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Vanadium Health Research Programme: Recent Published Literature

July – September 2016

Report to Vanitec

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

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Introduction

This report presents the bibliographic details of papers identified as being published during the period July 2016 – September 2016.

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

Jiang, M., Li, Y., Zhang, B.*, et al.* (2016) A nested case-control study of prenatal vanadium exposure and low birthweight. *Human Reproduction (Oxford, England),* 31(9):2135-2141.

Abstract:
Study Question: Is prenatal vanadium exposure associated with adverse birth outcomes?; Summary Answer: The odds of low birthweight (LBW) are increased 2.23-fold in mothers with a urinary vanadium of =2.91 μg/g creatinine compared with that in mothers with a urinary vanadium of =1.42 μg/g creatinine.; What Is Known Already: Human exposure to vanadium occurs through intake of food, water and polluted air. Vanadium has been suggested to have fetotoxicity and developmental toxicity in animal studies, and epidemiological studies have reported an association between a decrease in birthweight and vanadium exposure estimated from particulate matter.; Study Design, Size, Duration: A nested case-control study involving 816 study participants (204 LBW cases and 612 matched controls) was conducted with data from the prospective Healthy Baby Cohort between 2012 and 2014 in the province of Hubei, China.; Participants/materials, Setting, Methods: Vanadium concentrations in 816 maternal urine samples collected before delivery the median gestational age was 39 weeks (range 27-42 weeks)] were measured by inductively coupled plasma mass spectrometry. Information on the infants' birth outcomes was obtained from medical records. Conditional logistic regression was used to calculate the odds ratios (ORs) and 95% confidence intervals (CIs).; Main Results and the Role Of Chance: The median urinary vanadium concentration of the cases was much higher than that of the controls (3.04 μg/g creatinine versus 1.93 μg/g creatinine). The results revealed a significant positive trend between the odds of LBW and level of maternal urinary vanadium relative to the lowest tertile; adjusted OR = 1.69 (95% CI: 0.92, 3.10) for the medium tertile; adjusted OR = 2.23 (95% CI: 1.23, 4.05) for the highest tertile; P-trend = 0.02]. Additionally, the association was not modified by maternal age (P for heterogeneity = 0.70) or infant gender (P for heterogeneity = 0.21).; Limitations, Reasons For Caution: The maternal urine sample was collected before labor, and the maternal urinary vanadium levels measured at one point in time may not accurately reflect the vanadium burden during the entire pregnancy.; Wider Implications Of the Findings: The results of this study can enrich the biological monitoring data on urinary vanadium in pregnant women; and may be evidence that vanadium may affect fetal development.; Study Funding/competing Interests: This work was supported by the National Natural Science Foundation of China (21437002, 81372959 and 81402649), the R&D Special Fund for Public Welfare Industry (Environment) (201309048) and the Fundamental Research Funds for the Central Universities, HUST (2016YXZD043). The authors have no conflicts of interest to declare.;

2. HEALTH EFFECTS

del Carmen Garcia-Rodriguez, M., Montserrat Hernandez-Cortes, L. & Agustin Altamirano-Lozano, M. (2016) In Vivo Effects of Vanadium Pentoxide and Antioxidants (Ascorbic Acid and Alpha-Tocopherol) on Apoptotic, Cytotoxic, and Genotoxic Damage in Peripheral Blood of Mice. *Oxidative Medicine and Cellular Longevity, Article ID* : 6797851. Available at: http://downloads.hindawi.com/journals/omcl/aip/6797851.pdf

Abstract:
This study was conducted to investigate the effects of vanadium pentoxide (V2O5), ascorbic acid (AA), and alpha-tocopherol (alpha-TOH) on apoptotic, cytotoxic, and genotoxic activity. Groups of five Hsd:ICR mice were treated with the following: (a) vehicle, distilled water; (b) vehicle, corn oil; (c) AA, 100mg/kg intraperitoneally (ip); (d) alpha-TOH, 20mg/kg by gavage; (e) V2O5, 40mg/kg by ip injection; (f) AA + V2O5; and (g) alpha-TOH + V2O5. Genotoxic damage was evaluated by examining micronucleated polychromatic erythrocytes (MN-PCE) obtained from the caudal vein at 0, 24, 48, and 72 h after treatments. Induction of apoptosis and cell viability were assessed at 48 h after treatment in nucleated cells of peripheral blood. Treatment with AA alone reduced basal MN-PCE, while V2O5 treatment marginally increased MN-PCE at all times after injection. Antioxidants treatments prior to V2O5 administration decreased MN-PCE compared to the V2O5 group, with the most significant effect in the AA + V2O5 group. The apoptotic cells increased with all treatments, suggesting that this process may contribute to the elimination of the cells with V2O5-induced DNA damage (MN-PCE). The necrotic cells only increased in the V2O5 group. Therefore, antioxidants such as AA and alpha-TOH can be used effectively to protect or reduce the genotoxic effects induced by vanadium compounds like V2O5.

Jiang, M., Li, Y., Zhang, B.*, et al.* (2016) A nested case-control study of prenatal vanadium exposure and low birthweight. *Human Reproduction (Oxford, England),* 31(9): 2135-2141.

Abstract:
Study Question: Is prenatal vanadium exposure associated with adverse birth outcomes?; Summary Answer: The odds of low birthweight (LBW) are increased 2.23-fold in mothers with a urinary vanadium of =2.91 μg/g creatinine compared with that in mothers with a urinary vanadium of =1.42 μg/g creatinine.; What Is Known Already: Human exposure to vanadium occurs through intake of food, water and polluted air. Vanadium has been suggested to have fetotoxicity and developmental toxicity in animal studies, and epidemiological studies have reported an association between a decrease in birthweight and vanadium exposure estimated from particulate matter.; Study Design, Size, Duration: A nested case-control study involving 816 study participants (204 LBW cases and 612 matched controls) was conducted with data from the prospective Healthy Baby Cohort between 2012 and 2014 in the province of Hubei, China.; Participants/materials, Setting, Methods: Vanadium concentrations in 816 maternal urine samples collected before delivery the median gestational age was 39 weeks (range 27-42 weeks)] were measured by inductively coupled plasma mass spectrometry. Information on the infants' birth outcomes was obtained from medical records. Conditional logistic regression was used to calculate the odds ratios (ORs) and 95% confidence intervals (CIs).; Main Results and the Role Of Chance: The median urinary vanadium concentration of the cases was much higher than that of the controls (3.04 μg/g creatinine versus 1.93 μg/g creatinine). The results revealed a significant positive trend between the odds of LBW and level of maternal urinary vanadium relative to the lowest tertile; adjusted OR = 1.69 (95% CI: 0.92, 3.10) for the medium tertile; adjusted OR = 2.23 (95% CI: 1.23, 4.05) for the highest tertile; P-trend = 0.02]. Additionally, the association was not modified by maternal age (P for heterogeneity = 0.70) or

infant gender (P for heterogeneity = 0.21).; Limitations, Reasons For Caution: The maternal urine sample was collected before labor, and the maternal urinary vanadium levels measured at one point in time may not accurately reflect the vanadium burden during the entire pregnancy.; Wider Implications Of the Findings: The results of this study can enrich the biological monitoring data on urinary vanadium in pregnant women; and may be evidence that vanadium may affect fetal development.; Study Funding/competing Interests: This work was supported by the National Natural Science Foundation of China (21437002, 81372959 and 81402649), the R&D Special Fund for Public Welfare Industry (Environment) (201309048) and the Fundamental Research Funds for the Central Universities, HUST (2016YXZD043). The authors have no conflicts of interest to declare.

Park, E-J., Lee, G-H, Yoon, C.*, et al.* (2016) Comparison of distribution and toxicity following repeated oral dosing of different vanadium oxide nanoparticles in mice. *Environmental Research,* 150: 154-165.

Abstract:
Vanadium is an important ultra-trace element derived from fuel product combustion. With the development of nanotechnology, vanadium oxide nanoparticles (VO NPs) have been considered for application in various fields, thus the possibility of release into the environment and human exposure is also increasing. Considering that verification of bioaccumulation and relevant biological responses are essential for safe application of products, in this study, we aimed to identify the physicochemical properties that determine their health effects by comparing the biological effects and tissue distribution of different types of VO NPs in mice. For this, we prepared five types of VO NPs, commercial (C)-VO2 and -V2O5 NPs and synthetic (S)-VO2, -V2O3, and -V2O5 NPs. While the hydrodynamic diameter of the two types of C-VO NPs was irregular and impossible to measure, those of the three types of S-VO NPs was in the range of 125–170 nm. The S- and C-V2O5 NPs showed higher dissolution rates compared to other VO NPs. We orally dosed the five types of VO NPs (70 and 210 μg/mouse, approximately 2 and 6 mg/kg) to mice for 28 days and compared their biodistribution and toxic effects. We found that S-V2O5 and S-V2O3 NPs more accumulated in tissues compared to other three types of VO NPs, and the accumulated level was in order of heart>liver>kidney>spleen. Additionally, tissue levels of redox reaction-related elements and electrolytes (Na+, K+, and Ca2+) were most clearly altered in the heart of treated mice. Notably, all S- and C-VO NPs decreased the number of WBCs at the higher dose, while total protein and albumin levels were reduced at the higher dose of S-V2O5 and S-V2O3 NPs. Taken together, we conclude that the biodistribution and toxic effects of VO NPs depend on their dissolution rates and size (surface area). Additionally, we suggest that further studies are needed to clarify effects of VO NPs on functions of the heart and the immune system. © 2016 Elsevier Inc.

Pollitt, K.J.G., Maikawa, C.L., Wheeler, A.J.*, et al.* (2016) Trace metal exposure is associated with increased exhaled nitric oxide in asthmatic children. *Environmental Health,* 15(1): 94. Available at:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5009709/pdf/12940_2016_Article_173.pdf

Abstract:
BACKGROUND:
Children with asthma experience increased susceptibility to airborne pollutants. Exposure to traffic and industrial activity have been positively associated with exacerbation of symptoms as well as emergency room visits and hospitalisations. The effect of trace metals contained in fine particulate matter (aerodynamic diameter 2.5 μm and lower, PM2.5) on acute health

effects amongst asthmatic children has not been well investigated. The objective of this panel study in asthmatic children was to determine the association between personal daily exposure to ambient trace metals and airway inflammation, as measured by fractional exhaled nitric oxide (FeNO).

METHODS:

Daily concentrations of trace metals contained on PM2.5 were determined from personal samples (n = 217) collected from 70 asthmatic school aged children in Montreal, Canada, over ten consecutive days. FeNO was measured daily using standard techniques.

RESULTS:

A positive association was found between FeNO and children's exposure to an indicator of vehicular non-tailpipe emissions (8.9 % increase for an increase in the interquartile range (IQR) in barium, 95 % confidence interval (CI): 2.8, 15.4) as well as exposure to an indicator of industrial emissions (7.6 % increase per IQR increase in vanadium, 95 % CI: 0.1, 15.8). Elevated FeNO was also suggested for other metals on the day after the exposure: 10.3 % increase per IQR increase in aluminium (95 % CI: 4.2, 16.6) and 7.5 % increase per IQR increase in iron (95 % CI: 1.5, 13.9) at a 1-day lag period.

CONCLUSIONS:

Exposures to ambient PM2.5 containing trace metals that are markers of traffic and industrial-derived emissions were associated in asthmatic children with an enhanced FeNO response.

Roberts, G.K., Stout, M.D., Sayers, B.*, et al.* (2016) 14-day toxicity studies of tetravalent and pentavalent vanadium compounds in Harlan Sprague Dawley rats and B6C3F1/N mice via drinking water exposure. *Toxicology Reports,* 3: 531-538.

Abstract:

Background: The National Toxicology Program (NTP) performed short-term toxicity studies of tetra- and pentavalent vanadium compounds, vanadyl sulfate and sodium metavanadate, respectively. Due to widespread human exposure and a lack of chronic toxicity data, there is concern for human health following oral exposure to soluble vanadium compounds. Objectives: To compare the potency and toxicological profile of vanadyl sulfate and sodium metavanadate using a short-term in vivo toxicity assay. Methods: Adult male and female Harlan Sprague Dawley (HSD) rats and B6C3F1/N mice, 5 per group, were exposed to vanadyl sulfate or sodium metavanadate, via drinking water, at concentrations of 0, 125, 250, 500, 1000 or 2000 mg/L for 14 days. Water consumption, body weights and clinical observations were recorded throughout the study; organ weights were collected at study termination. Results: Lower water consumption, up to -80% at 2000 mg/L, was observed at most exposure concentrations for animals exposed to either vanadyl sulfate or sodium metavanadate and was accompanied by decreased body weights at the highest concentrations for both compounds. Animals in the 1000 and 2000 mg/L sodium metavanadate groups were removed early due to overt toxicity. Thinness was observed in high-dose animals exposed to either compound, while lethargy and abnormal gait were only observed in vanadate-exposed animals. Conclusions: Based on clinical observations and overt toxicity, sodium metavanadate appears to be more toxic than vanadyl sulfate. Differential toxicity cannot be explained by differences in total vanadium intake, based on water consumption, and may be due to differences in disposition or mechanism of toxicity. © 2016 The Author(s).

Rodriguez-Lara, V., Muñiz-Rivera Cambas, A., González Villalva, A.*, et al.* (2016) Sex-based differences in lymphocyte proliferation in the spleen after vanadium inhalation. *Journal of Immunotoxicology,*13(4): 498-508.

Abstract:
Abstract: Vanadium (V) is a transition metal often adhered to particulate matter and released into the atmosphere as vanadium pentoxide (V2O5) by the burning of fossil fuels. This air pollutant causes adverse effects in the immune system. Lymphocytosis and splenomegaly have been reported with increased white pulp in mice after V inhalation. The effect of V on the immune system as related to sex has been poorly investigated. This study sought to determine if V inhalation (a) produced lymphoproliferation that could explain the changes previously observed in the spleen and in peripheral blood lymphocyte counts and (b) whether any observed effects differed due to gender. Immunohistochemical analyses of Ki-67, a specific proliferation marker, was made in the spleens of CD-1 male and female mice exposed for 1 h, twice a week, over a 12-week period to V2O5 (at 1.4 mg V2O5/m3) by whole-body inhalation; similar analyses were performed on spleens of control mice exposed to vehicle (filtered air). The results showed that in male mice there was a significant increase in percentage of Ki-67 immunopositive lymphocytes starting from the second week and until the end of the exposure. The Ki-67 signal was cytoplasmic and nuclear in the exposed males, while in controls the signal was only nuclear. In female mice, V inhalation singificantly increased the percentage of proliferating lymphocytes only after 1 week of exposure. Ki-67 signal was observed only in the nucleus of lymphocytes from the control and exposed females. The results here help to explain the splenomegaly and lymphocytosis observed previously in male mice and support the lymphoproliferative effect induced by V. Lastly, the finding that there was a sex difference in the effect of vanadium on lymphocyte proliferation suggests a role for sex hormones in potential protection against V immunotoxicity; however, further studies are needed to support this hypothesis. © 2016 Informa UK Limited trading as Taylor & Francis Group.

Usende, I.L., Leitner, D.F., Neely, E.*, et al.* (2016) The Deterioration Seen in Myelin Related Morphophysiology in Vanadium Exposed Rats is Partially Protected by Concurrent Iron Deficiency. *Nigerian Journal of Physiological Sciences: Official Publication of the Physiological Society of Nigeria,* 31(1): 11-22.

Abstract:
Oligodendrocyte development and myelination occurs vigorously during the early post natal period which coincides with the period of peak mobilization of iron. Oligodendrocyte progenitor cells (OPCs) are easily disturbed by any agent that affects iron homeostasis and its assimilation into these cells. Environmental exposure to vanadium, a transition metal can disrupt this iron homeostasis. We investigated the interaction of iron deficiency and vanadium exposure on the myelination infrastructure and its related neurobehavioural phenotypes, and neurocellular profiles in developing rat brains. Control group (C) dams were fed normal diet while Group 2 (V) dams were fed normal diet and pups were injected with 3mg/kg body weight of sodium metavanadate daily from postnatal day (PND) 1-21. Group 3 (I+V) dams were fed iron deficient diet after delivery and pups injected with 3mg/kg body weight sodium metavanadate from PND1-21. Body and brain weights deteriorated in I+V relative to C and V while neurobehavioral deficit occurred more in V. Whereas immunohistochemical staining shows more astrogliosis and microgliosis indicative of neuroinflammation in I+V, more intense OPCs depletion and hypomyelination were seen in the V, and this was partially protected in I+V. In in vitro studies, vanadium induced glial cells toxicity was partially protected only at the LD 50 dose with the iron chelator, desferroxamine. The data indicate that vanadium promotes myelin damage and iron deficiency in combination with vanadium partially protects this neurotoxicological effects of vanadium.

Zhu, C.W., Liu, Y.X., Huang, C.J.*, et al.* (2016) Effect of vanadium exposure on neurobehavioral function in workers. *Zhonghua Lao Dong Wei Sheng Zhi Ye Bing Za Zhi = Zhonghua Laodong Weisheng Zhiyebing Zazhi = Chinese Journal of Industrial Hygiene and Occupational Diseases,* 34(2): 103-106.

Abstract:
OBJECTIVE: To establish the comprehensive indicators for neurobehavioral function test, and to investigate the possible adverse effect of long-time vanadium exposure on neurobehavioral function and its features in workers. METHODS: From July to November, 2012, The Neurobehavioral Core Test Battery(NCTB) recommended by WHO was used to conduct tests for 128 workers in vanadium exposure group and 128 workers in control group. The t-test and analysis of covariance were used to compare the differences in each indicator in NCTB between different populations, and the principal component analysis was used to establish the comprehensive neurobehavioral index(NBI) and investigate the effect of vanadium on workers' neurobehavioral function. RESULTS: The vanadium exposure group had significantly lower visual retention score(6.9+/-1.9), digit span(order) score(8.9+/-2.9), lifting and turning dexterity(the non-handed hand) score (14.1+/-3.6), pursuit aiming test(the number of correct dots) score(65.7+/-24.8), and digit symbol score (31.1+/-15.0) than the control group (8.2+/-1.3, 9.4+/-2.7, 15.5+/-3.0, 76.5+/-23.8, and 33.7+/-9.5)(all P<0.05). The vanadium exposure group also had a significantly lower NBI than the control group(-0.167+/-0.602 vs 0.168+/-0.564, P<0.05). CONCLUSION: Long-term vanadium exposure can influence the workers' neurobehavioral function, with the manifestations of decreased hearing and visual memory, movement velocity, accuracy, and coordination.

3. BIOLOGICAL MECHANISMS

Hosseini, M.-., Shahraki, J., Tafreshian, S.*, et al.* (2016) Protective effects of Sesamum indicum extract against oxidative stress induced by vanadium on isolated rat hepatocytes. *Environmental Toxicology,*31(8): 979-985.

Abstract:
Vanadium toxicity is a challenging problem to human and animal health with no entirely understanding cytotoxic mechanisms. Previous studies in vanadium toxicity showed involvement of oxidative stress in isolated liver hepatocytes and mitochondria via increasing of ROS formation, release of cytochrome c and ATP depletion after incubation with different concentrations (25-200 μM). Therefore, we aimed to investigate the protective effects of Sesamum indicum seed extract (100-300 μg/mL) against oxidative stress induced by vanadium on isolated rat hepatocytes. Our results showed that quite similar to Alpha-tocopherol (100 μM), different concentrations of extract (100-300 μg/mL) protected the isolated hepatocyte against all oxidative stress/cytotoxicity markers induced by vanadium in including cell lysis, ROS generation, mitochondrial membrane potential decrease and lysosomal membrane damage. Besides, vanadium induced mitochondrial/lysosomal toxic interaction and vanadium reductive activation mediated by glutathione in vanadium toxicity was significantly (P<0.05) ameliorated by Sesamum indicum extracts. These findings suggested a hepato-protective role for extracts against liver injury resulted from vanadium toxicity. © 2015 Wiley Periodicals, Inc.

Jacobs, F.A., Sadie-Van Gijsen, H., van de Vyver, M.*, et al.* (2016) Vanadate Impedes Adipogenesis in Mesenchymal Stem Cells Derived from Different Depots within Bone. *Frontiers in Endocrinology,* 7: 108.

Available at: http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4971437/pdf/fendo-07-00108.pdf

Abstract:
Glucocorticoid-induced osteoporosis (GIO) is associated with an increase in bone marrow adiposity, which skews the differentiation of mesenchymal stem cell (MSC) progenitors away from osteoblastogenesis and toward adipogenesis. We have previously found that vanadate, a non-specific protein tyrosine phosphatase inhibitor, prevents GIO in rats, but it was unclear whether vanadate directly influenced adipogenesis in bone-derived MSCs. For the present study, we investigated the effect of vanadate on adipogenesis in primary rat MSCs derived from bone marrow (bmMSCs) and from the proximal end of the femur (pfMSCs). By passage 3 after isolation, both cell populations expressed the MSC cell surface markers CD90 and CD106, but not the hematopoietic marker CD45. However, although variable, expression of the fibroblast marker CD26 was higher in pfMSCs than in bmMSCs. Differentiation studies using osteogenic and adipogenic induction media (OM and AM, respectively) demonstrated that pfMSCs rapidly accumulated lipid droplets within 1 week of exposure to AM, while bmMSCs isolated from the same femur only formed lipid droplets after 3 weeks of AM treatment. Conversely, pfMSCs exposed to OM produced mineralized extracellular matrix (ECM) after 3 weeks, compared to 1 week for OM-treated bmMSCs. Vanadate (10 μM) added to AM resulted in a significant reduction in AM-induced intracellular lipid accumulation and expression of adipogenic gene markers (PPARγ2, aP2, adipsin) in both pfMSCs and bmMSCs. Pharmacological concentrations of glucocorticoids (1 μM) alone did not induce lipid accumulation in either bmMSCs or pfMSCs, but resulted in significant cell death in pfMSCs. Our findings demonstrate the existence of at least two fundamentally different MSC depots within the femur and highlights the presence of MSCs capable of rapid adipogenesis within the proximal femur, an area prone to osteoporotic fractures. In addition, our results suggest that the increased bone marrow adiposity observed in GIO may not be solely due to direct effect of glucocorticoids on bone-derived MSCs, and that an increase in femur lipid content may also arise from increased adipogenesis in MSCs residing outside of the bone marrow niche.

Kobeasy, M.I., El-Naggar, A.Y. & Abdallah, A.A. (2015) A novel methods for protective role against reproductive toxicity of carbofuren in male rats using palm pollen grains and vanadyl(II) folate as a new compound. ***Journal of Chemical and Pharmaceutical Research,*** **7(4): 1142-1148.** Available at: http://jocpr.com/vol7-iss4-2015/JCPR-2015-7-4-1142-1148.pdf

Abstract:
The acute toxicity (LD 50) of insecticides carbofuran and its effects on male reproduction in rats were carried out. Carbofuran was given orally to dose (2.4 mg kg-1 b.wt, corresponding to 1/25 LD50) alone and in combination with date palm pollen grains extracts (60 mg/ kgb.wt) and vanadylfolate (50 mg /kg b.wt). Fertility index, weight of sexual organs, semen picture, serum testosterone level and activity of lactate dehydrogenase (LDH), acid phosphatase enzymes and fructose content in serum. Results showed that there was a correlation between carbofuran administration and the significant decrease of the fertility index, weight of the testes and accessory male sexual glands, serum testosterone level and sperm cell abnormality. Carbofuran increased significantly lactate dehydrogenase and acid phosphate activity and decreased the fructose content in the serum. In contrast Coadministration of date palm pollen grains or vanadylfolate to carbofuran treated rats restored almost of these biochemical parameters to normal levels and alleviates the toxic effects of carbofuran on reproductivefunctions in male rats.

León, I.E., Díez, P., Etcheverry, S.B.*, et al.* (2016) Deciphering the effect of an oxovanadium (IV) complex with the flavonoid chrysin (VOChrys) on intracellular cell signalling pathways in an osteosarcoma cell line. *Metallomics,* 8(8): 739-749.

Abstract:
Vanadium complexes were studied during recent years and considered as a representative of a new class of non-platinum metal antitumor agents in combination with their low toxicity. However, a few challenges still remain in the discovery of new molecular targets for these novel metal-based drugs. The study of cell signaling pathways related to vanadium drugs, which is highly critical for identifying specific targets that play an important role in the antitumor activity of vanadium compounds, is scarce. This research deals with the alterations in intracellular signaling pathways promoted by an oxovanadium(iv) complex with the flavonoid chrysin [VO(chrysin)2EtOH]2 (VOChrys) in a human osteosarcoma cell line (MG-63). Herein we report for the first time the effect of [VO(chrysin)2EtOH]2 on the relative abundance of 224 proteins, which are involved in the most common intracellular pathways. Besides, full-length human recombinant (FAK and AKT1) kinases are produced using an in situ IVTT system and then we have evaluated the variation of relative tyrosine-phosphorylation levels caused by the [VO(chrysin)2EtOH]2 compound. The results of the differential protein expression levels reveal that several proteins such as PKB/AKT, PAK, DAPK, Cdk 4, 6 and 7, FADD, AP2, NAK, and JNK, among others, were altered. Moreover, cell signaling pathways related to the PTK2B, FAK, PKC families suggests an important role associated with the antitumor activity of [VO(chrysin)2EtOH]2 was demonstrated. Finally, the effect of this compound on in situ expressed FAK and AKT1 is validated by determining the phosphorylation level, which decreased in the former and increased in the latter. © 2016 The Royal Society of Chemistry.

Sanna, D., Ugone, V., Fadda, A.*, et al.* (2016) Behavior of the potential antitumor VIVO complexes formed by flavonoid ligands. 3. Antioxidant properties and radical production capability. *Journal of Inorganic Biochemistry,* 161: 18-26.

Abstract:
The radical production capability and the antioxidant properties of some VIVO complexes formed by flavonoid ligands were examined. In particular, the bis-chelated species of quercetin (que), [VO(que)2]2 −, and morin (mor), [VO(mor)2], were evaluated for their capability to reduce the stable radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) and produce the hydroxyl radical •OH by Fenton-like reactions, where the reducing agent is VIVO2 +. The results were compared with those displayed by other VIVO complexes, such as [VO(H2O)5]2 +, [VO(acac)2] (acac = acetylacetonate) and [VO(cat)2]2 − (cat = catecholate). The capability of the VIVO flavonoids complexes to reduce DPPH is much larger than that of the VIVO species formed by non-antioxidant ligands and it is due mainly to the flavonoid molecule. Through the 5,5-dimethyl-1-pyrroline N-oxide (DMPO) trapping assay of the hydroxyl radical it was possible to demonstrate that in acidic solution VIVO2 + has an effectiveness in producing •OH radicals comparable to that of Fe2 +. When VIVO complexes of flavonoids were taken into account, the amount of hydroxyl radicals produced in Fenton-like reactions depends on the specific structure of the ligand and on their capability to reduce H2O2 to give •OH. Both the formation of reactive oxygen species (ROS) under physiological conditions by VIVO complexes of flavonoid ligands and their radical scavenging capability can be put in relationship with their antitumor effectiveness and it could be possible to modulate these actions by changing the features of the flavonoid coordinated to the VIVO2 + ion, such as the entity, nature and position of the substituents and the number of phenolic groups.

Ścibior, A. (2016) Vanadium (V) and magnesium (Mg) - In vivo interactions: A review. *Chemico-Biological Interactions,* 258: 214-233.

Abstract:
Abstract Vanadium (V) and magnesium (Mg) arouse interest of many research centres worldwide. Many aspects of their action have already been recognized but some of them have not been fully elucidated yet. Relatively little is known about the mechanisms of absorption, transport, and excretion of V. There is also a lack of sufficient data about the most sensitive biomarkers of V toxicity and the mechanisms of its toxic action, which have not been fully explained yet. There is also a lack of comprehensive research on the consequences, character, and mechanisms of mutual interactions of V (which has strong pro-oxidant properties) with elements with an antioxidant potential such as Mg, the recognition of which, besides the cognitive value, may have great practical importance. It should be highlighted that the question of interactions between elements is always up to date and it is still an important issue in toxicology. A comprehensive research on interactions of V with Mg can be particularly important in the studies of the usage of V (which has a narrow margin of safety) in the treatment of certain diseases in humans, especially diabetes, which is accompanied by changes in the level of Mg in the tissues and weakening of the antioxidant barrier and oxidative stress. Therefore, the aspect concerning the possible interaction of V (as a potent pro-oxidant) with Mg (as an antioxidant) was the subject of our special interest. In addition, the examination of the effects of the interactions between V and Mg is very important especially for extending the knowledge of the mechanism of the influence of V on the organism and a potential role of Mg (which is characterized by a wide therapeutic window) in prevention of V toxicity. This review summarizes the most important results obtained from our experiments in a rodent model referring to the interactions of V with Mg on the background of the in vivo experimental data published by other researchers of this issue. Our studies have shown that V and Mg supplied in combination are able to modulate the response in an interactive manner to produce a specific effect that is distinct from that observed during separate administration thereof. The present report also provides the most important information about the effects of the action of V and Mg with other metals.

Yang, J., Zhang, Z., Jiang, S.*, et al.* (2016) Vanadate-induced antiproliferative and apoptotic response in esophageal squamous carcinoma cell line EC109. *Journal of Toxicology and Environmental Health, Part A,* 79(19): 864-868.

Abstract:
Vanadate is a transition element that present in nature and was shown to be a nonspecific inhibitor of protein tyrosine phosphatases. It was reported that vanadium (Vd) compounds exhibit antitumor actions in several cancer cell lines. This study aimed to examine the antiproliferative and apoptotic actions of different concentrations of sodium vanadate (NaVd) (+5) in esophageal squamous carcinoma cell line EC109 by determining the protein expression levels of cyclin D1 and caspase-3 following incubation for various times from 15 min up to 4 h. In addition, cell proliferation of EC109 treated with different concentrations (NaVd) was also measured using the MTT assay at 4, 12, 24, and 48 h. The cell cycle of EC109 cells exposed to different concentrations of NaVd was detected using flow cytometry determination at 24 h. Data showed that NaVd greater than 100 μM significantly increased cyclin D1. In contrast, reduced caspase-3 protein expression levels occurred at 50 μM. Cellular proliferation was significantly decreased at 50uM. The cell cycle was arrested at S phase with 100 μM NaVd. Taken together, data indicate that NaVd produced concentration- and time-dependent antitumor actions in EC109 cell line.;

Zhang, L., Huang, Y., Liu, F.*, et al.* (2016) Vanadium(IV)-chlorodipicolinate inhibits 3T3-L1 preadipocyte adipogenesis by activating LKB1/AMPK signaling pathway. *Journal of Inorganic Biochemistry,* 162: 1-8.

Abstract:
Our previous studies demonstrated that vanadium(IV) complex with 4-chlorodipicolinic acid (VOdipic-Cl) alleviates lipid abnormalities in streptozotocin (STZ)-induced diabetic rats. However, the molecular mechanisms are not fully understood. In the present study, the effect of VOdipic-Cl on adipogenesis and mechanisms of action in 3T3-L1 preadipocytes were investigated. The 3T3-L1 preadipocytes were induced to differentiate in the presence or absence of VOdipic-Cl for 8 days. The cells were determined for proliferation, differentiation, lipid accumulation as well as the protein expressions of molecular targets that are involved in fatty acid synthesis. The results demonstrated that VOdipic-Cl at concentrations ranging from 2.5 μM to 10 μM reduced the intracellular lipid content by 10%, 22% and 30% compared to control. VOdipic-Cl down-regulated the expression of peroxisome proliferator-activated receptor (PPARγ), CCAAT element binding protein a (C/EBPα), sterol regulatory element binding protein 1c (SREBP-1c), fatty acid synthase (FAS) and fatty acid-binding protein 4 (FABP4) and activated the phosphorylation of acetyl coenzyme A carboxylase (ACC), adenosine monophosphate-activated protein kinase (AMPK) and liver kinase B1 (LKB1) in a dose-dependent manner. Further studies showed that AMPK small interfering RNA (siRNA) markedly up-regulated PPARγ, C/EBPα, FAS and FABP4 expression in the presence of VOdipic-Cl, respectively. When LKB1 was silenced with siRNA, the effect of VOdipic-Cl on AMPK phosphorylation was diminished. Taken together, these results suggested that VOdipic-Cl can inhibit 3T3-L1 preadipocyte differentiation and adipogenesis through activating the LKB1/AMPK-dependent signaling pathway. These findings raise the possibility that VOdipic-Cl may be a promising therapy in treatment of obesity.

4. USES OF VANADIUM

Domingo, J.L. & Gómez, M. (2016) Vanadium compounds for the treatment of human diabetes mellitus: A scientific curiosity? A review of thirty years of research. *Food and Chemical Toxicology,* 95: 137-141.

Abstract:
In the second part of the 1980s, and in the 1990s, a number of investigators demonstrated – mainly in streptozotocin-induced (STZ) diabetic rats-that the vanadate and vanadyl forms of vanadium possessed a number of insulin-like effects in various cells. It was hypothesized that oral vanadium could be an alternative treatment to parenteral insulin in the therapy of diabetes mellitus. However, the long-term and/or chronic administration of vanadium compounds should also mean tissue vanadium accumulation and risks of toxicity. The purpose of this review was to revise the current-state-of-the-art on the use of vanadium in the treatment of human diabetes. It has been conducted more than three decades after the first report on the beneficial insulin-mimetic effects of oral vanadium administration in STZ-diabetic rats. Although the antidiabetic effects of vanadium in STZ-diabetic rodents are well supported, in the few studies on human patients with positive results, that are available in the literature, vanadium compounds were administered during very short periods. We conclude that vanadium administration for the treatment of human diabetes is misplaced. © 2016 Elsevier Ltd.

Kannan, P., Vijayaraj, A., Sesh, P.S.L.*, et al.* (2016) Antioxidant status in streptozotocin induced diabetic rats treated with vanadium complex. *Indian Journal of Animal Research,* 50(1): 57-62. Available at: http://arccjournals.com/uploads/articles/ArticleFile-B-2815-12%20(57-62)%20B-2815.pdf

Abstract:
As lipid peroxidation and oxidative stress play a key role in the pathogenesis of diabetes, the antioxidant status of streptozotocin induced diabetic rats, treated with vanadium complex was explored in the present study. Diabetes was induced by single intraperitoneal injection of streptozotocin (STZ) at the dose rate of 45 mg per kg body weight. Diabetes was confirmed after 72 hours of STZ injection by estimating blood glucose level and those rats showing more than 250 mg/ dL were considered as diabetic. Vanadium complex at the dose rates of 5 and 10 mg / kg body weight was administered orally to normal control and STZ induced diabetic rats. Glimepiride was used as the positive control and was given orally at the dose rate of 800 µg / Kg body weight. The study on the hepatic, renal and pancreatic tissues showed that vanadium complex at both the predetermined dosages significantly increased the antioxidant activities of superoxide dismutase and glutathione peroxidase along with a significant increase in the level of glutathione and a significant decrease in the level of lipid peroxidation. The study also revealed that there is a significant reduction in the activity of catalase after treatment with vanadium complex at both the dosage levels. ABSTRACT FROM AUTHOR]; Copyright of Indian Journal of Animal Research is the property of Agricultural Research Communication Centre and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use. This abstract may be abridged. No warranty is given about the accuracy of the copy. Users should refer to the original published version of the material for the full abstract. (Copyright applies to all Abstracts.).

Ki, J., Mukherjee, A., Rangasamy, S.*, et al.* (2016) Insulin-mimetic and Anti-inflammatory Potential of a Vanadyl-Schiff Base Complex for its Application against Diabetes. *RSC Advances,* (6): 57530-57539.

Abstract:
Insulin signalling causes the translocation of glucose transporter 4 (GLUT4) to the plasma membrane to facilitate cellular glucose uptake. Numerous observations indicate that the prime cause of type 2 diabetes mellitus (T2DM) is inflammation, the occurrence of which increases in obese individuals. Inflammatory mediators induce an insulin-resistance (IR) state where impaired insulin signalling fails to promote the glucose transporters for intracellular uptake of glucose. Hence compounds, which possess insulin-mimetic and anti-inflammatory potentials, may be effective in the treatment of obesity-induced IR during T2DM. Previous studies showed that vanadium oxo complexes possess insulin-mimetic activities whereas the tryptamine moiety offers anti-inflammatory potential. Hence a vanadyl-Schiff base complex (VOTP) consisting of the tryptamine moiety was synthesized by condensation of pyridoxal hydrochloride and tryptamine and its subsequent complexation with $VOSO_4$. HEK-293 cells, expressing a GLUT4-myc-GFP fusion protein, were treated with VOTP and GLUT4 translocation was quantified by total internal reflection fluorescence (TIRF) microscopy. Results indicated that VOTP could efficiently act as an insulin-mimetic substance. A high-content cell based assay using quantum dot–antibody conjugates showed that VOTP restored insulin signaling during IR by the inactivation of c-Jun N-terminal kinase-1 (JNK-1) and subsequent phosphorylation and activation of the tyrosine moiety of insulin receptor substrate (IRS). Also, high levels of phosphorylated Forkhead box O1 (FOXO) indicated low levels of gluconeogenesis. Hence VOTP has insulin-mimetic and anti-inflammatory potentials.

Moreover, VOTP is highly effective at nanomolar treatment ranges, thus evades the toxicity issues. Collectively, these findings encourage us for future use of this compound as a potential anti-diabetic agent.

Pathak, P. & Lahkar, M. (2015) A Comperative Study of Vanadium Pentoxide and Chromium Oxide in Streptozotocin Induced Diabetes in Albino Rats. ***International Journal of Pharmaceutical Sciences and Research,*** **6(48464843).** Available at: http://ijpsr.com/bft-article/a-comperative-study-of-vanadium-pentoxide-and-chromium-oxide-in-streptozotocin-induced-diabetes-in-albino-rats/?view=fulltext

Abstract:
The present study was conducted to evaluate and compare the effect of vanadium pentoxide and chromium oxide in normal and streptozotocin induced diabetic albino rats. Methods: Diabetes was experimentally induced by injecting intraperitoneally with a single dose of 60mg/kg. The animals were considered as diabetic, if their blood glucose values were above 300 mg/dl on the 10th day after injection. The blood glucose estimation was done by glucose oxidase method. Glibenclamide was taken as standard drug. The one-way ANOVA followed by Dunnett's 't' test was used for statistical analysis. Results: The blood glucose levels were found to be significantly ($p<0.05$) decreased in vanadium pentoxide and chromium oxide treated groups. Conclusion: This study suggests that vanadium pentoxide and chromium oxide have antidiabetic effect in a dose dependent manner.

Refat, M.S., El-Megharbel, S.M., Kobeasy, M.I.*, et al.* (2016) Synthesis, spectroscopic characterizations and biological activities of vanadyl(II) folate compound as a new anti-DNA damage and antioxidant agent. ***Journal of Molecular Liquids,*** **220: 468-477.**

Abstract:
New oxovanadium(IV) folate [(VO)(2)(FO) (NH4)(2)(SO4)(2)] complex was synthesized by the reaction between vanadyl(II) sulfate and folic acid vitamin B-9 drug in an alkaline media. Elemental analysis shows 1:2 ligand to metal ion stoichiometry and the conductance data deduced that oxovanadium(IV) folate complex has non electrolytic nature. IR spectrum of oxovanadium(IV) complex reveal that folic acid acts as a binuclear chelate via deprotonation of both carboxylic groups. The biological section aimed to test the toxicity of carbofuran orally for male rat and oxidative stress of the sub-lethal (2.4 mg/kg b.w, 1/25 LD50) dose on the lipid peroxidation level (LPO), reduced glutathione content (GSH), antioxidant enzymes, superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx) and glutathione-S-transferase (GST) activities of testicular tissue. The protective efficiency of vanadylfolate (50 mg/kg b.w) only or combined together carbofuran was tested. The taken of carbofuran orally led to elevation in LPO level by 2.10 fold in comparable with control. The efficient of antioxidant enzymes using of vanadylfolate in combined with carbofuran or its only were decreased by (25.48%, 18.60%, 22.46% and 16.62%) but the GSH level increased by 37.18% in testicular tissue in comparison with controller sample. The DNA damaging of carbofuran and vanadylfolate were assessed using single cell gel electrophoresis (SCGE) data.

Yang, J., Zhang, Z., Jiang, S.*, et al.* (2016) Vanadate-induced antiproliferative and apoptotic response in esophageal squamous carcinoma cell line EC109. ***Journal of Toxicology and Environmental Health, Part A,*** **79(19): 864-868.**

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5. ENVIRONMENTAL EFFECTS in PLANTS and SOIL

No relevant papers identified.

6. ENVIRONMENTAL EFFECTS in TERRESTRIAL ORGANISMS

Yuan, Z.H., Zhang, K.Y., Ding, X.M.*, et al.* (2016) Effect of tea polyphenols on production performance, egg quality, and hepatic antioxidant status of laying hens in vanadium-containing diets. *Poultry Science,* 95(7): 1709-1717.

Abstract:
This study was conducted to determine the effect of tea polyphenols (TP) on production performance, egg quality, and hepatic-antioxidant status of laying hens in vanadium-containing diets. A total of 300 Lohman laying hens (67 wk old) were used in a 1 plus 3 x 3 experiment design in which hens were given either a diet without vanadium and TP supplementation (control) or diets supplemented with 5, 10, or 15 mg V/kg and TP (0, 600, 1,000 mg/kg) diets for 8 wk, which included 2 phases: a 5-wk accumulation phase and a 3-wk depletion phase. During the accumulation phase, dietary vanadium addition decreased (linear, $P < 0.01$) albumen height and Haugh unit (HU), and TP supplementation mitigated (linear effect, $P < 0.01$) this reduction effect induced by vanadium. Eggshell thickness (linear,

P < 0.01), redness (linear and quadratic, P < 0.05), and yellowness (linear and quadratic, P < 0.05) were decreased by vanadium and increased by the effect of TP when a vanadium-containing diet was fed. In the depletion phase, the bleaching effect on eggshells induced by vanadium disappeared one wk after vanadium withdrawal. Eggshell thickness, eggshell strength, albumen height, and HU were lower (P < 0.05) in the 15 mg/kg vanadium group compared with the control diet until 2 wk post vanadium challenge, but hens fed 15 mg/kg vanadium and 600 mg/kg TP showed no difference from the control diet only after 1 wk withdrawal. In the liver, the activity of glutathione S-transferases and glutathione peroxidase was increased (linear, P < 0.01) with the TP addition at 5 wk in the accumulation phase in the vanadium-containing diet; the malondialdehyde content increased (linear effect, P = 0.02) with the addition of vanadium. The results indicate that supplementation of 10 and 15 mg/kg vanadium resulted in reduced albumen quality, bleaching effect on eggshell color, and antioxidant stress in the liver. The effect of TP addition can prevent laying hens from the adverse effect of vanadium on egg quality, liver antioxidant stress and shorten the recovery time.

7. ENVIRONMENTAL EFFECTS in AQUATIC ORGANISMS

Mangal, V., Zhu, Y., Shi, Y.X.*, et al.* (2016) Assessing cadmium and vanadium accumulation using diffusive gradient in thin-films (DGT) and phytoplankton in the Churchill River estuary, Manitoba. *Chemosphere,* 163: 90-98.

Abstract:
Diffusive gradient in thin films (DGT) and phytoplankton communities were evaluated for the measurement of Cd and V at environmentally relevant concentrations in laboratory settings and in the Churchill River estuary (Manitoba, Canada) during an annual spring melt. Despite rapid changes in hydrology and water quality, DGT samplers and intracellular Cd and V concentrations were positively correlated (0.79 0.99). Principal component analysis (PCA) reinforced similarities between both metal monitoring techniques and assessed how changing environmental variables during the river discharge period influenced each monitoring technique. Cd accumulation was influenced by DOC concentrations and protein-like DOM whereas ionic strength (i.e. conductivity) and humic-like DOM influenced V accumulation. The present findings suggest that (1) DGT is a versatile tool for monitoring bioaccumulation of Cd and V in highly dynamic environmental systems and (2) DOC concentration, DOM composition, conductivity, pH, and river discharge influence the bioavailability of Cd and V in estuarine and riverine waters. © 2016 Elsevier Ltd.

Yamaguchi, N., Yoshinaga, M., Kamino, K.*, et al.* (2016) Vanadium-Binding Ability of Nucleoside Diphosphate Kinase from the Vanadium-Rich Fan Worm, Pseudopotamilla occelata. *Zoological Science,* 33(3): 266-271.

Abstract:
Polychaete fan worms and ascidians accumulate high levels of vanadium ions. Several vanadiumbinding proteins, known as vanabins, have been found in ascidians. However, no vanadium-binding factors have been isolated from the fan worm. In the present study, we sought to identify vanadiumbinding proteins in the branchial crown of the fan worm using immobilized metal ion affinity chromatography. A nucleoside diphosphate kinase (NDK) homolog was isolated and determined to be a vanadium-binding protein. Kinase activity of the NDK homologue, PoNDK, was suppressed by the addition of V(IV), but was unaffected by

V(V). The effect of V(IV) on PoNDK precedes its activation by Mg(II). This is the first report to describe the relationship between NDK and V(IV). PoNDK is located in the epidermis of the branchial crown, and its distribution is very similar to that of vanadium. These results suggest that PoNDK is associated with vanadium accumulation and metabolism in P. occelata.

8. MISCELLANEOUS

Okibe, N., Maki, M., Nakayama, D.*, et al.* (2016) Microbial recovery of vanadium by the acidophilic bacterium, Acidocella aromatica. *Biotechnology Letters,* 38(9): 1475-1481.

Abstract:
Objective: To investigate the bioreduction of toxic pentavalent vanadium [vanadate; V(V)] in the acidophilic, Fe(III)-reducing obligately heterotrophic bacterium, Acidocella aromatica PFBC. Results: Although the initial lag-phase of growth became extended with increasing initial V(V) concentrations, the final cell density during aerobic growth of A. aromatica PFBC was unaffected by up to 2 mM V(V). While strain PFBC is an aerobe, growth-decoupled PFBC cell suspensions directly reduced V(V) using fructose, both micro-aerobically and anaerobically, under highly acidic (pH 2) and moderately acidic (pH 4.5) conditions. Bio reduced V(IV) was subsequently precipitated even under micro-aerobic conditions, mostly by encrusting the cell surface. An anaerobic condition at pH 4.5 was optimal for forming and maintaining stable V(IV)-precipitates. Recovery of approx. 70 % of V(V) from the solution phase was made possible with V(V) at 1 mM. Conclusions: The first case of direct V(V) reducing ability and its subsequent V recovery from the solution phase was shown in acidophilic prokaryotes. Possible utilities of V(V) bioreduction in acidic conditions, are discussed. © 2016, Springer Science+Business Media Dordrecht.

Žižic, M., Miladinovic, Z., Stanic, M.*, et al.* (2016) 51V NMR investigation of cell-associated vanadate species in Phycomyces blakesleeanus mycelium. *Research in Microbiology,* 167(6): 521-528.

Abstract:
51V NMR spectroscopy was used for detection and identification of cell-associated vanadate (V5+) species after exposure of Phycomyces blakesleeanus mycelium, in exponential phase of growth, to sodium orthovanadate. Complete disappearance of monomer and dimer signals and decreased intensity of the tetramer signal were observed about 40 min after treatment. Simultaneously, a signal at -532 ppm, with increasing intensity, was detected in spectra. The time-dependent rise in this signal was connected to a decrease in the extracellular monomer signal, indicating its transport into the cell. The signal at -532 ppm did not belong to any known simple oxido-vanadate species, nor to a complex with any of the components of experimental medium. This signal was the only one present in spectrum of the mycelium washed 35 min after treatment, and the only one observed in mycelium cultivated on vanadate-contained medium. Therefore, its appearance can be attributed to intracellular complexation, and may represent an important detoxification mechanism of the cell exposed to a physiologically relevant concentration of vanadate. Experiments (51V NMR and polarography) performed with Cd-pretreated mycelium (inhibitor of an enzyme responsible for V5+ reduction) and ferricyanide-preincubated mycelium excluded the possibility of V5+ tetramer's entry into the cell. © 2016 Institut Pasteur.