

1 **Vanadium – a re-emerging environmental hazard**

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22 **Introduction**

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

32 **The re-emergence of vanadium as an environmental hazard**

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

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

52 **Addressing knowledge gaps in vanadium environmental behaviour**

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

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

82 **A call for preventative measures**

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

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

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

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