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Watt, JAJ, Burke, IT, Edwards, RA et al. (9 more authors) (2018) Vanadium: A Re-Emerging Environmental Hazard. Environmental Science and Technology, 52 (21). pp. 11973-11974. ISSN 0013-936X

https://doi.org/10.1021/acs.est.8b05560

Vanadium – a re-emerging environmental hazard

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Introduction

Vanadium (V) is a contaminant which has been long confined to the annals of regulatory history. This follows the reduction of its historical primary source (fossil fuel emissions) since the 1970s (e.g. by 80% in the UK). However, V is quickly becoming an important strategic resource which promises its return to environmental prominence because of changing industrial practices and emerging waste streams. We discuss below: (i) what makes V a re-emerging environmental and human health hazard of global interest, (ii) the knowledge gaps that currently restrict prediction of environmental effect and mitigation, and (iii) opportunities for the community to address these gaps towards reducing the risk of an impending environmental hazard.

The re-emergence of vanadium as an environmental hazard

Global anthropogenic releases to soil and water for V have been recently re-evaluated and the rate at which V is being deposited into the environment is increasing. As a result, V is again accumulating in the environment. In the atmosphere, V has the highest anthropogenic enrichment factor (AEF) of all trace elements (1) and has the fourth highest AEF in global rivers, behind Cd, Sb and Ni (2). This dominant anthropogenic signal reflects dispersed and pervasive environmental releases in the global V cycle as a result of changing societal demands.

Global V production has approximately doubled in the last 15 years to 80,000 t y^{-1} in 2017 (3), driven by increased demand for high grade steel. Emerging policy, in the People's Republic of China (policy number: GB/T 1499.2-2018), to increase V content in steel to improve its tensile qualities is expected to increase China's V consumption by 10,000 t y^{-1}. This was reflected in a 100% increase in mined V prices in 2017. There has been a global rise in discharges to the environment of V-rich industrial by-products including steel slags, ash from the expansion of waste incineration (e.g. in the European Union, EU), and bauxite processing residue which now reaches 120 million t y^{-1} globally (4). Emerging technologies are forecast to enhance global V production and environmental releases. Vanadium redox-flow batteries are being rapidly developed for power storage having the advantage of being able to charge and discharge simultaneously, making them ideal for use in off-grid locations to support renewable energy needs.

Addressing knowledge gaps in vanadium environmental behaviour

Despite the increasing prevalence of V in the environment, we still possess a relatively poor understanding of V geochemistry, relative to other contaminants. Vanadium has three stable oxidation states: V^{+3}, V^{+4} and V^{+5}, although it is most commonly found as V^{+4} or V^{+5}, with the latter showing greater solubility under oxic conditions. Vanadium has historically been regarded as a conservative element in surface environments, although there is growing evidence of greater mobility. In freshwater streams affected by the release of red mud in Ajka, Hungary, V exhibited cycling and attenuation behaviour with other ubiquitous elements e.g. aluminum, iron, and molybdenum. These results confirmed that V can disperse and persist in the environment to a greater degree than other contaminants such as arsenic or phosphorus. Vanadium exhibits multiple interactions within surface environments (5) including complexing to organic and inorganic matter in sediments and uptake into flora and fauna, some bacteria being known to scavenge V from refractory compounds. However, the complicated interactions between these processes, and responses to changes in chemical and physical conditions within environmental compartments are poorly understood.

Predicting the fate and behaviour of V in the environment requires that we understand its speciation and phase association. Powerful analytical methods, such as high-resolution transmission electron microscopy and synchrotron-based X-Ray spectroscopy, can provide molecular scale geochemical characterisation. However, these methods require concentrated samples and may not be applicable beyond highly contaminated materials. For the wider environment, methods more suited to lower concentration samples are required, such as ion chromatography-mass spectrometry for aqueous speciation and novel V-specific sequential extractions to understand solid partitioning. The potential to utilise $^{50/51}$V isotopic fractionation to trace V through environmental compartments represents an exciting opportunity to assess V behaviour and transport through ecosystems. Data on V in freshwater and sediment monitoring databases (e.g. the US Geological Survey and the Environmental Protection Agency) may be exploited to help describe regional distributions and trends of V in soils, sediments and waters. It is essential that these data are produced to underpin the development and validation of much needed geochemical models to support prediction of environmental risk and behaviour.

A call for preventative measures

We face an increasing likelihood of acute exposure to V that is largely unregulated (6). Some jurisdictions are now remedying this regulatory oversight although much is still to be achieved. In the USA, V is now on the Contaminant Candidate List 4 (CCL4) and is subject to more stringent monitoring in potable waters. Such regulatory attention is encouraging and needs to be adopted more broadly alongside measures to minimise environmental V release. For example, since current global recycling rates for V are estimated by UNEP at <1% (7), there is significant scope for V re-use and/or recycling to meet escalating anthropogenic demand and reduce environmental exposure.

Vanadium hazard and risk assessments must be improved. In the most comprehensive study to date, the W.H.O. concluded that V concentrations in environmental media are substantially lower than toxic concentrations reported in ecotoxicology studies, noting that the paucity of data from specific industrial sites prevented an accurate risk assessment. A review of ecotoxicology data commissioned by the Netherlands' Government has subsequently proposed water quality standards for dissolved V of 1.2 and 3.0 µg L^{-1} for long- and short-term exposure, respectively (8). These standards are similar to the reported background range of concentrations. For example, V concentrations in a large proportion of EU surface waters (range <0.05 µg L^{-1} to 19.5 µg L^{-1}; median 0.46 µg L^{-1}) (9) exceed or are near to these proposed standards, suggesting that any further increase in V losses to the environment will cause, at least, a major regulatory concern.

The emerging V sources described above, and the legacy of historic emissions represent a growing problem requiring wide scale intervention. The International Aluminium Institute has produced best practice guidance on the management of V-enriched bauxite residues to reduce the likelihood of un-controlled discharges on a global scale. There is a need for other industries to do the same. The global life-cycle of V must be comprehensively mapped and used to identify priority actions through which more sustainable V use can be achieved.

References

1. Schlesinger, W.H., Klein, E.M. and Vengosh, A. Global biogeochemical cycle of vanadium.

Proceedings of the National Academy of Sciences, **2017** p.201715500.

2. Viers, J.; Dupré, B.; Gaillardet, J. Chemical composition of suspended sediments in World Rivers: New insights from a new database. Science of the Total Environment, **2009**, 407: 853-868.

3. United States Geological Survey. Vanadium Statistics and Information. (2018). Available at https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2018-vanad.pdf (last accessed: 05.17.18)

4. Power, G., Gräfe, M.; Klauber, C. Bauxite residue issues: I. Current management, disposal and storage practices. Hydrometallurgy, **2011**, 108, 33-45.

5. Huang, J.H.; Huang, F.; Evans, L.; Glasauer, S. Vanadium: Global (bio) geochemistry. Chemical Geology, **2015**, 417, 68-89.

6. Rattner, B.A.; McKernan, M.A.; Eisenreich, K.M.; Link, W.A.;Olsen, G.H.; Hoffman, D.J.; Knowles, K.A.; McGowan, P.C. Toxicity and hazard of vanadium to mallard ducks (Anas platyrhynchos) and Canada geese (Branta canadensis). Journal of Toxicology and Environmental Health, **2006**, 69,331-351.

7. Graedel, T.E.; Allwood, J.; Birat, J.P. ; Buchert, M. ; Hagelüken, C. ; Reck, B.K. ; Sibley, S.F. ; Sonnemann, G. Recycling rates of metals: A status report, United Nations Environment Programme, **2011**

8. Smit, C.E. Environmental Risk Limits for Vanadium in Water: A Proposal for Water Quality Standards in Accordance with the Water Framework Directive. RIVM Letter Report 601714021/2012. **2012** National Institute for Public Health and the Environment, Bilthoven, 73.

9. Salminen, R. ; Batista, M.J. ; Bidovec, M. ; Demetriades, A. ; De Vivo, B. ; De Vos, W. ; Duris, M. ; Gilucis, A. ; Gregorauskiene, V. ; Halamić, J. ; Heitzmann, P. 2005. Geochemical atlas of Europe, part 1, background information, methodology and maps. Geological survey of Finland.