaolorun, F.A., Olopade, F.E.*, et al.* (2019) Trends in vanadium neurotoxicity. *Brain Research Bulletin,* 145: 75-80.
Keywords: Vanadium; Environmental pollution; Neurotoxicity; Neurodegeneration

Abstract
Vanadium, atomic number 23, is a transition metal widely distributed in nature. It is a major contaminant of fossil fuels and is widely used in industry as catalysts, in welding, and making steel alloys. Over the years, vanadium compounds have been generating interests due to their use as therapeutic agents in the control of diabetes, tuberculosis, and some neoplasms. However, the toxicity of vanadium compounds is well documented in literature with occupational exposure of workers in vanadium allied industries, environmental pollution from combustion of fossil fuels and industrial exhausts receiving concerns as major sources of toxicity and a likely predisposing factor in the aetiopathogenesis of neurodegenerative diseases. A lot has been done to understand the neurotoxic effects of vanadium, its mechanisms of action and possible antidotes. Sequel to our review of the subject in 2011, this present review is to detail the recent insights gained in vanadium neurotoxicity.

Kim, K., Wang, C-H., Ok, Y.S.*, et al.* (2019) Heart developmental toxicity by carbon black waste generated from oil refinery on zebrafish embryos (Danio rerio): Combined toxicity on heart function by nickel and vanadium. *Journal of Hazardous Materials,* 363: 127-137.
Keywords: Carbon black waste; Heart defects; Mixture toxicity; Vanadium; Zebrafish embryo

Abstract
This study assessed the developmental toxicities of water-soluble carbon black wastes (CBW) extract (1:5, w/v) in zebrafish embryos (Danio rerio). Acute embryonic toxicity was performed following OECD guideline 236. Analysis using ICP-OES revealed that nickel (Ni) and vanadium (V) were predominant in CBW. Embryos exposed to CBW exhibited developmental delay, along with pericardial and yolk sac edemas. Malformed heart chambers were found in the CBW-exposed embryos and heart rates were significantly reduced since 48 h post fertilization (hpf). After RT-qPCR analysis, two cardiac forming-related genes, amhc and nppa responsible for atrial cardiac myofibril assembly and cardiac muscle cell proliferation, were up-regulated after 96 hpf. The increased mortality and delayed yolk-sac development appeared related to CBW-induced decrease in pH to about 5.5. Individual treatments of Ni and V did not cause identical toxic effects as CBW showed. At 100 ppm, V had a pH of approximately 5.5, causing developmental delay and pericardial edema in zebrafish embryos. At the same pH, combined Ni and V induced morphological anomalies and reduced heart rates similar to CBW-exposed embryos. Conclusively, this study demonstrates that environmental runoff is a serious concern, and thus, CBW incineration bottom ash should be treated carefully before disposal in landfills. © 2018 Elsevier B.V.

Lewicka, I., Kocyłowski, R., Grzesiak, M.*, et al.* (2019) Relationship between pre-pregnancy body mass index and mineral concentrations in serum and amniotic fluid in pregnant women during labor. *Journal of Trace Elements in Medicine and Biology,* 52: 136-142.
Keywords: Amniotic fluid; Body mass index; Pregnancy; Pregnancy outcomes; Trace elements

Abstract
The aim of the study was to determine the correlations between body mass index (BMI) values before pregnancy and the concentrations of selected elements (Mg, Co, Cu, Zn, Sr, Cd, Ba, Pb, U, Ca, Cr, Al, Mn, V, Fe) in blood serum and amniotic fluid (AF) in pregnant women. Elemental analysis of serum and amniotic fluid in 225 Polish women (Caucasian/white) showed a relationship between the concentration of minerals in the above-mentioned samples and the pre-pregnancy BMI. Analysis of blood serum was performed by using ICP-MS and it demonstrated that iron concentration was significantly lower in overweight and obese women. Being underweight in pregnant women was associated with a significantly lower concentration of magnesium and cobalt in the blood serum. Both underweight and overweight women were associated with significantly lower concentrations of calcium and strontium in the blood serum. The concentration of cobalt was significantly higher in underweight women. The concentration of lead in the blood serum of overweight and obese women was significantly higher than in other groups. Analysis of the AF showed that the concentration of copper was significantly lower in overweight and obese women, and the concentration of manganese and vanadium significantly higher than in other groups of women. A deficiency in essential minerals and an excess of heavy metals in women may be associated with abnormal body weight and this is important in the etiopathogenesis of pregnancy and fetal development disorders. © 2018 Elsevier GmbH.

Liang, C.M., Wu, X.Y., Huang, K.*, et al.* (2019) Trace element profiles in pregnant women's sera and umbilical cord sera and influencing factors: Repeated measurements. *Chemosphere,* 218: 869-878.

Keywords: Birth cohort; China; Pregnant women; Repeated measurements; Trace elements

Abstract
In utero exposure to toxic heavy metals and deficient or excessive essential trace elements during pregnancy may have adverse effects on pregnant women and their offsprings, which are of great concern. The objective of the present study was to characterize serum concentrations of multiple trace elements at multiple time points during pregnancy in Chinese women. Three thousand four hundred and sixteen pregnant women in total were included from MABC (Ma'anshan Birth Cohort) study. Fasting sera in the morning and questionnaires were obtained at three separate follow-up visits. Nineteen trace elements from serum samples were analyzed, including aluminum (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), barium (Ba), thallium (Tl), lead (Pb), calcium (Ca), magnesium (Mg), mercury (Hg) and molybdenum (Mo). The total detection rates for most elements were 100% rather than Ni (99.98%), As (99.97%), Cd (99.6%), Ba (99.9%), Pb (99.8%), Hg (99.8%). The concentration distributions of 19 elements varied vastly. Median concentrations for all trace elements ranged from 38.5 ng/L to 102.9 mg/L. The moderate interclass correlation coefficients (ICCs) were observed for Co, Cu, Se and Hg, ranging from 0.40 to 0.62; the lower ICCs, ranging from 0.13 to 0.32 were for Fe, Zn, Cd, Ba, Tl, Mg and Mo. The intraclass correlation effects were not observed for the remaining elements, such as Al, V, Cr, Mn, Ni, As and Pb. The concentrations of each element between three time points were significantly different; significant differences were also found between any two time points except for Ni, Cd and Mo. Many factors could affect the levels of trace elements, and a very important factor of them was season. Consequently, a single measurement of elements in sera seems not enough to describe exposure levels throughout pregnancy; additionally, season affected exposure levels of trace elements with moderate ICCs showed certain regularity. Future analyses should take sampling seasons into consideration carefully.

Liu, L., Urch, B., Szyszkowicz, M.*, et al.* (2018) Metals and oxidative potential in urban particulate matter influence systemic inflammatory and neural biomarkers: A controlled exposure study. *Environment International,* 121: 1331-1340.
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https://www.sciencedirect.com/science/article/pii/S0160412018320014/pdfft?md5=5f7964304a63a141b04ae2c52a1c1eef&pid=1-s2.0-S0160412018320014-main.pdf

Abstract
Background: Oxidative stress and inflammation are considered to be important pathways leading to particulate matter (PM)-associated disease. In this exploratory study, we examined the effects of metals and oxidative potential (OP) in urban PM on biomarkers of systemic inflammation, oxidative stress and neural function. Methods: Fifty-three healthy non-smoking volunteers (mean age 28 years, twenty-eight females) were exposed to coarse (2.5–10 μm, mean 213 μg/m 3), fine (0.15–2.5 μm, 238 μg/m 3), and/or ultrafine concentrated ambient PM (<0.3 μm, 136 μg/m 3). Exposures lasted 130 min, separated by ≥2 weeks. Metal concentrations and OP (measured by ascorbate and glutathione depletion in synthetic airway fluid) in PM were analyzed. Blood and urine samples were collected pre-exposure, and 1-h and 21-h post exposure for assessment of biomarkers. We used mixed-regression models to analyze associations adjusting for PM size and mass concentration. Results: Results for metals were expressed as change (%) from daily pre-exposure biomarker levels after exposure to a metal at a level equivalent to the mean concentration. Exposure to various metals (silver, aluminum, barium, copper, iron, potassium, lithium, nickel, tin, and/or vanadium) was significantly associated with increased levels of various blood or urinary biomarkers. For

example, the blood inflammatory marker vascular endothelia growth factor (VEGF) increased 5.3% (95% confidence interval: 0.3%, 10.2%) 1-h post exposure to nickel; the traumatic brain injury marker ubiquitin C-terminal hydrolase L1 (UCHL1) increased 11% (1.2%, 21%) and 14% (0.3%, 29%) 1-h and 21-h post exposure to barium, respectively; and the systemic stress marker cortisol increased 1.5% (0%, 2.9%) and 1.5% (0.5%, 2.8%) 1-h and 21-h post exposure to silver, respectively. Urinary DNA oxidation marker 8-hydroxy-deoxy-guanosine increased 14% (6.4%, 21%) 1-h post exposure to copper; urinary neural marker vanillylmandelic acid increased 29% (3%, 54%) 1-h post exposure to aluminum; and urinary cortisol increased 88% (0.9%, 176%) 1-h post exposure to vanadium. Results for OP were expressed as change (%) from daily pre-exposure biomarker levels after exposure to ascorbate-related OP at a level equivalent to the mean concentration, or for exposure to glutathione-related OP at a level above the limit of detection. Exposure to ascorbate- or glutathione-related OP was significantly associated with increased inflammatory and neural biomarkers including interleukin-6, VEGF, UCHL1, and S100 calcium-binding protein B in blood, and malondialdehyde and 8-hydroxy-deoxy-guanosine in urine. For example, UCHL1 increased 9.4% (1.8%, 17%) in blood 21-h post exposure to ascorbate-related OP, while urinary malondialdehyde increased 19% (3.6%, 35%) and 8-hydroxy-deoxy-guanosine increased 24% (2.9%, 48%) 21-h post exposure to ascorbate- and glutathione-related OP, respectively. Conclusion: Our results from this exploratory study suggest that metal constituents and OP in ambient PM may influence biomarker levels associated with systemic inflammation, oxidative stress, perturbations of neural function, and systemic physiological stress. © 2018.

Mikelson, C.K., Troisi, J., LaLonde, A.*, et al.* (2019) Placental concentrations of essential, toxic, and understudied metals and relationships with birth outcomes in Chattanooga, TN. *Environmental Research,* 168: 118-129.

Keywords: Birth weight; Lead; Manganese; Metals; Placenta; Rhodium

Abstract

Background: Comprehensive examinations of placental metal concentrations and correlations with infant parameters are under-investigated. Chattanooga, Tennessee's consistently high incidence of low birth weight and potential for metal exposure provides an ideal opportunity to investigate potential correlations. Objectives: To investigate the associations between a wide variety of metals in placental tissue and multiple infant parameters. Methods: A total of 31 elements were screened via ICP-MS in 374 individual placental samples. Of those, 14 were quantifiable in > 86% of the samples. We examined correlations between metal concentrations and infant parameters (birth weight, gestational age, birth weight centile, placental weight, birth length and head circumference). We fit multivariable regression models to estimate the covariate-adjusted associations of birth weight with ln-transformed concentrations of each of the 14 metals and used generalized additive models to examine nonlinear relationships. Results: Some of the strongest relationships with infant parameters came from several lesser-studied metals. Placental rhodium concentrations were negatively correlated with almost all infant parameters. In the fully adjusted regression model, birth weight was significantly associated with several metals. On an IQR (25th to the 75th percentile) basis, estimated changes in birthweight were: for cobalt (82.5 g, IQR=6.05 μg/kg, p = 0.006), iron (−51.5 g, IQR = 171800 μg/kg, p = 0.030), manganese (−27.2 g, IQR=152.1 μg/kg, p = 0.017), lead (−72.7 g, IQR=16.55 μg/kg, p = 0.004) and rhodium (−1365.5 g, IQR = 0.33 μg/kg, p < 0.001). Finally, a generalized additive model showed significant nonlinear relationships between birth weight and concentrations of Co and Rh. Conclusions: Our comprehensive examination of placental metals illustrate many strong associations between lesser-studied metals and infant parameters. These data, in combination with our correlations

of well-studied metals, illustrate a need to consider in utero exposure to a broad array of metals when considering fetal development. © 2018 Elsevier Inc.

O'Brien, K.M., White, A.J., Sandler, D.P.*, et al.* (2019) Do Post-breast Cancer Diagnosis Toenail Trace Element Concentrations Reflect Prediagnostic Concentrations? *Epidemiology (Cambridge, Mass.),* 30(1): 112-119.

Abstract
BACKGROUND: Exposure to trace elements may affect health, including breast cancer risk. Trace element levels in toenails are potentially useful biomarkers of exposure, but their reliability is not established. We assessed the reproducibility of toenail element concentrations over time and whether concentrations change following a breast cancer diagnosis. METHODS: We assessed trace element levels in toenails collected at two time points from 221 women (111 with and 110 without an intervening breast cancer diagnosis). We measured levels of arsenic, cadmium, chromium, cobalt, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, selenium, tin, vanadium, and zinc using inductively coupled plasma mass spectrometry in samples collected at baseline and 4-10 years later. We compared trace element concentrations over time using Spearman's rank correlation coefficient (R). We used linear models to examine the magnitude and direction of changes and the influence of a breast cancer diagnosis. RESULTS: Overall, we observed positive correlations (R = 0.18-0.71) between paired samples for all trace elements. However, nickel (R = -0.02) and antimony (R = 0.12) were not correlated among cases. We observed decreases in cadmium, chromium, mercury, manganese, molybdenum, nickel, and lead between baseline and follow-up, but case status was unrelated to these changes. The declines are consistent with decreases over calendar time rather than age time. CONCLUSIONS: Toenail trace element concentrations were correlated over time, but many elements showed systematic decreases by calendar year. Aside from nickel and antimony, postdiagnostic toenail levels correlated with prediagnostic levels, providing support for using postdiagnostic toenail samples in retrospective studies.

Skalny, A.V., Simashkova, N.V., Skalnaya, A.A.*, et al.* (2018) Trace element levels are associated with neuroinflammatory markers in children with autistic spectrum disorder. *Journal of Trace Elements in Medicine and Biology,* 50: 622-628.
Keywords: Autism spectrum disorders; Cadmium; Magnesium; Manganese; Neuroinflammation

Abstract
The objective of the present study was to estimate the association between brain inflammatory markers and serum trace element levels as assessed by inductively coupled plasma mass spectrometry at NexION 300D. Leukocyte elastase (LE), α1-proteinase inhibitor (α1-PI) activity, anti-nerve growth factor-antibodies (anti-NGF-Ab), and anti-myelin basic protein-antibodies (anti-MBP-Ab) levels were assessed as inflammatory markers. The obtained data demonstrate that the increase in LE and α1-PI activity is associated with higher serum Cr and Cu levels, respectively. The increase in Anti-NGF-Ab levels was associated with a nearly significant 16% increase in serum Mn levels. Autistic children with high MBP-Ab levels were characterized by 28% higher serum Mn and lower Mg concentration. The results of correlation analysis were generally in agreement with the outcome of group comparisons. Regression analysis demonstrated that serum Mg was significantly negatively associated with LE activity, whereas both serum Fe and V concentrations were characterized by a positive influence on the parameter. In turn, serum Cu was a significant predictor of α1-PI, as well as Cr levels. At the same time, the serum concentrations of Cd and Fe were found to be inversely

associated with α1-PI levels. Serum Cd and Mn levels were significant positive predictors of anti-MBP-Ab levels, whereas Mg levels had a negative impact on anti-MBP-Ab values. Generally, the obtained data demonstrate the interrelationship between trace element homeostasis and neuroinflammation in autism. Hypothetically, modulation of trace element status may be used for reduction of neuroinflammatory response, although further studies are required to reveal the underlying mechanisms of the observed associations. © 2018 Elsevier GmbH.

Sobhanardakani, S. (2019) Ecological and Human Health Risk Assessment of Heavy Metal Content of Atmospheric Dry Deposition, a Case Study: Kermanshah, Iran. *Biological Trace Element Research,* 187(2): 602-610.
Keywords: Atmospheric dry deposition; Health risk assessment; Heavy metals; Iran; Potential ecological risk

Abstract
The present study was intended to investigate the ecological and human health risk of cobalt, nickel, and vanadium in the atmospheric dry deposition of the Kermanshah city, Iran, in 2015. Totally 54 samples of atmospheric dry deposition were collected from the three regions of the city with different traffic intensity, and after acid digestion of the samples with ultrapure concentrated HNO3, the total contents of the metals were determined using inductively coupled plasma optical emission spectrometer (ICP-OES). Also, all statistical analyses were performed using the SPSS statistical package. The atmospheric dry deposition element contents increase according to the following descending order for both autumn seasons: Ni > Co > V. The results of potential ecological risk analysis demonstrated that metals in the samples are in low ecological risk levels, whereas the results of human health risk assessment showed that ingestion is the main exposure pathway of heavy metals in the dust to the local residents compared with inhalation and dermal pathways. Also, the upper limit of the 95% confidence interval (95% UCL) of hazard indices for non-carcinogenic risks of all analyzed metals in the dust samples was within the safe level for both children and adults. On the other hand, the carcinogenic risk levels of Co and Ni were all lower than the acceptable range (10(-6)-10(-4)) to local citizens. Consequently, the results advocate the necessity of understanding the heavy metal content of atmospheric dry deposition and regular monitoring of air pollution.

Tinkov, A.A., Skalnaya, M.G., Simashkova, N.V.*, et al.* (2019) Association between catatonia and levels of hair and serum trace elements and minerals in autism spectrum disorder. *Biomedicine and Pharmacotherapy,* 109: 174-180.
Available at:
https://www.sciencedirect.com/science/article/pii/S0753332218360529/pdfft?md5=b073affbe2041c69b36187ce13628166&pid=1-s2.0-S0753332218360529-main.pdf
Keywords: Autism spectrum disorder; Catatonia; Children; Mercury; Neurotoxicity

Abstract
The objective of the study was to investigate the association between catatonia in autism spectrum disorder (ASD) and the levels of hair and serum trace elements and minerals in children with ASD. The levels of hair and serum trace elements and minerals of boys suffering from ASD with (n = 30) and without (n = 30) catatonia, as well as 30 age- and sex-matched neurotypical controls were assessed using ICP-MS. Hair calcium (Ca) and selenium (Se) levels were lower in ASD patients as compared to the controls. Hair mercury (Hg) levels in ASD patients were more than 3-fold and 2-fold higher as compared to the controls and children with catatonia in ASD. Hair iodine (I) and manganese (Mn) were the lowest and the highest in

ASD + Catatonia, respectively. Serum aluminium (Al) and cadmium (Cd) levels in healthy controls were significantly higher in comparison to the patients of both groups. Serum chromium (Cr), copper (Cu) levels were significantly increased in patients with ASD and catatonia, whereas vanadium (V) levels were elevated in patients both with and without catatonia. Multiple regression analysis demonstrated that hair Hg and serum Al and Cd levels were negatively associated with catatonia in ASD in crude and adjusted models. Although the etiology of catatonia in ASD is unclear, the obtained data demonstrate that catatonic symptoms in ASD may be at least partially mediated by altered trace element levels. Further studies are required to elucidate the role of trace elements in the potential signaling mechanisms of catatonia.

Ubaid Ali, M., Liu, G., Yousaf, B.*, et al.* (2019) Evaluation of floor-wise pollution status and deposition behavior of potentially toxic elements and nanoparticles in air conditioner dust during urbanistic development. *Journal of Hazardous Materials,* 365: 186-195.
Keywords: Air conditioner dust; nanoparticles; potential toxic elements; urban areas

Abstract
The study was undertaken to investigate deposition behaviors of various size-segregated particles and indoor air quality using dust accumulated on the air conditioner filter acting as a sink for PTEs and nanoparticles that can pose a significant health risk. However, the particulate matter size and chemical composition in AC dust and its relationship with PTEs remains uncertain. Current study aims to investigate the PTEs and nanoparticles composition of AC dust using different analytical approaches including ICP-MS, XRD, XPS, SEM/TEM along with EDS and Laser Diffraction particle size analyzer. The mean concentration of PTEs like Al, As, Cd, Cu, Li, Pb, Sb, Se, Sn, Ti, V and Zn exceeded the corresponding background value. Pb, As, Sn, Sb, Cd were categorizing under geo-accumulation index class IV. Most of the particles were found to be > 100 μm and it decreased significantly with increase in floor altitude. A significantly negative correlation was found between particles size and PTEs concentration showing a significant increase in PTEs content with decrease in particles size. The XPS results showed dominant peaks for TiO 2 , Ti-O-N, As 2 O 3 , Fe +3 , Fe +2 , Al-OH and Al 2 0 3 . Additionally, As, Pb, Si and Fe were dominant metallic nanoparticles identified using SEM/TEM along with EDS. © 2018 Elsevier B.V.

Vanska, M., Diab, S.Y., Perko, K.*, et al.* (2019) Toxic Environment of war: Maternal prenatal heavy metal load predicts infant emotional development. *Infant Behavior & Development,* 55: 1-9.
Keywords: Child development; Emotional development; Heavy metals; PTSD; War trauma

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

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

Wan, Z.Z., Chen, H.G., Lu, W.Q.*, et al.* (2019) Metal/metalloid levels in urine and seminal plasma in relation to computer-aided sperm analysis motion parameters. *Chemosphere,* 214: 791-800.

Keywords: Dimenhydrinate/chemistry; Humans; Male; Metalloids/urine; Semen/chemistry; Semen Analysis/methods; Spermatozoa/physiology; CASA motion parameters; epidemiology; metals; seminal plasma; urine

Abstract

BACKGROUND: Exposure to high levels of metals/metalloids may impair semen quality. Computer-aided sperm analysis (CASA) can be used for kinematic analysis of spermatozoa, which provides additional insights into sperm motion characteristics. OBJECTIVE: To explore the associations of urinary and seminal plasma metal/metalloid concentrations with CASA motion parameters and assess the degree of correspondence between the two sample types. METHODS: Eighteen metals/metalloids in seminal plasma and repeated urine samples were determined among 746 men recruited from a reproductive center. We assessed their associations with 6 CASA motion parameters [i.e., straight-line velocity (VSL), curvilinear velocity (VCL), average path velocity (VAP), linearity (LIN), straightness (STR) and amplitude head displacement (ALH)] using multivariable linear regression models. RESULTS: We found significantly inverse dose-dependent relationships between seminal plasma arsenic (As) and VSL, VCL and VAP, between seminal plasma selenium (Se) and VSL and VAP, between seminal plasma zinc (Zn) and STR and LIN, and between seminal plasma manganese (Mn) and LIN in single-metal models [all false discovery rate (FDR) adjusted P for trend<0.05]. These dose-response relationships remained statistically significant based on multiple-metal models and restricted cubic spline functions. Metal/metalloid concentrations in urine poorly predicted the same-day seminal plasma concentrations [coefficient of determination (R(2))<0.15]. We didn't find any significant associations between urinary metal/metalloid concentrations and the CASA motion parameters. CONCLUSION: Exposure to high levels of As, Se, Mn and Zn may impair sperm motion capacity. Concentrations of metals/metalloids in spot urine samples cannot accurately predict same-day seminal plasma exposure levels.

Wang, L., Chen, M., He, P.*, et al.* (2019) Composition and spatial distribution of elements and isotopes of a giant human bladder stone and environmental implications. *Science of the Total Environment,* 650: 835-846.

Keywords: Carbon and nitrogen isotopes; Environmental implications; Spatial distribution; Trace elements; Urinary stone

Abstract

The composition and spatial distribution of minerals, trace elements, as well as carbon and nitrogen isotopes from the outer crust to inner nucleus of a 20-year old giant human bladder stone comprising thirteen layers were intensively investigated. Calcium oxalate monohydrate

(COM) was found to concentrate in the inner and middle layers, struvite was concentrated in middle and outer layers, and fluorapatite occurred in almost all layers. The spatial distribution of minerals has the potential to provide preliminary knowledge regarding the long-term urine composition, or even the physiological condition of the patient. The stable carbon isotope ratio (δ 13 C) and stable nitrogen isotope ratio (δ 15 N) were measured in each layer and significant correlation was found between δ 13 C with calcium oxalate monohydrate content and between δ 15 N and struvite content. Nearly constant values of −23.2‰ and 7.1‰ for δ 13 C and δ 15 N, respectively, were found in the organic components of the stone. Both isotope ratios indicate a long-term fixed diet consisting mainly of C3 plants, such as rice and wheat, for the 20-year time period of the stone formation. In addition, eighteen elements (Ca, P, Mg, K, Na, Al, Fe, Zn, Pb, Cu, Sr, Ba, Ti, V, Cr, Ni, Mn and Co) were measured in all the layers. The trace elements Al, Fe, Cu, Zn, Pb, Sr, Ba and Ti showed a similar spatial distribution pattern from the outer crust to the inner core. Although there were complex correlations between elements and minerals, Factor Analysis suggests that the occurrence of these elements in stones may be mainly the result of environmental exposure to metals during the formation of the stone, indicating that urinary stones may serve as potential long-term biomonitors. In particular, Ni and Cr showed a distinct distribution pattern in the stone, which may relate to human metabolic activities.

Wang, Y-X., Chen, H-G., Li, X-D.*, et al.* (2018) Concentrations of vanadium in urine and seminal plasma in relation to semen quality parameters, spermatozoa DNA damage and serum hormone levels. *Science of the Total Environment,* 645: 441-448.
Keywords: DNA damage; Reproductive hormone; Semen quality; Vanadium

Abstract
Widespread human exposure to vanadium has been well documented. Vanadium exposure was reported to induce male reproductive toxicity in toxicological studies, yet human epidemiologic studies are lacking. Here we determined the associations between environmental exposure to vanadium and semen quality, spermatozoa DNA damage and serum reproductive hormones. Concentrations of vanadium in seminal plasma and repeated urine samples were determined among 764 men recruited from a reproductive medicine centre. Associations of vanadium concentrations with semen quality parameters (n = 764), DNA integrity measures (n = 404) and serum reproductive hormones (n = 381) were assessed by logistic or linear regression models with adjustment for potential confounders. Significant positive dose–response relationships were observed between vanadium concentrations in seminal plasma and tail length and serum estradiol, as well as odds ratios for a below-reference-value sperm concentration; whereas inverse relationships between seminal plasma vanadium with total testosterone (T) and free T (all p values for trends <0.05) were observed. These relationships were maintained after adjusting for seminal plasma concentrations of other elements (i.e., arsenic, cadmium, copper, selenium, or tin). No significant associations was revealed between urinary vanadium concentrations and semen quality, spermatozoa DNA integrity and reproductive hormones. Our findings suggested that elevated vanadium exposure may be adversely associated with male reproductive health, and that seminal plasma vanadium may be a more direct exposure biomarker for the male reproductive system than urinary vanadium.

Yang, Y., Ruan, Z., Wang, X.*, et al.* (2018) Short-term and long-term exposures to fine particulate matter constituents and health: A systematic review and meta-analysis. *Environmental Pollution (Barking, Essex : 1987),* 247: 874-882.
Keywords: Air pollution; Constituents of fine particulate matter; Morbidity; Mortality; PM(2.5)

Abstract
BACKGROUND: Fine particulate matter (Particulate matter with diameter</=2.5mum) is associated with multiple health outcomes, with varying effects across seasons and locations. It remains largely unknown that which components of PM2.5 are most harmful to human health. METHODS: We systematically searched all the relevent studies published before August 1, 2018, on the associations of fine particulate matter constituents with mortality and morbidity, using Web of Science, MEDLINE, PubMed and EMBASE. Studies were included if they explored the associations between short term or long term exposure of fine particulate matter constituents and natural, cardiovascular or respiratory health endpoints. The criteria for the risk of bias was adapted from OHAT and New Castle Ottawa. We applied a random-effects model to derive the risk estimates for each constituent. We performed main analyses restricted to studies which adjusted the PM2.5 mass in their models. RESULTS: Significant associations were observed between several PM2.5 constituents and different health endpoints. Among them, black carbon and organic carbon were most robustly and consistently associated with all natural, cardiovascular mortality and morbidity. Other potential toxic constituents including nitrate, sulfate, Zinc, silicon, iron, nickel, vanadium, and potassium were associated with adverse cardiovascular health, while nitrate, sulfate and vanadium were relevant for adverse respiratory health outcomes. CONCLUSIONS: Our analysis suggests that black carbon and organic carbon are important detrimental components of PM2.5, while other constituents are probably hazardous to human health. However, more studies are needed to further confirm our results.

Yu, Y-Q. & Yang, J-Y. (2019) Oral bioaccessibility and health risk assessment of vanadium(IV) and vanadium(V) in a vanadium titanomagnetite mining region by a whole digestive system in-vitro method (WDSM). *Chemosphere,* 215: 294-304.
Keywords: Oral bioaccessibility; Oral ingestion; Vanadium(IV); Vanadium(V); Whole digestive system in-vitro method (WDSM)

Abstract
Oral bioaccessibility of vanadium(IV) and vanadium(V) in soil, dust and concentrate fines from a vanadium titanomagnetite mining region was assessed by a whole digestive system in-vitro scheme. The scheme including the addition of sweat and the large intestinal digestion was used to estimate the oral bioaccessibility of vanadium(IV) and vanadium(V) in the whole digestive system for the first time. Higher oral bioaccessibility of vanadium(IV) and vanadium(V) was determined in gastric and small intestinal phases demonstrating that their major roles for vanadium digestion and absorption. The decreasing order of the oral bioaccessibility of vanadium(IV) and vanadium(V) in each digestive phase was stomach, small intestine, large intestine and mouth. Higher oral bioaccessibility of vanadium(V) in the whole digestion indicated its higher risk potential for human than vanadium(IV). Lower oral bioaccessibility of vanadium(IV) and vanadium(V) determined in bionic digestion illustrated detoxicity potential of human body for ingested vanadium. Compared with soil and dust, higher digestion rate of vanadium in vanadium titanomagnetite concentrate fines indicated its higher risk for human, especially for mining workers. Based on vanadium oral bioaccessibility, hazard quotients of the vanadium were much less than the critical level suggested for no non-carcinogenic risks to the populations surrounding the sampling sites. Indeed, compared with the estimations based on total vanadium content, the incorporation of oral vanadium bioaccessibility into risk assessments could give more realistic information.

3. BIOLOGICAL MECHANISMS

Erratum to: Inflammatory cytokine release from human peripheral blood mononuclear cells exposed to polyetheretherketone and titanium-6 aluminum-4 vanadium in vitro (Journal of Biomaterials Applications, (2018), 33, 2, (245-258), 10.1177/0885328218786005) (2019) *J Biomater Appl,* : 0885328219827162.
Available at: https://doi.org/10.1177/0885328219827162

Costa, B.C., Tokuhara, C.K., Rocha, L.A.*, et al.* (2019) Vanadium ionic species from degradation of Ti-6Al-4V metallic implants: In vitro cytotoxicity and speciation evaluation. *Materials Science & Engineering.C, Materials for Biological Applications,* 96: 730-739.
Keywords: Cytotoxicity; Ionic speciation; Oxidovanadium(IV); Ti-6Al-4V; Tribocorrosion; Vanadate(V)

Abstract
Among the metallic materials used in biomedical industry, the most common choice for orthopedics and dental implants is titanium (Ti) and its alloys, mainly due to their superior corrosion and tribocorrosion resistance and biocompatibility. Under different conditions in vivo, such as different pH levels, composition of body fluid and mechanical loads, metallic materials may suffer from degradation, resulting in the release of undesired wear particles and ions. In particular, the Ti-6Al-4V system represents almost half of the production of Ti as a biomaterial and many concerns have been raised about titanium, aluminum and vanadium ions releasing. This work evaluates the cytotoxic effects of vanadium ionic species generated from Ti-6Al-4V surfaces regarding mouse pre-osteoblasts and fibroblasts. In our cell viability tests, we noticed a significant decrease in the fibroblasts' cell viability with vanadium concentrations (23muM) close to those previously reported to be observed in vivo in patients with poor functioning of their medical devices based on Ti-6Al-4V (30muM). Speciation modelling was carried-out, for the first time, to this system. Results of the modelling reveal that vanadates(V), namely $H_2VO_4^-$ and HVO_4^{2-}, are the main species present in cell culture media. Otherwise, in synovial fluids of individuals with poorly functioning implants, wherein the concentration of vanadium may go up to ca. 30muM, the tentative theoretical speciation data indicates a high occurrence probability for V(V)- and V(IV)-species bound to albumin and hyaluronic acid. In conclusion, even though relatively low concentrations of vanadium may be released from Ti-6Al-4V implants in vivo, the continuous contact with peri-implant cells for long periods of time may represent a potentially hazardous situation.

Domingo-Relloso, A., Grau-Perez, M., Galan-Chilet, I.*, et al.* (2019) Urinary metals and metal mixtures and oxidative stress biomarkers in an adult population from Spain: The Hortega Study. *Environment International,*123: 171-180.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018312947/pdfft?md5=59346fc87b7c17341a269ec52bc3118c&pid=1-s2.0-S0160412018312947-main.pdf
Keywords: Metal mixtures; Oxidative stress; Population-based; Urine metals

Abstract
Introduction: Few studies have investigated the role of exposure to metals and metal mixtures on oxidative stress in the general population. Objectives: We evaluated the cross-sectional association of urinary metal and metal mixtures with urinary oxidative stress biomarkers, including oxidized to reduced glutathione ratio (GSSG/GSH), malondialdehyde (MDA), and 8-oxo-7,8-dihydroguanine (8-oxo-dG), in a representative sample of a general population from Spain (Hortega Study). Methods: Urine antimony (Sb), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), vanadium (V) and zinc (Zn) were

measured by ICPMS in 1440 Hortega Study participants. Results: The geometric mean ratios (GMRs) of GSSG/GSH comparing the 80th to the 20th percentiles of metal distributions were 1.15 (95% confidence intervals [95% CI]: 1.03–1.27) for Mo, 1.17 (1.05–1.31) for Ba, 1.23 (1.04–1.46) for Cr and 1.18 (1.00–1.40) for V. For MDA, the corresponding GMRs (95% CI) were 1.13 (1.03–1.24) for Zn and 1.12 (1.02–1.23) for Cd. In 8-oxo-dG models, the corresponding GMR (95% CI) were 1.12 (1.01–1.23) for Zn and 1.09 (0.99–1.20) for Cd. Cr for GSSG/GSH and Zn for MDA and 8-oxo-dG drove most of the observed associations. Principal component (PC) 1 (largely reflecting non-essential metals) was positively associated with GSSG/GSH. The association of PC2 (largely reflecting essential metals) was positive for GSSG/GSH but inverse for MDA. Conclusions: Urine Ba, Cd, Cr, Mo, V and Zn were positively associated with oxidative stress measures at metal exposure levels relevant for the general population. The potential health consequences of environmental, including nutritional, exposure to these metals warrants further investigation. (Note: This was also in December update but with the wrong year, it should be 2019 not 2018.)

Guerrero-Palomo, G., Rendon-Huerta, E.P., Montano, L.F.*, et al.* (2019) Vanadium compounds and cellular death mechanisms in the A549 cell line: The relevance of the compound valence. *Journal of Applied Toxicology : JAT,* 39(3): 540-552.
Keywords: A549; NSCLC; ROS; caspases; lung cancer; sodium metavanadate; vanadyl sulfate

Abstract
Non-small lung cell carcinoma has a high morbidity and mortality rates. The elective treatment for stage III and IV is cisplatinum that conveys serious toxic side effects. Vanadium compounds are metal molecules with proven antitumor activity that depends on its valence. Therefore, a better understanding of the mechanism of action of vanadium compounds is required. The aim of our study was to investigate the mechanisms of cell death induced by sodium metavanadate (NaVO3 [V(+5)]) and vanadyl sulfate (VOSO4 [(+4)]), both of which have reported apoptotic-inducing activity. We exposed the A549 cell line to various concentrations (0-100 muM) and to different exposure times to each compound and determined the cell viability and expression of caspases, reactive oxygen species (ROS) production, Bcl2, Bax, FasL and NO. Our results showed that neither compounds modified the basal expression of caspases or pro- and anti-apoptotic proteins. The only change observed was the 12- and 14-fold significant increase in ROS production induced by NaVO3 and VOSO4 , respectively, at 100 mum concentrations after 48 hours. Our results suggest that classical apoptotic mechanisms are not related to the cell death induced by the vanadium compounds evaluated here, and showed that the higher ROS production was induced by the [(+4)] valence compound. It is possible that the difference will be secondary to its higher oxidative status and thus higher ROS production, which leads to higher cell damage. In conclusion, our results suggest that the efficacy of the cell death mechanisms induced by vanadium compounds differ depending on the valence of the compound.

Halevas, E., Papadopoulos, T.A., Swanson, C.H.*, et al.* (2019) In-depth synthetic, physicochemical and in vitro biological investigation of a new ternary V(IV) antioxidant material based on curcumin. *Journal of Inorganic Biochemistry,* 191: 94-111.
Keywords: Bioreactivity profile and antioxidant agent; Cell metabolism inhibition and DNA degradation; Crystal structure and DFT calculations; Hybrid metallopharmaceutical; ROS-suppression; Vanadium-curcumin complex

Abstract
Curcumin is a natural product with a broad spectrum of beneficial properties relating to pharmaceutical applications, extending from traditional remedies to modern cosmetics. The

biological activity of such pigments, however, is limited by their solubility and bioavailability, thereby necessitating new ways of achieving optimal tissue cellular response and efficacy as drugs. Metal ion complexation provides a significant route toward improvement of curcumin stability and biological activity, with vanadium being a representative such metal ion, amply encountered in biological systems and exhibiting exogenous bioactivity through potential pharmaceuticals. Driven by the need to optimally increase curcumin bioavailability and bioactivity through complexation, synthetic efforts were launched to seek out stable species, ultimately leading to the synthesis and isolation of a new ternary V(IV)-curcumin-(2,2'-bipyridine) complex. Physicochemical characterization (elemental analysis, FT-IR, Thermogravimetry (TGA), UV–Visible, NMR, ESI-MS, Fluorescence, X-rays) portrayed the solid-state and solution properties of the ternary complex. Pulsed-EPR spectroscopy, in frozen solutions, suggested the presence of two species, cis- and trans-conformers. Density Functional Theory (DFT) calculations revealed the salient features and energetics of the two conformers, thereby complementing EPR spectroscopy. The well-described profile of the vanadium species led to its in vitro biological investigation involving toxicity, cell metabolism inhibition in S. cerevisiae cultures, Reactive Oxygen Species (ROS)-suppressing capacity, lipid peroxidation, and plasmid DNA degradation. A multitude of bio-assays and methodologies, in comparison to free curcumin, showed that it exhibits its antioxidant potential in a concentration-dependent fashion, thereby formulating a bioreactivity profile supporting development of new efficient vanado-pharmaceuticals, targeting (extra)intra-cellular processes under (patho)physiological conditions. © 2018.

Kongot, M., Dohare, N., Reddy, D.S.*, et al.* (2019) In vitro apoptosis-induction, antiproliferative and BSA binding studies of a oxidovanadium(V) complex. *Journal of Trace Elements in Medicine and Biology: Organ of the Society for Minerals and Trace Elements (GMS),* 51: 176-190.

Keywords: Animals; Antineoplastic Agents/chemical synthesis/chemistry/pharmacology; Apoptosis/drug effects; Cattle; Cell Line, Tumor; Cell Proliferation/drug effects; Coordination Complexes/chemical synthesis/chemistry/pharmacology; Dose-Response Relationship, Drug; Humans; MCF-7 Cells; Molecular Structure; Serum Albumin, Bovine/chemistry; Structure-Activity Relationship; Vanadium Compounds/chemistry/pharmacology; BSA binding; Bovine serum albumin; Fluorescence spectroscopy; Human breast adenocarcinoma; Human lung carcinoma; Oxidovanadium complex

Abstract

In our ongoing efforts to develop novel trace metal complexes with therapeutically interesting properties, a neutral mono nuclear oxidomethoxidovanadium(V) complex, [V(V)O(OCH3)(hpdbal-sbdt)] (1) and a mu-O bridged dinuclear oxidovanadium(V) complex, [{V(V)O(hpdbal-sbdt)}2mu-O] (2) [H2hpdbal-sbdt (I) is a tridentate and dibasic ONS(2-) donor ligand obtained through the Schiff base reaction of 2-hydroxy-5-(phenyldiazenyl)benzaldehyde (Hhpdbal) and S-benzyldithiocarbazate (Hsbdt)] have been synthesized and characterized by various analytical techniques such as TGA, EDS, ATR-IR, UV-Vis, CV, (1)H NMR, (13)C NMR and (51)V NMR. Single-crystal X-ray diffraction analysis of 1 confirms the coordination of phenolate oxygen, imine nitrogen and thioenolate sulfur of the ligand to the vanadium center with a distorted tetragonal-pyramidal geometry. The compound 2 triggered apoptotic and reproductive death of the cancer cells in vitro with 76% and 62% growth inhibition of human breast adenocarcinoma (MCF-7) and human lung carcinoma cells (A549) respectively. The compound 2 was found to be sufficiently stable over a wide window of physiological pH. The complex 2 was studied further for its interaction with a drug carrier protein BSA with the aid of spectroscopic techniques viz. fluorescence, temperature controlled UV-vis and deconvoluted IR techniques.

Liu, L., Urch, B., Szyszkowicz, M.*, et al.* (2018) Metals and oxidative potential in urban particulate matter influence systemic inflammatory and neural biomarkers: A controlled exposure study. *Environment International,* 121: 1331-1340.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018320014/pdfft?md5=5f7964304a63a141b04ae2c52a1c1eef&pid=1-s2.0-S0160412018320014-main.pdf

Abstract
Background: Oxidative stress and inflammation are considered to be important pathways leading to particulate matter (PM)-associated disease. In this exploratory study, we examined the effects of metals and oxidative potential (OP) in urban PM on biomarkers of systemic inflammation, oxidative stress and neural function. Methods: Fifty-three healthy non-smoking volunteers (mean age 28 years, twenty-eight females) were exposed to coarse (2.5–10 μm, mean 213 μg/m 3), fine (0.15–2.5 μm, 238 μg/m 3), and/or ultrafine concentrated ambient PM (<0.3 μm, 136 μg/m 3). Exposures lasted 130 min, separated by ≥2 weeks. Metal concentrations and OP (measured by ascorbate and glutathione depletion in synthetic airway fluid) in PM were analyzed. Blood and urine samples were collected pre-exposure, and 1-h and 21-h post exposure for assessment of biomarkers. We used mixed-regression models to analyze associations adjusting for PM size and mass concentration. Results: Results for metals were expressed as change (%) from daily pre-exposure biomarker levels after exposure to a metal at a level equivalent to the mean concentration. Exposure to various metals (silver, aluminum, barium, copper, iron, potassium, lithium, nickel, tin, and/or vanadium) was significantly associated with increased levels of various blood or urinary biomarkers. For example, the blood inflammatory marker vascular endothelia growth factor (VEGF) increased 5.3% (95% confidence interval: 0.3%, 10.2%) 1-h post exposure to nickel; the traumatic brain injury marker ubiquitin C-terminal hydrolase L1 (UCHL1) increased 11% (1.2%, 21%) and 14% (0.3%, 29%) 1-h and 21-h post exposure to barium, respectively; and the systemic stress marker cortisol increased 1.5% (0%, 2.9%) and 1.5% (0.5%, 2.8%) 1-h and 21-h post exposure to silver, respectively. Urinary DNA oxidation marker 8-hydroxy-deoxy-guanosine increased 14% (6.4%, 21%) 1-h post exposure to copper; urinary neural marker vanillylmandelic acid increased 29% (3%, 54%) 1-h post exposure to aluminum; and urinary cortisol increased 88% (0.9%, 176%) 1-h post exposure to vanadium. Results for OP were expressed as change (%) from daily pre-exposure biomarker levels after exposure to ascorbate-related OP at a level equivalent to the mean concentration, or for exposure to glutathione-related OP at a level above the limit of detection. Exposure to ascorbate- or glutathione-related OP was significantly associated with increased inflammatory and neural biomarkers including interleukin-6, VEGF, UCHL1, and S100 calcium-binding protein B in blood, and malondialdehyde and 8-hydroxy-deoxy-guanosine in urine. For example, UCHL1 increased 9.4% (1.8%, 17%) in blood 21-h post exposure to ascorbate-related OP, while urinary malondialdehyde increased 19% (3.6%, 35%) and 8-hydroxy-deoxy-guanosine increased 24% (2.9%, 48%) 21-h post exposure to ascorbate- and glutathione-related OP, respectively. Conclusion: Our results from this exploratory study suggest that metal constituents and OP in ambient PM may influence biomarker levels associated with systemic inflammation, oxidative stress, perturbations of neural function, and systemic physiological stress. © 2018.

Trevino, S., Diaz, A., Sanchez-Lara, E.*, et al.* (2019) Vanadium in Biological Action: Chemical, Pharmacological Aspects, and Metabolic Implications in Diabetes Mellitus. *Biological Trace Element Research,* 188(1): 68-98.
Keywords: Biological action; Diabetes mellitus; Metabolic aspects; Metabolic implications; Metallopharmaceuticals; Vanadium

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

Wei, Q., Muhammad, U., Jiang, P.-*, et al.* (2018) Vanadyl trehalose-induced oxidative stress in mouse gastrointestinal tract and the protective functions of vitamin C and reduced glutathione. *Journal of Xi'an Jiaotong University (Medical Sciences),* 39(6): 810-815. [Chinese]
Keywords: GSH/GSTs; Oxidative stress; Reduced glutathione (GSH); Vanadyl trehalose (VT); Vitamin C

Abstract
Objective: To investigate the effects of vanadyl trehalose (VT) on oxidative stress and GSH/GSTs pathway gene expression in mouse gastrointestinal tract as well as the protective effects of vitamin C and reduced glutathione (GSH). Methods: Thirty male Kunming mice were randomly divided into five groups: normal control group (group A), VT group (group B), Vc+VT group (group C), GSH +VT group (group D), and Vc+GSH+VT group (group E). The treatment groups were fed with vanadyl trehalose (125 mg/kg) every day, while the control group was given the same amount of normal saline daily. Vc and GSH were administered one hour before vanadyl trehalose treatment via gavage. The treatment lasted 15 days. Then, all mice were killed and the stomach and duodenum were isolated. The content of reduced GSH was measured by DTNB method, the activity of glutathione peroxidase was determined by glutathione oxidase method. Real-time fluorescence quantitative PCR was used to detect the expressions of GCLC, GSS, GSR and GSTpi in GSH/GSTs pathway. Results: The content of GSH and GSH-Px activity and the expressions of GCLC, GSS, GSR and GSTpi in the stomach and duodenum in VT-treated group were lower than those in group A ($P<0.05$). In groups C, D and E the above indicators were significantly improved, but those only in the stomach in group E reached the level of the normal control group. In groups C and D, except for the amount of GSR expressed in the duodenum, there was no significant difference in the other indexes. Conclusion: VT can cause oxidative stress damage to the gastrointestinal tract of mice, which affects GSH content and GSH-Px activity, and interferes with the normal expressions of

GSH/GSTs pathway related genes. Exogenous Vc and GSH and the combination of the two can play a certain role in antioxidant protection and reduce the toxicity of VT. The combination of the two is better than one used alone, and the related indicators in the stomach can reach the normal level.

4. USES OF VANADIUM

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

Abstract
Islet Amyloid Polypeptide (IAPP), also known as amylin, is a 37-amino-acid peptide hormone that is secreted by pancreatic islet β-cells. Amylin is complementary to insulin in regulating and maintaining blood glucose levels in the human body. The misfolding and aggregation of amylin is primarily associated with type 2 diabetes mellitus, which is classified as an amyloid disease. Recently, the interactions between amylin and specific metal ions, e.g., copper(II), zinc(II), and iron(II), were found to impact its performance and aggregation processes. Therefore, the focus in this review will be on how the chemistry and structural properties of amylin are affected by these interactions. In addition, the impact of amylin and other amyloidogenic peptides interacting with metal ions on the cell membranes is discussed. In particular, recent studies on the interactions of amylin with copper, zinc, iron, nickel, gold, ruthenium, and vanadium are discussed. © 2018 The Authors.

Cheng, Y., Sun, T., Yin, C.*, et al.* (2019) Downregulation of PTEN by sodium orthovanadate protects the myocardium against ischemia/reperfusion injury after chronic atorvastatin treatment. *Journal of Cellular Biochemistry,* 120(3): 3709-3715.
Keywords: Akt signaling; atorvastatin; ischemia/reperfusion injury; PTEN; sodium orthovanadate

Abstract
Acute statin treatment has been reported to be critical in protecting the cardiac cells against ischemia/reperfusion injury by activating PI3K/Akt signal pathway. In vitro rat myocardial ischemia/reperfusion model, chronic statin treatment led to upregulation of phosphatase and tensin homolog (PTEN). This has been potentially indicated the correlation in PTEN and protective effect of statin on myocardium. In this current study, we evaluated the role of sodium orthovanadate a nonspecific inhibitor to PTEN and its correlation with atorvastatin on protecting myocardium against ischemia/reperfusion injury. We found a long-term statin treatment could increase the PTEN level, and this process was counteracted in the presence of sodium orthovanadate. However, the phosphotyrosine level was not affected by this statin. Besides, this process was mediated by Akt signaling since phosphorylated Akt level was altered by statin and sodium orthovanadate treatment. In a conclusion, this study showed a potential mechanism underlying PTEN-induced attenuation in long-term statin's therapeutic effect, which provided the new insight into the synergic role of PTEN and atorvastatin in protecting cardiac cells against ischemia/reperfusion injury. © 2018 Wiley Periodicals, Inc.

Dong, Y., Stewart, T., Zhang, Y.*, et al.* (2019) Anti-diabetic vanadyl complexes reduced Alzheimer's disease pathology independent of amyloid plaque deposition. *Science China.Life Sciences,* 62(1): 126-139.
Available at: http://engine.scichina.com/publisher/scp/journal/SCLS/62/1/10.1007/s11427-018-9350-1?slug=fulltext
Keywords: Alzheimer's disease; Abeta oligomerization; Grp75; PPARgamma-AMPK; neuroprotection; vanadyl (IV) acetylacetonate

Abstract
Association of Alzheimer's disease (AD) with cerebral glucose hypometabolism, likely due to impairments of insulin signaling, has been reported recently, with encouraging results when additional insulin is provided to AD patients. Here, we tested the potential effects of the anti-diabetic vanadium, vanadyl (IV) acetylacetonate (VAC), on AD in vitro and in vivo models. The experimental results showed that VAC at sub-micromolar concentrations improved the viability of neural cells with or without increased beta-amyloid (Abeta) burden; and in APP/PS1 transgenic mice, VAC treatment (0.1 mmol kg(-1) d(-1)) preserved cognitive function and attenuated neuron loss, but did not reduce brain Abeta plaques. Further studies revealed that VAC attenuated Abeta pathogenesis by (i) activation of the PPARgamma-AMPK signal transduction pathway, leading to improved glucose and energy metabolism; (ii) up-regulation of the expression of glucose-regulated protein 75 (Grp75), thus suppressing p53-mediated neuronal apoptosis under Abeta-related stresses; and (iii) decreasing toxic soluble Abeta peptides. Overall, our work suggested that vanadyl complexes may have great potential for effective therapeutic treatment of AD.

El-Deen, I.M., Shoair, A.F. & El-Bindary, M.A. (2019) Synthesis, characterization and biological properties of oxovanadium(IV) complexes. *Journal of Molecular Structure,* 1180: 420-437.
Keywords: Antimicrobial activities; Antitumor activities; DNA binding; Molecular structure; VO(II) complexes

Abstract
The complexes of oxovanadium(IV) with bidentate heterocyclic azo pyrazolone were synthesized and characterized by elemental analyses, IR, UV–Visible, EPR and magnetic measurements as well as thermal analysis and X-ray diffraction. Reaction of [V IV O(acac) 2] (where acac = acetylacetonate) in methanol with azo pyrazolones (HL n) produced mononuclear vanadium(IV) oxo complexes with general formula [VO(L n) 2]H 2 O. The molar conductance measurements proved that all the complexes are non-electrolytes. IR spectra showed that the ligands (HL n) acts as a monobasic bidentate ligand by coordinating via the nitrogen atom of the pyrazole ring (–HN–N =) and deprotonated hydroxyl O, thereby forming a square pyramidal chelating ring. Analytical data revealed that all the complexes exhibited 1:2 (metal-ligand) ratio. The thermal data confirm that the complexes have water molecule outside the coordination sphere and the complexes show similar thermogravimetric decomposition fragments which are consistent with the proposed structures. The thermodynamic parameters of VO(II) complexes are calculated using Coats–Redfern and Horowitz-Metzger methods. The optimized bond lengths, bond angles and the calculated quantum chemical parameters for VO(II) complexes (1–3) were investigated. Their interactions with calf thymus DNA were investigated by absorption spectra and viscosity measurements. The results suggest that these complexes bind to DNA in an intercalative mode (K b = 4.58–8.96 × 10 5 M −1). All VO(II) complexes (1–3) were evaluated against human cancer cell lines, MCF-7 and HepG-2 as compared with the positive controls in the viability assay of colchicine and vinblastine. Complex 2 (IC 50 = 30.5 ± 2.3 and 20.1 ± 1.9 μg/ml) exhibit

moderate activities against the two cell lines MCF-7 and HepG-2, respectively as compared to the Colchicine (IC 50 = 17.7 ± 0.03 and 10.6 ± 0.01 µg/mL). The antimicrobial activities of VO(II) complexes were tested against gram negative bacteria (Escherichia coli), gram positive bacteria (Staphylococcus aureus) and fungal (Candida albicans). © 2018 Elsevier B.V.

Farias, C.L.A., Martinez, G.R., Cadena, S.M.S.C.*, et al.* (2019) Cytotoxicity of xyloglucan from Copaifera langsdorffii and its complex with oxovanadium (IV/V) on B16F10 cells. *International Journal of Biological Macromolecules,* 121: 1019-1028.
Keywords: B16F10 cells; Melanoma; Metal complexes; Oxovanadium; Polysaccharides; Xyloglucan

Abstract:
The aim of this study was to investigate the effects of xyloglucan extracted from Copaifera langsdorffii seeds (XGC) and its complex with oxovanadium (XGC:VO) in murine melanoma B16F10 cells. The formation of complexes was followed by potentiometric titration and further demonstrated by 51 V RMN. The viability and proliferation of B16F10 cells were reduced up 50% by the xyloglucan and its complex, both at 200 µg/mL, from 24 to 72 h. Cytotoxic effects of XGC and XGC:VO do not involve changes in cell cycle progression. Only XGC:VO (200 µg/mL) promoted the cell death evidenced by annexin V stain. XGC increased the respiration and lactate levels in melanoma cells, while XGC:VO reduced about 50% the respiration and levels of pyruvate, without alter the lactate levels, indicating that both xyloglucan preparations interfere with the metabolism of B16F10 cells. No change in activity of the enzyme hexokinase and expression of pyruvate kinase M2 was observed. XGC:VO (200 µg/mL) negatively modulated the expression of the β subunit of ATP synthase. The results demonstrate that the cytotoxicity of XGC and XGC:VO on murine melanoma B16F10 cells can be related to the impairment of the mitochondrial functions linked to energy provision. © 2018.

Li, J., Liu, W., Zhang, X.*, et al.* (2019) Temperature-responsive tungsten doped vanadium dioxide thin film starves bacteria to death. *Materials Today,* 22: 35-49.
Available at:
https://www.sciencedirect.com/science/article/pii/S1369702118301445/pdfft?md5=70671ed136cbb53610998ace4ec5b49e&pid=1-s2.0-S1369702118301445-main.pdf
Keywords: metal-insulator-transition; phase-transition; antibiotic-resistance; electron-transfer; semiconductor; biofilms; nanoparticles; environment; reduction; coatings; Materials Science

Abstract:
The colonization of microorganisms on material surfaces, or namely biofouling, is a challenging matter in both the medical and marine industries. With the inspiration of the metabolism cascade of microorganisms, this study develops a new antifouling material surface that enables the drainage of extracellular electrons from the electron transfer chain in microbial metabolism, thereby interrupting the energy metabolism and subsequent microbial viability. This thought has been realized by tungsten-doped vanadium dioxide (VO2) thin film using customized magnetron-sputtering deposition. The aim of tungsten doping is to tune the semiconductor-to-metal phase change of the VO2 thin film and then endow the temperature-responsive electrical conductivity (band structure). While contacting with microorganisms, the electrically conductive VO2 can disrupt the membrane respiration function of bacteria. This antifouling phenomenon can be explained by a three-step mechanism. The initial step is the microbial adhesion onto the metallic VO2 film to form the direct microbe-VO2 physical contact, which leads to the destructive extraction of electrons

from the transmembrane protein complex of the respiratory chain (a discharge process); this induces oxidative stress and energy starvation and, eventually, interrupts the microbial membrane function. Finally, the microbial membrane integrity is destroyed, which leads to intracellular matter leakage (electrocution). This study demonstrates that the temperature-dependent VO2 electrical conductivity or band structure serves as a key factor to modulate the antimicrobial capability of tungsten-doped VO2 thin film. It is believed that the current findings can provide a new insight for the development of new antifouling surfaces.

Lu, L-P., Liu, J-H., Cen, S-H.*, et al.* (2019) Discovery of vanadium complexes bearing tridentate schiff base ligands as novel LSD1 inhibitors. *Bioorganic and Medicinal Chemistry Letters,* 29(4): 681-683.
Keywords: Anticancer; LSD1; MAO; Vanadium complex

Abstract
Lysine specific demethylase (LSD1) plays a pivotal role in epigenetic modulation of gene expression. Abberrant expression of LSD1 was associated with the progress and oncogenesis of multiple human cancers. Herein, we report the preliminary anti-LSD1 evaluation of the synthetic vanadium (V) complexes. Among them, complex 2 showed a moderate inhibitory effect against LSD1 with IC 50 value of 19.0 μM, as well as good selectivity over MAO-A/B. Complex 2 is the first vanadium based LSD1 inhibitor, which provides a novel scaffold for the development of LSD1 inhibitor. © 2018.

Monfort, O. & Plesch, G. (2018) Bismuth vanadate-based semiconductor photocatalysts: a short critical review on the efficiency and the mechanism of photodegradation of organic pollutants. *Environmental Science and Pollution Research International,* 25(20): 19362-19379.
Keywords: Bismuth/chemistry; Environmental Pollutants/chemistry/radiation effects; Photolysis; Reactive Oxygen Species; Semiconductors; Sunlight; Vanadates/chemistry/radiation effects; BiVO4; Efficiency; Mechanism; Organic pollutant; Photocatalysis

Abstract
The number of publications on photocatalytic bismuth vanadate-based materials is constantly increasing. Indeed, bismuth vanadate is gaining stronger interest in the photochemical community since it is a solar-driven photocatalyst. However, the efficiency of BiVO4-based photocatalyst under sunlight is questionable: in most of the studies investigating the photodegradation of organic pollutants, only few works identify the by-products and evaluate the real efficiency of BiVO4-based materials. This short review aims to (i) present briefly the principles of photocatalysis and define the photocatalytic efficiency and (ii) discuss the formation of reactive species involved in the photocatalytic degradation process of pollutants and thus the corresponding photodegradation mechanism could be determined. All these points are developed in a comprehensive discussion by focusing especially on pure, doped, and composite BiVO4. Therefore, this review exhibits a critical overview on different BiVO4-based photocatalytic systems with their real efficiency. This is a necessary knowledge for potential implementation of BiVO4 materials in environmental applications at larger scale than laboratory conditions.

Naglah, A.M., Al-Omar, M.A., Almehizia, A.A.*, et al.* (2018) A Novel Oxidovanadium (IV)-Orotate Complex as an Alternative Antidiabetic Agent: Synthesis, Characterization, and Biological Assessments. *BioMed Research International,* 2018: 8108713.

Available at: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6323442/pdf/BMRI2018-8108713.pdf

Abstract
Diabetes is an increasingly common metabolic disorder with high comorbidity and societal and personal costs. Insulin replacement therapy is limited by a lack of oral bioavailability. Recent studies suggest vanadium has therapeutic potential. A newly synthesized complex between oxidovanadium (IV) and orotic acid (OAH3), [(OAH1)(VO)(NH3)2].3H2O, was characterized using spectroscopic and thermogravimetric techniques. In vivo potential was assessed in a streptozocin-induced rat model of diabetes. OAH3 acts as a bidentate ligand in the formation of the dark green, crystalline oxidovanadium (IV) complex in a square pyramidal configuration. Treatment with oxidovanadium (IV)-orotate in vivo significantly improved many biochemical parameters with minimal toxicity and restored pancreatic and hepatic histology. The results of the present work describe a safe, new compound for the treatment of diabetes.

Ortega-Pacheco, D., Jiménez-Pérez, M.M., Serafín-López, J.*, et al.* (2018) Vanadyl Sulfate Effects on Systemic Profiles of Metabolic Syndrome in Old Rats with Fructose-Induced Obesity. *International Journal of Endocrinology,* 2018.
Available at: http://downloads.hindawi.com/journals/ije/2018/5257216.pdf

Abstract
Background
Currently, energy obtained from hypercaloric diets has been part of the obesity and type 2 diabetes mellitus (T2DM) epidemics from childhood to old age. Treatment alternatives have been sought from plants, minerals, and trace elements with metabolic effects. Vanadyl sulfate (VS) has been investigated as a hypoglycemic compound in animal and human studies showing effective insulin-mimetic properties. This characteristic encompasses several molecules that have beneficial pleiotropic effects. *The aim* was to determine the antiobesity, hypoglycemic, and hypolipidemic effects of VS on fructose-induced metabolic syndrome in aged rats.
Material and Methods
Five groups of male Wistar rats were made, each with six rats: two groups with normal diet (ND) and three with high-fructose diet (HFD). The first ND group was treated with saline solution (SS), the second with VS; treatment for HFD groups was in the first group with SS, second with VS, and third with metformin. Weight, body mass index (BMI), blood glucose, and lipidic profile were measured; water, food, fructose and energy consumption were also determined. All parameters were compared among groups.
Results and Discussion
Although obese rats treated with VS presented anorexia, oligodipsia, and a marked weight loss in the first two weeks. They recovered food and water intake in the third week with a slow recovery of some weight weeks later. VS normalized blood glucose level and decreased triglyceride and insulin levels in obese rats. These results suggest that vanadyl sulfate shows antiobesity, hypoglycemic, and hypolipidemic properties in old obese rats and could be useful as an alternative, additional, and potent preventive treatment for obesity and T2DM control in elderly obese and poorly controlled diabetic patients.
Conclusion
VS could play an important role in the treatment of metabolic syndrome, contributing to a decrease in obesity and T2DM, through different ways, such as euglycemia, satiety, weight loss, and lipid profile optimization, among others. However, more research is needed to confirm this suggestion.

Sarhan, A.M., Elsayed, S.A., Mashaly, M.M.*, et al.* (2019) Oxovanadium(IV) and ruthenium(II) carbonyl complexes of ONS-donor ligands derived from dehydroacetic acid and dithiocarbazate: Synthesis, characterization, antioxidant activity, DNA binding and in vitro cytotoxicity. *Applied Organometallic Chemistry,* 33(2), e4655.
Keywords: anticancer; antioxidant; DNA binding; oxovanadium(IV); ruthenium(II) complexes

Abstract
A series of new complexes of oxovanadium(IV) [VO(L)(B)] and ruthenium(II) [Ru(CO)(PPh3)2(L)] (1.1- 1.3, 2.1–2.3) (H2L = dehydroacetic acid Schiff base of S-methyldithiocarbazate, H2smdha (1) or S-benzyldithiocarbazate, H2sbdha (2); B = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) have been synthesized. The structure of these complexes was authenticated using elemental analyses and spectroscopic techniques, and their magnetic properties and electrochemical behaviour were studied. The molecular structures of oxovanadium(IV) complexes [VO(smdha)(bpy)]·CH2Cl2 (1.1) and [VO(sbdha)(phen)]·2H2O (2.2) were confirmed using single-crystal X-ray crystallography. Analytical data showed that the ligands 1 and 2 are chelated to the metal centres in a bi-negative tridentate fashion through azomethine N, thiol S and deprotonated hydroxyl group. The antioxidant activity of the synthesized compounds was tested against 2,2-diphenyl-1-picrylhydrazyl) radical, which showed that the complexes demonstrate a better scavenging activity than their corresponding ligands. The cupric ion reducing antioxidant capacity method was also employed and the total equivalent antioxidant capacity values were found to be higher for the oxovandium(IV) complexes. DNA binding affinity of the compounds was determined using UV–visible and fluorescence spectra, revealing an intercalation binding mode. Higher cytotoxicity for the complexes compared to their ligands was found against human liver hepatocellular carcinoma (HepG2) and breast adenocarcinoma (MCF7) cell lines using MTT assay. © 2018 John Wiley Sons, Ltd.

Trevino, S., Diaz, A., Sanchez-Lara, E.*, et al.* (2019) Vanadium in Biological Action: Chemical, Pharmacological Aspects, and Metabolic Implications in Diabetes Mellitus. *Biological Trace Element Research,* 188(1): 68-98.
Keywords: Biological action; Diabetes mellitus; Metabolic aspects; Metabolic implications; Metallopharmaceuticals; Vanadium

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

ability of vanadium-based compounds and their role for the treatment of diabetes mellitus, specifically on that of vanadate- and polioxovanadate-containing compounds. We aim at shedding light on the prevailing gaps between primary scientific data and information from animal models and human studies.

Yang, C., Yu, H., Gao, Y.*, et al.* (2019) Surface-engineered vanadium nitride nanosheets for an imaging-guided photothermal/photodynamic platform of cancer treatment. *Nanoscale,* 11(4): 1968-1977.
Keywords: Animals; Biocompatible Materials/chemistry/pharmacology/therapeutic use; Cattle; Cell Survival/drug effects; Female; Hep G2 Cells; Humans; Hyperthermia, Induced; Mice; Mice, Inbred BALB C; Mice, Nude; Nanostructures/chemistry; Neoplasms/diagnostic imaging/drug therapy/pathology; Photochemotherapy; Photosensitizing Agents/chemistry/pharmacology/therapeutic use; Polyamines/chemistry; Reactive Oxygen Species/metabolism; Serum Albumin, Bovine/chemistry; Theranostic Nanomedicine; Vanadium/chemistry

Abstract
Of the many strategies for precise tumor treatment, near-infrared (NIR) light-activated "one-for-all" theranostic modality with real-time diagnosis and therapy has attracted extensive attention from researchers. Herein, a brand-new theranostic nanoplatform was established on versatile vanadium nitride (VN) nanosheets, which show significant NIR optical absorption, and resultant photothermal effect and reactive oxygen species activity under NIR excitation, thereby realizing the synergistic action of photothermal/photodynamic co-therapy. As expected, systematic in vitro and in vivo antitumor evaluations demonstrated efficient cancer cell killing and solid tumor removal without recurrence. Meanwhile, the surface modification of VN nanosheets with poly(allylamine hydrochloride) and bovine serum albumin enhanced the biocompatibility of VN and made it more suitable for in vivo delivery. Moreover, VN has been ascertained as a potential photoacoustic imaging contrast for in vivo tumor depiction. Thus, this work highlights the potential of VN nanosheets as a single-component theranostic nanoplatform.

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: Accumulation; BCF; Essential element; Plant growth; Setaria viridis; Vanadium
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.

Aihemaiti, A., Jiang, J., Blaney, L.*, et al.* (2019) The detoxification effect of liquid digestate on vanadium toxicity to seed germination and seedling growth of dog's tail grass. *Journal of Hazardous Materials,* 369: 456-464.
Keywords: Detoxification; Vanadium toxicity; Liquid digestate; Soil solution; dog's tail grass

Abstract
Dog's tail grass (Setaria viridis) presented strong tolerance and high accumulation of vanadium in field conditions. Liquid digestate containing high levels of nutrients could alleviate vanadium toxicity and accelerate the growth of dog's tail grass. To elucidate the detoxification potential and mechanism of liquid digestate, dog's tail grass was grown in soil solution containing 0.14–55.8 mg L-1 of vanadium. Parameters including germination index (GI), tolerance index (TI), seedlings' fresh weight, seedlings' vanadium accumulation, antioxidant enzymes activity, malonaldehyde (MDA) content, and V5+ species, were measured after addition of 1%, 5%, 10% and 15% liquid digestate. The results showed that a vanadium level of 10.9 mg L-1was a threshold value for toxicity; furthermore, the GI and TI decreased by 50% when vanadium content reached 36.8 mg L-1. The MDA content was reduced, and the other parameters were markedly enhanced, after addition of 5% and 10% liquid digestate with vanadium levels above 36.8 mg L-1. V5+ species was the dominant vanadium species in solution and the addition of liquid digestate reduced V5+ concentrations. The detoxification of vanadium by liquid digestate was a combined effect of direct reduction of V5+ species and plant nutrition.

Bai, L., Liu, X-L., Hu, J.*, et al.* (2018) Heavy metal accumulation in common aquatic plants in rivers and lakes in the Taihu Basin. *International Journal of Environmental Research and Public Health,* 15(12).
Available at: https://www.mdpi.com/1660-4601/15/12/2857/pdf
Keywords: Aquatic plants; Bioaccumulation capability; Heavy metals; Taihu lake

Abstract
We investigated the concentrations of 10 heavy metals in Potamogeton malaianus, Nymphoides peltata, Eichhornia crassipes, and Hydrilla verticillata to evaluate their potential to bioaccumulate heavy metals and related influencing factors in Taihu Lake. Enrichment factor (EF) values of Cu, Cr, Mn, Ni, Zn, Co, Pb, and V were above 2.0, indicating moderate to significant contamination in sediment. Most of Ti, V, Cr, Mn, and Ni in P. malaianus, E. crassipes, and H. verticillata and V in N. peltata were within excess/toxic level in plants, but higher than normal level. Even though no aquatic plants in this study were identified as a hyperaccumulator, relatively higher concentrations in aquatic plants were found in Taihu Lake than have been found in other previous studies. Heavy metal in submerged plants, especially in their stems, seemed to be more closely related to metals in water and sediment than those in floating-leaf plants. Ratios of metals in stem versus leaves in all plants ranged from 0.2 to 25.8, indicating various accumulation capabilities of plant organs. These findings contribute

to the application of submerged aquatic plants to heavy metal removal from moderately contaminated lakes. © 2018 by the authors. Licensee MDPI, Basel, Switzerland.

Barouchas, P.E., Akoumianaki-Ioannidou, A., Liopa-Tsakalidi, A.*, et al.* (2019) Effects of Vanadium and Nickel on Morphological Characteristics and on Vanadium and Nickel Uptake by Shoots of Mojito (Mentha x villosa) and Lavender (Lavandula anqustifolia). *Notulae Botanicae Horti Agrobotanici Cluj-Napoca,* 47(2): 487-492.
Keywords: culinary herbs; heavy metals accumulators; medicinal herbs; ACCUMULATION; CADMIUM; GROWTH; METABOLISM; YIELD; Plant Sciences

Abstract
Vanadium and Nickel may enter the human food chain through medicinal and culinary plants which in great doses are toxic to human, so it is important to determine their potential toxicity and health risk. Therefore, the objective of this work was to study the effects of Vanadium and Nickel on morphological characteristics and on Vanadium and Nickel uptake by shoots of mojito (Mentha x vilosa) and lavender (Lavandula anqustifolia). A completely randomized block design with five Vanadium treatments (0, 5, 10, 20, 40 mg V L-1) and five replications per treatment and another one with five Nickel treatments (0, 5, 10, 20 and 40 mg Ni L-1) and five replications per treatment for mojito and lavender were conducted in pots. No visible toxic or inhibitory symptoms were observed on the plants due to the increasing amounts of Vanadium or Nickel. Shoot dry matter and root dry matter of mojito and lavender decreased with increasing Vanadium rates. Vanadium uptake by shoots of mojito and lavender increased linearly with increasing Vanadium rates. Nickel uptake by shoots of lavender increased linearly with increasing rates of Nickel. Mojito is a Nickel accumulator.

Cánovas, C.R., Caro-Moreno, D., Jiménez-Cantizano, F.A.*, et al.* (2019) Assessing the quality of potentially reclaimed mine soils: Environmental implications for the construction of a nearby water reservoir. *Chemosphere,* 216: 19-30.
Keywords: Acid mine drainage; Iberian pyrite belt; Restoration measures; Soil pollution

Abstract
The cementation complex of Las Viñas (SW Spain) is a partially reclaimed abandoned mine site located in the drainage basin of a water reservoir currently under construction. The aim of this investigation was to analyze these mine soils to evaluate their potential environmental impact, especially on the final reservoir water quality. Results evidence the extremely high acidity of soils (pH of 3.4 and maximum potential acidity of 47 kg CaCO3/ton), with high concentrations of trace elements, especially As, Pb and Cu. Sequential extraction data reveal the potential release of significant quantities of Mn, Cd, Cu and other easily-soluble trace elements by rainfalls. The weathering and transport of soils to the bottom sediments of the planned reservoir could lead to the release of significant quantities of toxic trace elements to the water column if anoxic (mainly As, Sb, Cr, Ni, Cu and Pb) or oxic (mainly Hg, Pb, V, Cu and As) conditions are found in the sediments. The acidity and metals released from these soils could jeopardize the quality of the reservoir waters. Remediation measures must be therefore adopted, focused on the cleanup and liming of soils in order to promote colonization and vegetation succession, thus avoiding soil erosion and limiting metal release to the hydrosphere. This study proposes the use of different low-cost materials to improve the soil quality, limiting the metal transfer to the planned reservoir water. The information contained in this study could be of great importance in other watersheds affected by abandoned mine sites. © 2018 Elsevier Ltd.

Dong, B., Zhang, R., Gan, Y.*, et al.* (2019) Multiple methods for the identification of heavy metal sources in cropland soils from a resource-based region. *Science of the Total Environment,* 651: 3127-3138.
Keywords: Heavy metal; Loess Plateau; Positive matrix factorization (PMF); Soil pollution; Source appointment

Abstract
Examination of heavy metal sources in soils from a resource-based region is essential for source identification and implementation of restoration strategies regarding soil contamination. A total of 1069 samples were collected from cropland soils in the Baiyin District (Loess Plateau, Northwest China), a characteristically resource-based region to investigate the sources of arsenic (As), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). Source identification was analyzed by multiple methods including spatial deviation (SD), correlation analysis (CA), enrichment factor (EF), principal component analysis (PCA), geographic information system (GIS), and positive matrix factorization (PMF). The results showed the combined applications of PMF, GIS, and PCA were accurate, pragmatic, and effective for source apportionment. Three origins were identified and the contribution rates were calculated as follows: approximately 95% of As came from wastewater irrigation; 75, 88, 60, and 76% of Cr, Mn, Ni, and V were separately derived from natural origins; and 81, 93, and 70% of Cu, Pb, and Zn originated from industrial sources, respectively. Natural origins, industrial sources, and wastewater irrigation were the three main contributors of heavy metals to cropland soils in this region. © 2018 Elsevier B.V.

Fordyce, F.M., Everett, P.A., Bearcock, J.M.*, et al.* (2019) Soil metal/metalloid concentrations in the Clyde Basin, Scotland, UK: Implications for land quality. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh,* 108(2-3): 191-216.
Keywords: arsenic; cadmium; chromium; land contamination; lead; nickel; selenium; topsoil

Abstract
An assessment of topsoil (5-20cm) metal/metalloid (hereafter referred to as metal) concentrations across Glasgow and the Clyde Basin reveals that copper, molybdenum, nickel, lead, antimony and zinc show the greatest enrichment in urban versus rural topsoil (elevated 1.7-2.1 times; based on median values). This is a typical indicator suite of urban pollution also found in other cities. Similarly, arsenic, cadmium and lead are elevated 3.2-4.3 times the rural background concentrations in topsoil from the former Leadhills mining area. Moorlands show typical organic-soil geochemical signatures, with significantly lower ($P<0.05$) concentrations of geogenic elements such as chromium, copper, nickel, molybdenum and zinc, but higher levels of cadmium, lead and selenium than most other land uses due to atmospheric deposition/trapping of these substances in peat. In farmland, 14% of nickel and 7% of zinc in topsoil samples exceed agricultural maximum admissible concentrations, and may be sensitive to sewage-sludge application. Conversely, 5% of copper, 17% of selenium and 96% of pH in farmland topsoil samples are below recommended agricultural production thresholds. Significant proportions of topsoil samples exceed the most precautionary (residential/allotment) human-exposure soil guidelines for chromium (18% urban; 10% rural), lead (76% urban; 45% rural) and vanadium (87% urban; 56% rural). For chromium, this reflects volcanic bedrock and the history of chromite ore processing in the region. However, very few soil types are likely to exceed new chromiumVI-based guidelines. The number of topsoil samples exceeding the guidelines for lead and vanadium highlight the need for further investigations and evidence to improve human soil-exposure risk assessments to better inform land contamination policy and regeneration. Copyright © British Geological Survey UKRI 2018.

Gustafsson, J.P. (2019) Vanadium geochemistry in the biogeosphere –speciation, solid-solution interactions, and ecotoxicity. *Applied Geochemistry,* 102: 1-25.
Available at:
https://www.sciencedirect.com/science/article/pii/S0883292718303883/pdfft?md5=b344530895d4b91e801b0e6424b6a14c&pid=1-s2.0-S0883292718303883-main.pdf
Keywords: Vanadate; Vanadyl; Water; Soil; Sediment; Bioavailability

Abstract
Vanadium is a metal that receives increasing attention due to its possible toxicity and its increased use in society, i.e. in high-grade steel and in vanadium redox-flow batteries. Already today, the global biogeochemical cycle of vanadium is heavily impacted by human activities, and these impacts will probably increase. The total V concentration in the upper part of the Earth's crust, and in soils, is near 100 mg V kg−1. Usually, the dissolved V concentration is low. In seawater the mean dissolved V concentration is 1.8 μg L−1, and in freshwaters the concentration is commonly below 1 μg L−1 although in areas with volcanic and sedimentary rocks it may be much higher, i.e. at the slopes of Mt. Etna, Italy, concentrations of up to 180 μg V L−1 have been recorded. Vanadium is a redox-sensitive element, which occurs in three oxidation states (+III, +IV and +V) in the environment. Whereas vanadium(V) usually occurs as the oxyanion vanadate(V) under most environmental conditions, vanadyl(IV) is an oxocation that is stable at low pH and/or mildly reducing conditions, particularly when the organic matter concentration is high. Vanadium(III), which is the least studied form of vanadium, occurs under strongly reducing conditions. All vanadium forms are strongly bound to environmental sorbents: vanadate(V) is bound as a bidentate complex to iron, aluminium, and titanium (hydr)oxides, and with a stronger affinity than that of orthophosphate (o-phosphate). Vanadyl(IV) is strongly complexed to natural organic matter, while vanadium(III) may substitute for other trivalent ions in mineral structures. Despite this, vanadium may be mobilized to the aqueous phase, for example under high-pH conditions. Studies with V K-edge XANES spectroscopy have shown that most oxic soils usually contain a mixture of vanadium(IV) that is octahedrally coordinated in primary minerals, and surface-bound vanadate(V) on iron and aluminium (hydr)oxides, although acid organic soils are dominated by organically complexed vanadyl(IV). In reduced environments, such as in sediments and black shales, available evidence suggests that the V consists of a mixture of organically complexed vanadyl(IV) and unknown vanadium(III) species. However, considerable uncertainty exists on the V speciation under reducing conditions, and additional research is recommended. Vanadium is essential for some species of cyanolichens and algae due to its presence in vanadium nitrogenase, which can be important for N fixation in boreal ecosystems, and in vanadium haloperoxidases, which mediate the oxidation of halides, particularly iodine and bromine. In certain organisms vanadium is accumulated for unknown reasons, e.g. in ascidians, where V accumulates as a vanadium(III) complex with organic S, and in Amanita mushrooms, in which amavadin, a stable vanadium(IV)-organic complex, is accumulated. However, at high concentrations vanadium is toxic to many organisms. This is mostly due to its interference with o-phosphate in a number of biomolecules. Available evidence shows that toxic effects appear in the mg V L−1 range for most studied species. However, some organisms, i.e. algae and possibly some soil bacteria, are more sensitive. In soils, the toxic response is related to the soil solution V concentration, rather than to the solid-phase concentration. The o-phosphate concentration has been identified as a parameter that influences toxicity, but the relationship between the P status and the environmental risk of V toxicity is not yet well determined – as a result risk-based guidelines remain uncertain. There is urgent need for more research on this topic. Vanadium, being a redox-sensitive element, responds to sudden environmental change such as flooding that leads to decreased redox

potential. In most, but not all, cases, an increased solubilisation of vanadium is observed after flooding, which can be attributed to reductive dissolution of vanadate(V)-sorbing iron (hydr)oxides and to vanadate(V) reduction to vanadyl(IV) that forms stable complexes with dissolved organic matter. The vanadium redox conversions are carried out by a large number of genera of bacteria. Bioremediation methods are being developed that may reduce vanadate(V) to vanadyl(IV), which may reduce the bioavailability of vanadium in many soils.

Hou, M., Li, M., Yang, X.*, et al.* (2019) Responses of Nonprotein Thiols to Stress of Vanadium and Mercury in Maize (Zea mays L.) Seedlings. *Bulletin of Environmental Contamination and Toxicology,* 102(3): 425-431.
Keywords: Accumulation; Glutathione; Maize seedlings; Nonprotein thiol; Phytochelatins

Abstract
The heavy metal pollution in ecosystems is of increasing global concern. This study investigated firstly the responses of phytochelatins (PCs), glutathione (GSH) and other nonprotein thiols (NPT) in maize seedlings under vanadium (V), mercury (Hg) or their combined stress. With V or V-Hg combined stress, the contents of PCs, GSH and NPT in shoots and roots both increased with increasing the V stress level, and reached the maximum when the V stress level was 5 mg/L. Accumulation of V in all organs of maize seedlings was in sequence as follows: roots >> shoots, while Hg inhibited the accumulation of V. Results show that the root of plant has stronger tolerance to V, and the low V stress level can promote the synthesis of thiol groups to reduce the toxicity of Hg for plants.

Jeon, S.H., Kuppusamy, S., Yoon, Y.-*, et al.* (2019) Are There as Many Essential and Non-essential Minerals in Hydroponic Strawberry (Fragaria ananassa L.) Compared to Those Grown in Soil? *Biological Trace Element Research,* 187(2): 562-567.
Keywords: Macro-elements; Micro-elements; Open field; Plant nutrition; Soil-free cultivation

Abstract
The present study aims to compare the contents of minerals (essential major—K, Ca, Mg, Na, P, S; essential trace—Fe, Mn, Zn, Cu, B, Mo, As, Se, Ni, V, Cr, Co; non-essential—Sn, Ga, Li, Be, Rb, Sr, Al, Pd, Cd, Hg, Pb, Ge) in strawberry (stem, leaf, and fruit) cultivated in two different cultivation systems, soil and hydroponic. The concentrations of 30 minerals in the acid-digested strawberry samples were determined by ICP-MS and ICP-OES. Hydroponic strawberry (leaf > fruit > stem) indicated higher values for most minerals which were below the plant toxicity levels. In leaves collected from the hydroponic system, it was observed there were larger amounts of Fe, Zn, B, As, Se, Ni, V, Cr, Al, Cd, and Pd. Hydroponic fruits were the significant sources of K, P, Mn, Zn, Cr, and Co. Hydroponic strawberry leaves could contribute twice as many higher and safe daily intake of minerals to humans than other fruits. This analysis shows that, firstly, higher quality and safely edible produce can be provided by the hydroponic system; and secondly, strawberry leaf is a potential mineral source. © 2018, Springer Science+Business Media, LLC, part of Springer Nature.

Jin, Y., O'Connor, D., Ok, Y.S.*, et al.* (2019) Assessment of sources of heavy metals in soil and dust at children's playgrounds in Beijing using GIS and multivariate statistical analysis. *Environment International,* 124: 320-328.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018328757/pdfft?md5=d4c9da959d56c8ced8534ff69e7f45d4&pid=1-s2.0-S0160412018328757-main.pdf
Keywords: Air pollution; Atmospheric deposition; GIS; Heavy metals; Soil contamination

Abstract:
Potentially toxic elements such as heavy metals are ubiquitous in the environment. Risk-based environmental management relies upon identifying pollution sources, pathways, and the exposed population. In a Chinese urban setting, many residents live in high-rise buildings without private gardens. Therefore, the main residential risk of exposure to contaminated soils and dusts may be associated with public open spaces. As children are the most vulnerable receptor, playgrounds represent an important yet often overlooked exposure point. The present study assessed plausible sources of heavy metals at children's playgrounds in a representative metropolitan environment. Soil and equipment dust samples were collected from 71 playgrounds across Beijing, which were analyzed for 11 different heavy metals. Principal component analysis (PCA) was used to identify the latent constructs which control heavy metal variability and reflect potential sources. Cluster analysis (CA) was conducted to group sampled locations, which provided further insights on plausible sources. The main factors extracted from the PCA were then subject to geostatistical analysis. The systematic combination of GIS with multivariate statistical analysis proved valuable for elucidating anthropogenic and natural sources. Elevated Be, V, Cr, Mn, Co, Ni, As in playground soils were found to derive mainly from the natural background (spatial autocorrelation = 2 km), while elevated Cu and Pb was attributed to traffic activities (spatial autocorrelation = 17 km), especially along the routes of Beijing's inner ring-roads, the major roads toward the northwest and northeast, and the international airport. These results suggest that heavy metals in playground equipment dust may derive mainly from atmospheric deposition of air pollution of both natural and anthropogenic origin (spatial autocorrelation = 11–13 km). Among them, Be, V, Mn, Co, Cu, As, Pb were attributed to atmospheric pollution deriving from the north of Beijing, brought by the prevailing northern wind in the winter season; whereas, Cr and Ni may possibly be brought from the southeast by the summer season winds. Knowledge of anthropogenic vs. natural origins of heavy metals in playgrounds is critical in assessing health impact and designing policy instruments for metropolitan areas. © 2019 The Authors.

Karbassi, A.R., Tajziehchi, S. & Khoshghalb, H. (2018) Speciation of heavy metals in coastal water of Qeshm Island in the Persian Gulf. *Global Journal of Environmental Science and Management,* 4(1): 91-98.
Available at:
https://www.gjesm.net/article_26317_e35207020e4c51ba3f4cac3537795393.pdf
Keywords: Entropy; Heat capacity; Multivariate statistical package (MVSP); Oil tank; Water pollution

Abstract
Fuel storage tanks are one of the main sources of water pollution as well as loss of crude oil and oil products in refineries. In the process of utilization of these tanks, considerable amounts of hydrocarbons may find their way into the coastal water, which eventually lead to loss of valuable hydrocarbons. Oil type, climatic condition and characteristics of oil tanks are among the main variables in computing evaporative losses. The present study brings out the results of a project that was carried out to investigate the adverse effects of oil terminal on coastal waters of Qeshm Island and aims to elaborate on speciation of metals in coastal waters. For this purpose, 12 stations were sampled. Water chemistry software was used to draw Eh-pH diagrams. Along with the speciation of heavy metals, cluster analysis was carried out by MVSP software. According to the results, HSC diagrams showed that Cu and Cd were present as free ions. Lead, manganese, cobalt, zinc and nickel were respectively present as PbOH, MnOH, ZnOH, CoOH and NiOH in the Persian Gulf. Speciation of Cu and Ni was in the form of Cu2O and NiO. Vanadium was also present in combination with hydroxide. Since all the studied elements were within the water stability range, they were stable, and there were

no environmental risks of contamination and toxicity. The results of cluster analysis did not show any relation between Eh and pH. This clearly showed that Eh-pH was governed by different mechanisms in coastal waters of Qeshm Island. Vanadium and Ni concentration was governed by pH, while Cu and Cd concentration was controlled by Eh. © 2015 Iran Solid.

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).
Available at: https://www.nature.com/articles/s41598-018-34888-5.pdf

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. © 2018, The Author(s).

Li, T., Sun, G., Yang, C.*, et al.* (2019) Source apportionment and source-to-sink transport of major and trace elements in coastal sediments: Combining positive matrix factorization and sediment trend analysis. *Science of the Total Environment,* 651: 344-356.
Keywords: Major and trace elements; Positive matrix factorization; Sediment trend analysis; Source apportionment; Taiwan Strait

Abstract
Major and trace elemental concentrations in coastal marine sediments were incorporated into positive matrix factorization (PMF) to identify potential sources and source contributions. Transport pathways of fine-grained sediments and sediment-bound elements were inferred from sediment trend analysis (STA). The spatial distribution patterns of 21 elements (Co, Cu, Ni, Sr, Zn, V, Ba, Sc, Ga, Pb, Cr, Zr, SiO 2 , Al 2 O 3 , Fe 2 O 3 , MgO, CaO, K 2 O, MnO, TiO 2 , and P 2 O 5) coupled with sediment grain sizes were investigated. The natural and anthropogenic sources of the elements were distinguished by their medium enrichment factors (EFs). Seven sources were recognized by PMF: weathering products, anthropologic emissions, sand, older sediment, biogenic carbonates, products of siliceous organisms, and mine exploitation. Some land-derived elements, including weathering products, anthropogenic-related elements, and mining-related elements, had a significant positive correlation with sediment silt, clay, and organic carbon contents. The spatial patterns of the land-derived elements' concentrations and source contributions were consistent with the sediment transport pathways inferred from the STA. This result revealed that the delivery of the land-derived elements was determined by marine current flows and the associated sediment transport processes. Conversely, elements originating from marine sources, such as

sand and older sediment, and from the biological activities of calcareous and siliceous organisms showed little response to sediment transport and deposition processes. Our study links the outputs of statistically oriented approaches (e.g., PMF) to a process-based understanding of elemental transport in marine environments. © 2018 Elsevier B.V.

Lin, H., Liu, J., Dong, Y.*, et al.* (2019) The effect of substrates on the removal of low-level vanadium, chromium and cadmium from polluted river water by ecological floating beds. *Ecotoxicology and Environmental Safety,* 169: 856-862.
Keywords: Antioxidant enzyme; Ecological floating beds; Heavy metals; Substrates; Vanadium

Abstract
Ecological floating beds (EFBs) is one of the effective methods lately used to remove heavy metals pollutions in water. However, the role of substrate in EFBs was mainly focused on the study of microorganisms, and the effect of substrates on plants enrichment of heavy metals was rarely investigated. This study aimed to investigate the promotion of different substrates (green zeolite, sepiolite, absorbent paper, and ceramsite) on the removal of multi-heavy metals (V, Cr, and Cd) by Acorus calamus L. It also investigated the plant growth status. Results showed that the relative increase rate of Acorus calamus L. fresh weight increased the most in EFBs with green zeolite group (EFB-GZ), which was 60.50%, higher than 38.17% in EFBs with Acorus calamus L. (EFB-A). The enrichment ability of multi-metals in Acorus calamus L. was stronger in EFBs with substrates than in EFB-A, and green zeolite was the best. After 34 days, the total removal efficiency of V, Cr and Cd in EFB-GZ were 79.91%, 95.24% and 91.80%, respectively. Heavy metals translocation from root to shoot influenced by the kinds of substrates. In EFB-GZ, the translocation factor (TF) of V, Cr and Cd were 0.081, 0.263 and 0.180, respectively (0.024, 0.608 and 0.032 in EFB-A). The ability of Acorus calamus L. to resist multi-metals stress was significantly higher in EFBs with substrates than that in EFB-A and the activity of SOD, POD and CAT were increased by heavy metals stress. Our results acquired that green zeolite was the best substrate to promote multi-metals uptake by Acorus calamus L., which could effectively maintain the pH of water, provide a stable environment and nutriment for Acorus calamus L. Green zeolite can promote the translocation of V and Cd from root to shoot in Acorus calamus L., but is not conducive to Cr.

Mikkonen, H.G., van de Graaff, R., Collins, R.N.*, et al.* (2019) Immobilisation of geogenic arsenic and vanadium in iron-rich sediments and iron stone deposits. *Science of the Total Environment,* 654: 1072-1081.
Keywords: Arsenic; Vanadium; Iron stone; Synchrotron; X-ray fluorescence; X-ray absorption near edge spectroscopy

Abstract
Determination of how geogenic arsenic (As) and vanadium (V) is mobilised from naturally-enriched soils and iron (Fe) stones is integral for understanding the potential risk to the environment from changed land use conditions. Thus, the association of As, V and Fe in As-enriched sediments and Fe stones in Tertiary sediments of Melbourne, Australia, was assessed using chemical extraction methods, micro focused X-ray fluorescence and X-ray absorption spectroscopy. We show that the selective association of As with Fe during Fe stone formation has resulted in As enrichment of up to 60 times the concentration of surrounding soils, and 1000 times higher than mean As concentrations in world soils. In both soil and Fe stones, As was distributed with goethite as arsenate and relatively immobile under oxic conditions. The presence of V on the outer edge of the assessed Fe stone provided evidence of differences in historical As and V solubility; that is, As was immobilised by Fe during an earlier stage of Fe stone formation than V.

Modabberi, S., Tashakor, M., Sharifi Soltani, N.*, et al.* (2018) Potentially toxic elements in urban soils: source apportionment and contamination assessment. *Environmental Monitoring and Assessment,* 190(12)

Keywords: Contamination factor; Enrichment factor; Environmental geochemistry; Multivariate statistics; Soil contamination; Urban geochemistry

Abstract

Soils play a vital role in the quality of the urban environment and the health of its residents. City soils and street dusts accumulate various contaminants and particularly potentially toxic elements (PTEs) from a variety of human activities. This study investigates the current condition of elemental concentration in the urban soils of Hamedan, the largest and the fastest-growing city in western Iran. Thirty-four composite soil samples were collected from 0 to 10 cm topsoil of various land uses in Hamedan city and were analyzed for total concentration of 63 elements by ICP-MS. The possible sources of elemental loadings were verified using multivariate statistical methods (principal component analysis and cluster analysis) and geochemical indices. The spatial variability of the main PTEs was mapped using geographic information system (GIS) technique. The results revealed a concentration for As, Co, Cr, Mn, Mo, Ni, and V in the soil samples comparable to the background values as well as a range of associations among these elements in a single component suggesting geogenic sources related to geological and pedogenic processes, while the soils mostly presented a moderate to considerable enrichment/contamination of Cd, Zn, Pb, and Sb and moderate enrichment/contamination of Cu, Zn, and Mo. It was found that anthropogenic factors, vehicular traffic in particular, control the concentration of a spectrum of elements that are typical of human activities, i.e., Cd, Cu, Hg, Pb, Sb, and Zn. Lead and Sb were both the most enriched elements in soils with no correlation with land use highlighting general urban emissions over time and the impact of transport networks directly on soil quality. The highest concentrations of As were recorded in the southern part of the city reflecting the influence of metamorphic rocks. The effect of the geological substrate on the Co and Ni contents was confirmed by their maximum concentrations in the city's marginal areas. However, high spatial variability of urban elements' contents displayed the contribution of various human activities. In particular, the increased concentration of Cd, Sb, and Pb was found to be consistent with the areas where vehicular traffic is heaviest. © 2018, Springer Nature Switzerland AG.

Nguyen, C.T.T., Wasson, R.J., Estrada, E.S.*, et al.* (2019) Soil elemental analysis in a high conservation tropical forest in Singapore. *Journal of Environmental Management,* 232: 999-1011.

Keywords: Elemental distribution; Forest catchment; Land uses/land covers; Trace metal; Tropics

Abstract

To understand the distribution of soil elemental concentrations and their potential sources of trace metal contamination in the high-conservation Nee Soon freshwater swamp forest in Singapore, we analyzed samples from 227 surface and 35 subsurface (auger profiles) locations. Our assessment involved distribution maps, principle component analysis, cluster analysis, and correlation analysis of element concentrations determined from a mixed acid digestion and measurement on an ICP-MS. We found a distinct zonation in the distribution of several elements (Ba, Cr, Cu, Fe, Mn, Pb, Sr, Ti, V, and Zn) between the upper and lower catchment that gives an erroneous notion of widespread contamination in the lower catchment. We believe this zonation is natural, likely related to differences in the underlying geology. However, Cu, Pb, and Sb concentrations were greatly enriched by anthropogenic

activities on military training lands in the lower catchment, firing ranges in particular. Barium, Sr, and Zn also appear to be enriched in the lower part of the catchment, possibly from anthropogenic activities including military activity and roads. Although soils in the catchment are not highly contaminated, isolated areas with high concentrations of Cu, Pb and Sb may warrant management attention given the sensitive nature of the urban forest, which includes the last remaining fresh water swamp forest in Singapore. © 2018 Elsevier Ltd.

Ogunlaja, A., Ogunlaja, O.O., Okewole, D.M.*, et al.* (2019) Risk assessment and source identification of heavy metal contamination by multivariate and hazard index analyses of a pipeline vandalised area in Lagos State, Nigeria. *Science of the Total Environment,* 651: 2943-2952.

Keywords: Groundwater contamination; Health hazard assessment; Heavy metals; Multivariate analyses; Petroleum contamination

Abstract

Petroleum contamination is a significant contributor of elevated level of toxic heavy metals, which are of great concern to human health, due to their non-biodegradable nature. Agaye community has experienced frequent gasoline spills due to pipeline vandalisation, resulting in the contamination of soil and water sources. The concentrations of metals (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn) in groundwater, surface-water and soil were determined from a total of 216 samples acquired bi-monthly for two years by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to evaluate the impact of oil spills. Multivariate analyses using principal component analysis (PCA) and cluster analysis (CA) were also used to study the interactions between metals and identify the possible sources of contamination. The concentrations of heavy metals in soil and water samples (surface and groundwater) were in decreasing order of Mn > Ni > Zn > Cu > V > Cr > Pb > Cd and Ni > Zn > V > Cu > Mn > Pb > Cr > Cd respectively. Ni concentration ranged from 0.42–8.05 mg kg−1 and 0.10–2.85 mg L−1 for soil and groundwater respectively. Ni and V were more enhanced ($P < 0.05$) in soil samples. This study showed that there was significant relationship between elevated levels of Cr, Cu, Ni and Zn and oil spillage, due to petroleum spills and that residents were vulnerable to and at greater risk of non-carcinogenic hazards if they consumed groundwater. Multivariate analyses showed significant anthropogenic intrusions of two diagnostic heavy metals (Ni and V) for petroleum contamination in the soils and water sources. © 2018 Elsevier B.V.

Przydatek, G. (2019) The analysis of the possibility of using biological tests for assessment of toxicity of leachate from an active municipal landfill. *Environmental Toxicology and Pharmacology,* 67: 94-101.

Keywords: Municipal waste; Landfill; Leachate; Toxicity

Abstract

One of the consequence of municipal waste deposition is the production of landfill leachate. Its volume and composition is determined by numerous factors, including waste composition, landfill age and the volume of precipitation. Leachate may contain a number of mineral and organic compounds, the volume of which must be controlled regularly. One of the methods of determining the toxicity of substances contained in landfill leachate is the use of biological tests, based − among others − on aquatic organisms sensitive to environmental contamination. The purpose of this study was to analyse the possibility of using ecotoxicological tests (supplementing the physical and chemical tests) for the purpose of assessment of landfill leachate toxicity. The tests were conducted at an operating municipal landfill in Stary Sącz (southern Małopolska Region, Poland N: 49°55'33"76, E: 20°65'68'70) from December 2015 to October 2016. The scope of the tests included the analysis of physical

and chemical indicators as part of the landfill monitoring process, and also the analysis of additional selected indicators: namely the boron, barium and vanadium content. The selected ecotoxicological tests included tests using Daphnia magna Straus (Cladocera, Crustacea). Leachate tests conducted with the use of physical and chemical indicators have, for nearly twenty years, mainly demonstrated changes related to the age of the used landfill; besides increased boron and barium values, no evident contamination has been found, excluding the case of boron. However, a statistically significant correlation between the B and Ba contents and the amount of precipitation was determined. In two cases, the used biological tests have confirmed the toxicity of the leachate: in January and June 2016. In the same months, the highest and abnormal boron contents were measured, which could cause a toxic effect of leachates.

Rinklebe, J., Antoniadis, V., Shaheen, S.M.*, et al.* (2019) Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International,* 126: 76-88.
Available at:
https://www.sciencedirect.com/science/article/pii/S0160412018324954/pdfft?md5=5cfea4ef254356ae57dbf4b647181f6b&pid=1-s2.0-S0160412018324954-main.pdf
Keywords: Heavy metals; Risk assessment; Riverine ecosystems; Trace elements; Wetland soil

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

Saarikoski, S., Reyes, F., Vázquez, Y.*, et al.* (2019) Characterization of submicron aerosol chemical composition and sources in the coastal area of Central Chile. *Atmospheric Environment,* 199: 391-401.

Keywords: Aerosol Mass Spectrometer; Chemical composition; Source apportionment; South America; Submicron particles

Abstract
Chemical characteristics and the sources of submicron particles (<1 μm in diameter) were investigated in Valle Alegre, the coastal area of Central Chile. The chemical composition of particles was studied by using a Soot particle Aerosol Mass Spectrometer and Multi-Angle Absorption Photometer. Submicron particles were dominated by organics (42% of mass) and sulfate (39% of mass) while the mass fractions of ammonium, nitrate and black carbon were much smaller (13, 2 and 4% of mass, respectively). Additionally, several metals (V, Zn, Fe, Cd, Cu, K, Na and Mg) were detected in submicron particles and also some of their inorganic salts (e.g. NaCl+, MgCl2 +, CaCl2 +, KCl+ and KNO3 +). The sources of particles were examined by using Positive Matrix Factorization (PMF). Organic aerosol (OA) was divided into five factors by using PMF; hydrocarbon-like OA (HOA), biomass burning OA (BBOA), low-volatility oxygenated OA (LV-OOA), semi-volatile OA (SV-OOA) and marine oxygenated OOA (MOOA). Oxygenated factors (LV-OOA; SV-OOA and MOOA) comprised 75% of total OA with LV-OOA being the dominant factor (38% of OA). Sulfate had two major sources in Valle Alegre; ∼70% of sulfate was related to anthropogenic sources through the oxidation of gas phase SO2 whereas ∼24% of sulfate was associated with biogenic origin related to the oxidation of dimethyl sulfide in the marine environment. Regarding total submicron particle mass (campaign-average 9.5 μg m−3), the contribution of anthropogenic sources was at least as large as that of biogenic origin. © 2018 The Authors.

Shaheen, S.M., Alessi, D.S., Tack, F.M.G.*, et al.* (2019) Redox chemistry of vanadium in soils and sediments: Interactions with colloidal materials, mobilization, speciation, and relevant environmental implications - A review. *Advances in Colloid and Interface Science,* 265: 1-13.
Keywords: Colloidal materials; Redox potential; Sediments; Vanadium; Wetland soils

Abstract
Vanadium (V), although serving as an important component of industrial activities, has bioinorganic implications to pose highly toxic hazards to humans and animals. Soils and sediments throughout the world exhibit wide ranges of vanadium concentrations. Although vanadium toxicity varies between different species, it is mainly controlled by soil redox potential (EH). Nonetheless, knowledge of the redox geochemistry of vanadium lags in comparison to what is known about other potentially toxic elements (PTEs). In particular, the redox-induced speciation and mobilization of vanadium in soils and sediments and the associated risks to the environment have not been reviewed to date. Therefore, this review aims to address 1) the content and geochemical fate of vanadium in soils and sediments, 2) its redox-induced release dynamics, 3) redox-mediated chemical reactions between vanadium and soil organic and inorganic colloidal materials in soil solution, 4) its speciation in soil solution and soil-sediments, and 5) the use of advanced geochemical and spectroscopic techniques to investigate these complex systems. Vanadium (+5) is the most mobile and toxic form of its species while being the thermodynamically stable valence state in oxic environments, while vanadium (+3) might be expected to be predominant under euxinic (anoxic and sulfidic) conditions. Vanadium can react variably in response to changing soil EH: under anoxic conditions, the mobilization of vanadium can decrease because vanadium (+5) can be reduced to relatively less soluble vanadium (+4) via inorganic reactions such as with H2S and organic matter and by metal-reducing microorganisms. On the other hand, dissolved concentrations of vanadium can increase at low EH in many soils to reveal a similar pattern to that of Fe, which may be due to the reductive dissolution of Fe(hydr)oxides and the release of the associated vanadium. Those differences in vanadium release dynamics might occur as a

result of the direct impact of EH on vanadium speciation in soil solution and soil sediments, and/or because of the EH-dependent changes in soil pH, chemistry of (Fe)(hydr)oxides, and complexation with soil organic carbon. Release dynamics of vanadium in soils may also be affected positively by soil pH and the release of aromatic organic compounds. X-ray absorption spectroscopy (XAS) is a powerful tool to investigate the speciation of vanadium present in soil. X-ray absorption near edge structure (XANES) is often used to constrain the average valence state of vanadium in soils and sediments, and in limited cases extended X-ray absorption fine structure (EXAFS) analysis has been used to determine the average molecular coordination environment of vanadium in soil components. In conclusion, this review presents the state of the art about the redox geochemistry of vanadium and thus contributes to a better understanding of the speciation, potential mobilization, and environmental hazards of vanadium in the near-surface environment of uplands, wetlands, and agricultural ecosystems as affected by various colloidal particles. Further research is needed to elucidate the geochemistry and speciation of vanadium in the dissolved, colloidal, and soil sediments phases, including the determination of factors that control the redox geochemistry of vanadium.

Wang, S., Cai, L-M., Wen, H-H.*., et al.* (2019) Spatial distribution and source apportionment of heavy metals in soil from a typical county-level city of Guangdong Province, China. *Science of the Total Environment,* 655: 92-101.
Keywords: Positive matrix factorization; Soil heavy metals; Source apportionment; Spatial distribution

Abstract
The contents of ten heavy metals (Cr, Hg, As, Pb, Ni, Cd, Ti, Cu, Zn and V) in 413 topsoil samples from Puning City, Guangdong Province, China were investigated. Obvious enrichment of Hg, As, Pb, Cd and Zn were presented, and the contents of Hg and As in 5.8% and 3.4% samples respectively were higher than the guideline values recommended by the Chinese Environmental Quality Standard for Soils. Chromium and V were presented no enrichment and no pollution. According to one-way analysis of variance, the mean contents of Hg, Pb, Cu and Zn in land for construction were significantly higher than farmland and natural vegetation, but the land use had no obvious effect on other heavy metals. Furthermore, the potential sources of ten heavy metals were identified and apportioned in combination with geostatistics, correlation analysis and positive matrix factorization model. The results were following as: a) Pb, Zn and Cu mainly origin from vehicle emission and atmosphere deposition, and the hotspots approximately distributed in the areas of intensive traffic and near main roads; b) Hg and Cd were derived to industrial activities related to pharmaceutical industries, the textile and dyeing industries and e-waste recycling industries, and high-value areas were mainly concentrated in the northeast of the urban area where the industrial parks have been distributed; c) Soil parent material (Jurassic shale) was the main source of Cr, Ni, V and Ti; d) As mainly came from agricultural inputs such as pesticides or herbicides, livestock and fertilizers. Meanwhile, the contributions of four sources were 33.08%, 24.04%, 27.11% and 15.77% of the total contribution, respectively. © 2018 Elsevier B.V.

Yu, Y-Q. & Yang, J-Y. (2019) Oral bioaccessibility and health risk assessment of vanadium(IV) and vanadium(V) in a vanadium titanomagnetite mining region by a whole digestive system in-vitro method (WDSM). *Chemosphere,* 215: 294-304.
Keywords: Oral bioaccessibility; Oral ingestion; Vanadium(IV); Vanadium(V); Whole digestive system in-vitro method (WDSM)

Abstract

Oral bioaccessibility of vanadium(IV) and vanadium(V) in soil, dust and concentrate fines from a vanadium titanomagnetite mining region was assessed by a whole digestive system in-vitro scheme. The scheme including the addition of sweat and the large intestinal digestion was used to estimate the oral bioaccessibility of vanadium(IV) and vanadium(V) in the whole digestive system for the first time. Higher oral bioaccessibility of vanadium(IV) and vanadium(V) was determined in gastric and small intestinal phases demonstrating that their major roles for vanadium digestion and absorption. The decreasing order of the oral bioaccessibility of vanadium(IV) and vanadium(V) in each digestive phase was stomach, small intestine, large intestine and mouth. Higher oral bioaccessibility of vanadium(V) in the whole digestion indicated its higher risk potential for human than vanadium(IV). Lower oral bioaccessibility of vanadium(IV) and vanadium(V) determined in bionic digestion illustrated detoxicity potential of human body for ingested vanadium. Compared with soil and dust, higher digestion rate of vanadium in vanadium titanomagnetite concentrate fines indicated its higher risk for human, especially for mining workers. Based on vanadium oral bioaccessibility, hazard quotients of the vanadium were much less than the critical level suggested for no non-carcinogenic risks to the populations surrounding the sampling sites. Indeed, compared with the estimations based on total vanadium content, the incorporation of oral vanadium bioaccessibility into risk assessments could give more realistic information.

6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

Alvarez, M.D.P. & Carol, E. (2019) Geochemical occurrence of arsenic, vanadium and fluoride in groundwater of Patagonia, Argentina: Sources and mobilization processes. ***Journal of South American Earth Sciences,*** **89: 1-9.**

Keywords: Groundwater; Hydrogeochemical processes; Península valdés; Sediment interaction; Trace elements; Water supply

Abstract

Contamination of groundwater in different parts of the world is a result of natural and/or anthropogenic sources, leading to adverse effects on human health and the ecosystem. In Península Valdés, where groundwater is the only source of supply, high concentrations of As and F- were registered. Since it is a region without industrial activity, an analysis of possible natural sources of contamination is necessary. The aim of this study is to analyse the hydrological processes that determines the presence and mobilization of those elements through the analysis of the mineralogy of the aquifer sediments and the ionic water relationships. The productive aquifer, dominated by psamites, coquinas and siltstone is located between 29 and 42 m below ground surface. The hydrochemistry studied from 105 sampling points, shows that groundwater is dominated by Na-Cl ions and, in the fresh water sectors, the ionic type is Na-HCO3 to Na-Cl. In 17 of these samples, Zn, Cr, Mn, As, V, Sr, Fe, F ions were measured and As and F contents above the potability limit were recorded. These contents vary between 0.01 and 0.40 mg/L in As and between 0.31 and 4 in F- which are both associated with elevated V values. The optical petrographic microscope observations and the X-ray diffraction measurements show that the sediments are dominated by volcanic lithic fragments, volcanic glass shards and quartz, plagioclase, pyroxenes and magnetite clasts. The scanning electron microscopy, combined with the energy dispersive X-ray analysis, shows that the highest concentrations of As are associated with volcanic shards and iron oxides. The combined analysis of all these elements leads to conclude that the processes which explain the presence of those ions are a result of the interaction of groundwater with the components of the aquifer sediments. At alkaline pH, the high solubility of the amorphous silica of vitreous shards allows the release of As, V and F- ions towards the solution. Thus, adsorption-

desorption processes can also control the presence of these ions in groundwater. Both As and V (in solution in the form of oxyanions) can be adsorbed by iron oxides, while F- anions have more affinity to be adsorbed by the carbonate facies, some of them re-precipitated as a result of the increase in pH. The identified hydrogeological processes provide information for the planning of water purification measures that tend to improve the water resources management in a large arid region of Patagonia. © 2018 Elsevier Ltd.

van Aswegen, J.D., Nel, L., Strydom, N.A.*, et al.* (2019) Comparing the metallic elemental compositions of Kelp Gull Larus dominicanus eggs and eggshells from the Swartkops Estuary, Port Elizabeth, South Africa. *Chemosphere,* 221: 533-542.
Keywords: Chromium; Cobalt; Copper; Indian ocean; Laridae; Mercury; Vanadium; Zinc

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

7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS

Gholizadeh, M. & Patimar, R. (2018) Ecological risk assessment of heavy metals in surface sediments from the Gorgan Bay, Caspian Sea. *Marine Pollution Bulletin,* 137: 662-667.
Available at:
https://www.researchgate.net/profile/Mohammad_Gholizadeh/publication/329191249_Ecological_risk_assessment_of_heavy_metals_in_surface_sediments_from_the_Gorgan_Bay_Caspian_Sea/links/5c02efe692851c63cab32ae8/Ecological-risk-assessment-of-heavy-metals-in-surface-sediments-from-the-Gorgan-Bay-Caspian-Sea.pdf
Keywords: Bays; Caspian Sea; Ecology; Environmental Monitoring; Geologic Sediments/analysis; Metals, Heavy/analysis/toxicity; Risk Assessment; Water Pollutants, Chemical/analysis; Enrichment factor; Gorgan Bay; Metal; Pollution; Sediment

Abstract:
This study was conducted to investigate the amounts of heavy metals in the Gorgan Bay. For this purpose, 12 sediment samples were taken from the Gorgan Bay, and then, the amounts of metals were determined using the ICP-OES spectrometer. Accordingly, the average value of the metals aluminum (Al), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn) was 1.3+/-0.2%, 8.1+/-3.8ppm, 17.9+/-4.3ppm, 16.8+/-4.2ppm, 16.6+/-4ppm, 7.4+/-1.3ppm, 17.6+/-3.7ppm, and 29.5+/-6.9ppm, respectively. According to the Pearson test, a significant correlation was observed among all metals (except arsenic) in this study (P0.05). This positive correlation probably indicates that these metals enter the aquatic environment along with organic matter or that they are of the same origin (organic

matter and metals). On the basis of the PER index, all the measured metals had a low ecological risk at all stations.

Lin, H., Liu, J., Dong, Y.*, et al.* (2019) The effect of substrates on the removal of low-level vanadium, chromium and cadmium from polluted river water by ecological floating beds. *Ecotoxicology and Environmental Safety,* 169: 856-862.
Keywords: Antioxidant enzyme; Ecological floating beds; Heavy metals; Substrates; Vanadium

Abstract
Ecological floating beds (EFBs) is one of the effective methods lately used to remove heavy metals pollutions in water. However, the role of substrate in EFBs was mainly focused on the study of microorganisms, and the effect of substrates on plants enrichment of heavy metals was rarely investigated. This study aimed to investigate the promotion of different substrates (green zeolite, sepiolite, absorbent paper, and ceramsite) on the removal of multi-heavy metals (V, Cr, and Cd) by Acorus calamus L. It also investigated the plant growth status. Results showed that the relative increase rate of Acorus calamus L. fresh weight increased the most in EFBs with green zeolite group (EFB-GZ), which was 60.50%, higher than 38.17% in EFBs with Acorus calamus L. (EFB-A). The enrichment ability of multi-metals in Acorus calamus L. was stronger in EFBs with substrates than in EFB-A, and green zeolite was the best. After 34 days, the total removal efficiency of V, Cr and Cd in EFB-GZ were 79.91%, 95.24% and 91.80%, respectively. Heavy metals translocation from root to shoot influenced by the kinds of substrates. In EFB-GZ, the translocation factor (TF) of V, Cr and Cd were 0.081, 0.263 and 0.180, respectively (0.024, 0.608 and 0.032 in EFB-A). The ability of Acorus calamus L. to resist multi-metals stress was significantly higher in EFBs with substrates than that in EFB-A and the activity of SOD, POD and CAT were increased by heavy metals stress. Our results acquired that green zeolite was the best substrate to promote multi-metals uptake by Acorus calamus L., which could effectively maintain the pH of water, provide a stable environment and nutriment for Acorus calamus L. Green zeolite can promote the translocation of V and Cd from root to shoot in Acorus calamus L., but is not conducive to Cr.

Ogunlaja, A., Ogunlaja, O.O., Okewole, D.M.*, et al.* (2019) Risk assessment and source identification of heavy metal contamination by multivariate and hazard index analyses of a pipeline vandalised area in Lagos State, Nigeria. *Science of the Total Environment,* 651: 2943-2952.
Keywords: Groundwater contamination; Health hazard assessment; Heavy metals; Multivariate analyses; Petroleum contamination

Abstract
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This study showed that there was significant relationship between elevated levels of Cr, Cu, Ni and Zn and oil spillage, due to petroleum spills and that residents were vulnerable to and at greater risk of non-carcinogenic hazards if they consumed groundwater. Multivariate analyses showed significant anthropogenic intrusions of two diagnostic heavy metals (Ni and V) for petroleum contamination in the soils and water sources. © 2018 Elsevier B.V.

Ranjbar Jafarabadi, A., Riyahi Bakhtiari, A., Spanò, N.*, et al.* (2018) First report of geochemical fractionation distribution, bioavailability and risk assessment of potentially toxic inorganic elements in sediments of coral reef Islands of the Persian Gulf, Iran. *Marine Pollution Bulletin,* 137: 185-197.
Keywords: Bioavailability index; Coral reef sediment; Ecological risk assessment; Fractionation; Persian Gulf; Potentially toxic inorganic elements (PTIEs)

Abstract
Metal contamination is a serious environmental concern in the Middle East. Herein, geochemical fractionation distribution and potential sources of thirteen metals (Fe, Al, Mn, Zn, Cu, Co, Cr, Ni, V, As, Hg, Pb and Cd) were investigated in sediments from ten coral reef Islands in the Persian Gulf, Iran. To properly assess availability and mobility of elements, enrichment factor (EF), pollution load index (PLI), pollution index (PI), contamination index (CI), sediment pollution index (SPI) and ecological risk assessment were provided. Sediment grain size showed an outstanding role in controlling the levels of potentially toxic inorganic elements (PTIEs). The highest values of total organic matter (TOM) were detected in Kharg and Lavan Islands. Different metals fractionation distribution was found across sites. As was noticed in carbonate (F2), exchangeable (F1), Fe-Mn oxy-hydroxide (F3), organic (F4) and residual (F5) fractions, Hg primarily associated with F2 and F1, whereas Pb and Cd with F2, followed by F1, F3, F5 and F4. Conversely, Ni and V accumulated in F1, suggesting their high mobility and bioavailability, and thus environmental risk to aquatic biota. All metals (except Al, Fe and As) had geological and anthropogenic sources. Based on modified risk assessment analysis, the sediments from Kharg, Lavan, Siri and Lark Islands showed medium adverse effects. Overall, results from this study corroborate that petroleum industry is the main source of pollution of PTIEs in the Persian Gulf and offer a scientific basis for monitoring and preventing metal pollution in the environment. © 2018.

Rodríguez-Saldaña, V., González-Farías, F. & Miranda-Navarro, S.V. (2018) Bioaccumulation of metal(loid)s in Cardisoma crassum and pollution assessment in a mangrove protected area in Mexico. *Environmental Monitoring and Assessment,* 190(12)
Keywords: Bioaccumulation factors; Mangrove; Metals; Mouthless crab; Sediments

Abstract
The bioaccumulation of several elements in “mouthless crabs” (Cardisoma crassum) and their concentrations in environmental samples were assessed in a mangrove forest within a natural protected area located in the middle of Puerto Vallarta, Mexico. The concentrations of Al, As, Ba, Cd, Cr, Cu, Fe, Ni, Pb, Sr, Si, V, and Zn in sediments, mangrove litterfall, and pore water and their bioaccumulations in the muscle and shell tissue of C. crassum were determined during rainy and dry seasons. Two different sampling sites were compared, selected according to the influence of the tide. The samples were analyzed by ICP-OES. In pore water, half of the elements of interest were below the limits of detection. Pb and Cd concentrations were only detected in the sedimentary phase. Al and Fe presented the highest concentrations at both sampling sites in the sediments and mangrove litterfall. There were no significant differences between sampling seasons in water samples ($P > 0.05$). Only Cu presented significant differences between sampling seasons in the mangrove litterfall samples and V in the

sediment samples (P < 0.05). The sediment quality guidelines indicated that only Cd was above the threshold effect limit. As, Cd, Cr, Ni, and Pb remained below the limits of detection in muscle tissue and shell samples. The biota–sediment accumulation factors (BSAFs) determined for Cu and Zn were above 1.0, indicating the accumulation of these elements in the muscle tissue of C. crassum, while the BSAF values in the shell were above the threshold for Ba, Si, and Sr.

Smalling, K.L., Anderson, C.W., Honeycutt, R.K.*, et al.* (2019) Associations between environmental pollutants and larval amphibians in wetlands contaminated by energy-related brines are potentially mediated by feeding traits. *Environmental Pollution (Barking, Essex : 1987),* 248: 260-268.

Keywords: Amphibian; Brines; Energy development; Metals; Prairie Pothole Region; Wetland

Abstract

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

Zhou, Y., Gao, L., Xu, D.*, et al.* (2019) Geochemical baseline establishment, environmental impact and health risk assessment of vanadium in lake sediments, China. *Science of the Total Environment,* 660: 1338-1345.

Keywords: Vanadium; Poyang Lake; Sediments; Geochemical baseline; Sediment resuspension; Health risk assessment

Abstract

Lakes are essential water resources in China and their water quality are vital to its sustainability. However, the geochemical processes of trace elements, especially those of seldom-monitored trace elements, have not been adequately studied. Here, the regional geochemical baseline (RGB) of vanadium (V) was established using cumulative frequency and

normalization methods. Then, the RGB was applied to quantitatively calculate the anthropogenic contribution rate in sediments of the Poyang Lake (PYL), which is the largest freshwater lake in China. The pollution level and ecological risk of V were evaluated using the geoaccumulation index (Igeo) and potential ecological risk index (EI) with respect to three different reference values, namely local soil background values (BV), the RGB, and the median value of V concentrations. The health risk of V accumulation in residents through fish consumption during sediment resuspension was assessed by combining the environmental impact assessment model and health risk assessment model. The mean concentration of V in PYL sediments was 94.37 mg/kg (33.80–148.53 mg/kg), which was slightly higher than the levels in stream sediments in China, but lower than the local BV. The calculated RGB was slightly higher than the average V content in PYL sediments, but similar to the local BV. The average anthropogenic contribution rate was calculated as 11.48%, demonstrating low anthropogenic influence. Moreover, the result of Igeo and EI showed that V in PYL sediments was uncontaminated and posed a low ecological risk. In addition, based on the calculation by the two models, the human health risk result (target hazard quotient <1) indicated that the average human health risk from fish consumption due to sediment resuspension was negligible.

8. MISCELLANEOUS

Boukhobza, I. & Crans, D.C. (2017) Application of HPLC to measure vanadium in environmental, biological and clinical matrices. ***Arabian Journal of Chemistry***
Keywords: Vanadium; HPLC separation; Speciation; Characterization; Quantitation; Environmental samples; Biological samples; Clinical samples

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

Donner, M.W., Arshad, M., Ullah, A.*, et al.* (2019) Unravelled keratin-derived biopolymers as novel biosorbents for the simultaneous removal of multiple trace metals from industrial wastewater. ***Science of the Total Environment,*** **647: 1539-1546.**
Keywords: Biopolymer; Biosorbent; Keratin; Trace metals; Wastewater

Abstract
Biopolymers derived from modified poultry feathers (KB) were developed to target a broad range of potentially toxic trace elements for their removal from synthetic wastewater and industrial process affected water. The chemical modifications increased surface functionality of KBs for enhanced metal adsorption. Unmodified KB (SM-03) added to synthetic wastewater spiked with nine transition and redox sensitive elements (30–50 μg L−1 each) removed >82% of Pb, Ni, Co and Zn, whereas modified KBs (SM-01 and SM-06) removed 68–100% of SeIV, VV and CrVI. Similar results were observed when spiked process water was used. Experimental observation suggested chemical reduction of redox sensitive elements on the modified KB surfaces to their non-toxic/non-mobile redox states. Biopolymer SM-06 showed a maximum adsorption capacity of 17 mg g−1 for VV and 15 mg g−1 for CrVI at ~20 °C. Due to the abundance of raw material and simplicity of the modifications presented here, modified KBs may serve as a useful option for large-scale water treatment. © 2018 Elsevier B.V.

Hettiarachchi, E., Paul, S., Cadol, D.*, et al.* (2019) Mineralogy Controlled Dissolution of Uranium from Airborne Dust in Simulated Lung Fluids (SLFs) and Possible Health Implications. *Environmental Science and Technology Letters,* 6(2): 62-67.

Abstract
The recent increase in cardiovascular and metabolic disease in the Navajo population residing close to the Grants Mining District (GMD) in New Mexico is suggested to be due to exposure to environmental contaminants, in particular uranium in respirable dusts. However, the chemistry of uranium-containing-dust dissolution in lung fluids and the role of mineralogy are poorly understood, as is their impact on toxic effects. The current study is focused on the dissolution of respirable-sized U-containing-dust, collected from several sites near Jackpile and St. Anthony mines in the GMD, in two simulated lung fluids (SLFs): Gamble's solution (GS) and Artificial Lysosomal Fluid (ALF). We observe that the respirable dust includes uranium minerals that yield the uranyl cation, UO 2 2+ , as the primary dissolved species in these fluids. Dust rich in uraninite and carnotite is more soluble in GS, which mimics interstitial conditions of the lungs. In contrast, dust with low uraninite and high kaolinite is more soluble in ALF, which simulates the alveolar macrophage environment during phagocytosis. Moreover, geochemical modeling, performed using PHREEQC, is in good agreement with our experimental results. Thus, the current study highlights the importance of site-specific toxicological assessments across mining districts with the focus on their mineralogical differences. © 2018 American Chemical Society.

Mori, N., Sugitani, K., Yamamoto, M.*, et al.* (2018) Major and minor elemental compositions of streambed biofilms and its implications of riverine biogeochemical cycles. *Environmental Pollution,* 243: 308-317.
Keywords: Chemical compositions; Dam reservoir; Heavy metals; Streambed biofilm

Abstract
Chemical compositions of streambed biofilms from a major river of central Japan (the Kushida River) were obtained, with data of associated sediments (fine-grained fractions < 63 μm) and dissolved components of waters, in order to provide preliminary information about biogeochemical significance of streambed biofilms. During the sampling period (July 31st to August 3rd, 2013), dissolved components of the river waters were influenced by the dam reservoir. Concentrations of NO3 −, silica (as Si), SO4 2−, PO4 3− and Ca2+ decreased across the dam, whereas Fe and Mn increased across the dam, and then decreased downstream rapidly. Streambed biofilms contain significant amount of non-nutrient elements such as Al (up to 21% as Al2O3 on water and others-free basis), indicating that they are contaminated as siliciclatic (silt and clay) materials. Siliciclastic materials in the biofilms are basically

compositionally similar to fine-grained (<63 μm) fractions of streambed sediments. However, some elements such as Ca, P, Mn, and Zn are markedly enriched in the biofilms. Particularly, Mn concentrations in the biofilm samples collected just below the dam reservoir are very high (∼4.0 wt %), probably due to accumulation from the discharged water. Concentrations of trace elements such as P, Cr, Cu, Zn and V appear to be controlled by amounts of Fe-oxides and/or Mn-oxides in biofilms. Numbers of factors are involved in controlling chemical compositions of streambed biofilms, including amount of contaminated siliciclastics, authigenic mineral formation, adsorption of dissolved materials and microbial metabolisms. As demonstrated by this study, systematic analyses including major elements and comparison with associated sediments and waters could reveal biogeochemistry of this complex system. Chemical compositions of streambed biofilms can be interpreted by contaminated silts and clays, bioaccumulation and adsorption onto Fe- and Mn- oxides.

Natzke, J., Noar, J. & Bruno-Bárcena, J.M. (2018) Azotobacter vinelandii nitrogenase activity, hydrogen production, and response to oxygen exposure. *Applied and Environmental Microbiology,* 84(16)
Keywords: Hydrogen; In vivo nitrogenase activity; Iron; Molybdenum; Vanadium

Abstract
Azotobacter vinelandii selectively utilizes three types of nitrogenase (molybdenum, vanadium, and iron only) to fix N2, with their expression regulated by the presence or absence of different metal cofactors in its environment. Each alternative nitrogenase isoenzyme is predicted to have different electron flux requirements based on in vitro measurements, with the molybdenum nitrogenase requiring the lowest flux and the iron-only nitrogenase requiring the highest. Here, prior characterized strains, derepressed in nitrogenase synthesis and also deficient in uptake hydrogenase, were further modified to generate new mutants lacking the ability to produce poly-β-hydroxybutyrate (PHB). PHB is a storage polymer generated under oxygen-limiting conditions and can represent up to 70% of the cells' dry weight. The absence of such granules facilitated the study of relationships between catalytic biomass and product molar yields across different adaptive respiration conditions. The released hydrogen gas observed during growth, due to the inability of the mutants to recapture hydrogen, allowed for direct monitoring of in vivo nitrogenase activity for each isoenzyme. The data presented here show that increasing oxygen exposure limits equally the in vivo activities of all nitrogenase isoenzymes, while under comparative conditions, the Mo nitrogenase enzyme evolves more hydrogen per unit of biomass than the alternative isoenzymes. © 2018 American Society for Microbiology.

Omidinasab, M., Rahbar, N., Ahmadi, M.*, et al.* (2018) Removal of vanadium and palladium ions by adsorption onto magnetic chitosan nanoparticles. *Environmental Science and Pollution Research,* 25(34): 34262-34276.
Keywords: Chitin; Chitosan coated magnetic iron oxide nanoparticles; Palladium; Shrimp shell; Vanadium

Abstract
Chitosan (CS), synthesized from chitin chemically extracted from shrimp shells, was used for the synthesis of magnetic chitosan nanoparticles (Fe3O4-CSN), which makes the adsorbent easier to separate. Fe3O4-CSN was used for the removal of toxic metals such as vanadium (V(V)) and palladium (Pd(II)) ions from aqueous solutions. Influencing factors on the adsorption process such as pH, contact time, adsorbent dosage, and agitation speed were investigated. A competitive adsorption of V(V) and Pd(II) ions for the active sites was also studied. The monolayer maximum adsorption capacities (Qm) of 186.6 and 192.3 mg/g were

obtained for V(V) and Pd(II) ions, respectively. The pseudo-second-order equation gave the best fit for the kinetic data, implying that chemisorption was the determining step. Freundlich model yielded a much better fit than the other adsorption models assessed (Langmuir, Temkin and Dubinin-Radushkevich). Thus, the adsorption of V(V) and Pd(II) ions onto Fe3O4-CSN is a combination of physical and chemical adsorption, as based on the kinetics and equilibrium study. Generally, physical adsorption is the mechanism that governs the system, while chemical adsorption is the slowest adsorption step that takes place. Thermodynamic studies displayed that the adsorption process was exothermic and spontaneous. Removal efficiencies of 99.9% for V(V) and 92.3% for Pd(II) ions were achieved, implying that Fe3O4-CSN adsorbent had an excellent ability for the removal of the metal ions from real industrial wastewaters without remarkable matrix effect. [Figure not available: see fulltext.].

Robertson, J.M., Nesbitt, J.A. & Lindsay, M.B.J. (2019) Aqueous- and solid-phase molybdenum geochemistry of oil sands fluid petroleum coke deposits, Alberta, Canada. *Chemosphere,* 217: 715-723.

Keywords: Geochemistry; Molybdenum; Oil sands; Petroleum coke; Water; X-ray absorption spectroscopy

Abstract

Fluid petroleum coke generated at oil sands operations in the Athabasca Oil Sands Region of northern Alberta, Canada, contains elevated concentrations of molybdenum (Mo) and other metals including nickel (Ni) and vanadium (V). Solid-phase Mo concentrations in fluid petroleum coke are typically 10 to 100 times lower than V and Ni, yet dissolved Mo concentrations in associated pore waters are often comparable with these metals. We collected pore water and solids from fluid petroleum coke deposits in the AOSR to examine geochemical controls on Mo mobility. Dissolved Mo concentrations increased with depth below the water table, reaching maxima of 1.4–2.2 mg L −1 , within a mixing zone between slightly acidic and oxic meteoric water and mildly alkaline and anoxic oil sands process-affected water (OSPW). Dissolved Mo concentrations decreased slightly with depth below the mixing zone. X-ray absorption spectroscopy revealed that Mo(VI) and Mo(IV) species were present in coke solids. The Mo(VI) occurred as tetrahedrally coordinated MoO 4 2− adsorbed via inner- and outer-sphere complexation, and was coordinated in an environment similar to Fe-(hydr)oxide surface complexes. The OSPW likely promoted desorption of outer-sphere Mo(VI) complexes, resulting in higher dissolved Mo concentrations in the mixing zone. The principal Mo(IV) species was MoS 2 , which originated as a catalyst added upstream of the fluid coking process. Although MoS 2 is likely stable under anoxic conditions below the mixing zone, oxidative weathering in the presence of meteoric water may promote long-term Mo release. © 2018 Elsevier Ltd.

Yayayürük, A.E., Shahwan, T., Şxanli-Mohamed, G.*, et al.* (2018) Trypsin-immobilized silica: A novel adsorbent for V(IV) and V(V) removal from water. *Water Environment Research,* 90(12): 2056-2065.

Keywords: Inductively coupled plasma mass spectrometry; Removal; Silica; Trypsin; Vanadium

Abstract

In the present study, trypsin-immobilized silica was employed for the removal of V(IV) and V(V) ions from water. The synthesized sorbent was first characterized and then investigated for the removal of V(IV) and V(V) under various experimental conditions. The adsorption performance of the sorbent was tested as a function of pH, sorbent amount, initial vanadium concentration, contact time, and temperature. The sorption process was then investigated,

both from a kinetic perspective and also in terms of isotherm models. The Langmuir adsorption isotherm was the best model to describe the sorption process. Sorption thermodynamics were spontaneous and exothermic. The proposed method was successfully applied to real samples for the removal of V(IV)and V(V) with sufficient accuracy and precision.