Global biogeochemical cycle of vanadium

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Synthesizing published data, we provide a quantitative summary of the global biogeochemical cycle of vanadium (V), including both human-derived and natural fluxes. Through mining of V ores (130 × 10⁹ g V/y) and extraction and combustion of fossil fuels (600 × 10⁹ g V/y), humans are the predominant force in the geochemical cycle of V at Earth's surface. Human emissions of V to the atmosphere are now likely to exceed background emissions by as much as a factor of 1.7, and, presumably, we have altered the deposition of V from the atmosphere by a similar amount. Excessive V in air and water has potential, but poorly documented, consequences for human health. Much of the atmospheric flux probably derives from emissions from the combustion of fossil fuels, but the magnitude of this flux depends on the type of fuel, with relatively low emissions from coal and higher contributions from heavy crude oils, tar sands bitumen, and petroleum coke. Increasing interest in petroleum derived from unconventional deposits is likely to lead to greater emissions of V to the atmosphere in the near future. Our analysis further suggests that the flux of V in rivers has been incremented by about 15% from human activities. Overall, the budget of dissolved V in the oceans is remarkably well balanced—with about 40 × 10⁹ g V/y to 50 × 10⁹ g V/y inputs and outputs, and a mean residence time for dissolved V in seawater of about 130,000 y with respect to inputs from rivers.

vanadium | petroleum | geochemical cycle | aerosols | rock weathering

Vanadium (V) occurs in a wide range of earth materials and is a relatively abundant trace metal, with an average concentration in the upper continental crust (97 mg/kg) more than double those of nickel (Ni) and copper (Cu) (1). In modern society, the majority of V is used to improve the strength and corrosion resistance of steel; it is also of increasing strategic and technological interest as a specialty metal in electronics and batteries. V is an essential trace element in prokaryotic biochemistry, where it is found as an alternative to molybdenum in the molecular structure of nitrogenase, the enzyme of N fixation (2–4). It also appears in the structure of enzymes in the marine algae responsible for the formation of bromoform (5) and methyl bromide (6), which contributes to the depletion of stratospheric ozone. Whether V is an essential trace element in higher plants and animals is unknown (7), with some evidence favoring an essential role in at least some higher organisms (e.g., refs. 8 and 9). Higher plants accumulate about 1 mg/kg in their tissues (10).

The mean concentration of V in the continental crust is about 97 mg/kg (1, 11), and ~20 × 10⁹ g V/y enters biogeochemical cycles at Earth's surface through chemical weathering (12). V, which can exist in three common oxidation states, is largely found as the vanadate ion ($H_2VO_4^-$) in natural oxidized waters of near-neutral pH. The dissolved concentration in river water is about 0.7 μg/L, less than half of the concentration of ~1.8 μg/L in seawater (13).

V is widely recognized as a trace contaminant in coal and oil and is released to the atmosphere through particle emissions associated with their combustion (14–17). While V has not received as much attention as other anthropogenically mobilized elements, data presented here show that the human perturbation of V cycling through the atmosphere may exceed that of mercury (Hg) and a variety of other metals (Table 1). V is not viewed as a

problematic environmental contaminant, but high concentrations of V can be toxic to humans and other organisms (18, 19). Reflecting a new level of concern, the State of California has recently imposed a new standard (15 μg/L) for V in drinking water (https://oehha.ca.gov/water/notification-level/proposed-notification-level-vanadium). In some regions, the release of V to the atmosphere and its deposition in natural ecosystems have declined in recent decades due to changes in fuel use and industrial practices (20, 21).

Vanadium's primary commercial use is in the manufacture of steel alloys to increase hardness and corrosion resistance. An emerging application is the development of V redox batteries as an alternative for lithium-ion batteries for storage of renewable energy. Worldwide, about 82 × 10⁹ g of V are produced from virgin ore annually, and, at current rates of consumption, reserves (~15 × 10¹² g) are expected to meet demand into the next century (22). In the United States, recycling of products and fly ash provides as much as 40% of the V in commercial use, including exports (23).

Huang et al. (13) provide a comprehensive review of the oxidation and reduction processes that transform V in Earth's surface environments, and Hope (24) quantifies the movement of V on the present-day and future Earth, based on its mobilization by human activities. In this paper, we provide an updated, quantitative summary of the global biogeochemical cycle of V, including both human and natural fluxes. Using published data, we compile and calculate global-scale estimates of the flux of V in nature, especially as modified by recent changes in the combustion of coal and petroleum products and byproducts. Due to limited data, many of these estimates must be presented without boundaries of uncertainty, but we are encouraged by the general internal consistency that emerges when the independent flux estimates produce a roughly balanced global budget.

Mobilization of V from Earth's Crust

Natural Sources. Natural V mobilization from Earth's crust occurs dominantly through mechanical and chemical rock weathering, with lesser contributions from other pathways such as volcanic emissions and aeolian processes. For mechanical weathering, Hope (24) estimates that 2,300 × 10⁹ g V/y is transported to the sea in suspended sediments. We suggest a somewhat (30%)

Significance

Human emissions of vanadium to atmosphere exceed natural sources by a factor of 1.7 and are destined to rise dramatically as we switch to the use of heavy oils, tar sands, and bitumen as combustion sources. Breathing vanadium-rich aerosols has unknown but potentially adverse health impacts. The human impacts on the global vanadium cycle parallel impacts on the global cycles for Pb and Hg.

Table 1. Movement of certain crustal elements through the atmosphere

Element	Continental dust	Sea spray	Volcanic emissions	Biomass burning	Volatilization Natural	Volatilization Human induced	Industrial particles	Fossil fuel combustion	Ratio anthropogenic: natural
V	155	0.52	7	5				100 to 287	0.59 to 1.71
Hg	0.12	0.009	0.5	0.6	3.7	4.1		3.4	1.52
Pb	32	5	4.1	38			32	85	1.48
Cu	50	14	9	27			43	4	0.47
Zn	100	51	10	147			88	5	0.30
Ag	2.3	0.01	0.01	1.2			0.44	0.05	0.14
Fe	55,000	200	8,800	830			641	4,200	0.07
Al	96,000	810	4,500	2,125			397	5,900	0.06

From Rauch and Pacyna (88), except for V (this paper) and Hg (107, 108). All data in 10^9 grams per year.

lower value, $1,625 \times 10^9$ g V/y, derived from the transport of total suspended sediment, 12.6×10^{15} g/y (25), and the mean concentration of 129 mg V/kg in sediments (26).

With respect to chemical weathering, Shiller and Mao (12) observed that world rivers are characterized by relatively constant dissolved V/Si ratio ($\sim 66 \times 10^{-6}$ mol V/mol Si), suggesting that dissolved V and Si are dominantly derived from chemical weathering of silicate rocks (27). In a detailed study of global weathering, Gaillardet et al. (28) concluded that virtually all dissolved silica in rivers derives from silicate weathering. Following the approach of Shiller and Mao (12), we calculate the V flux from chemical weathering as $\sim 21 \times 10^9$ g/y, using their V/Si correlation and a recent estimate of global dissolved silicate flux (380×10^{12} g/y; ref. 29). Our calculated value for chemical weathering of V is in the middle of the range of earlier estimates for the transport of dissolved V to the oceans in rivers, 8×10^9 g/y to 32×10^9 g/y (12, 30–32).

Anthropogenic Sources from Earth's Crust. We estimate the global anthropogenic V flux from the mining and combustion of coals, exploitation and utilization of petroleum and its products, and direct extraction and processing of V compounds. In general, the exploitation of these resources has increased significantly during the last few decades, which has contributed to a greater mobilization of V through time. Worldwide, $\sim 85\%$ of V is used as an additive in steel alloys; V is also used as a catalyst in the chemical industry and, increasingly, in V redox batteries (33).

Coal production. Global coal production has doubled, from 3,800 million tons/y in the early 1980s to about 8,000 million tons/y in 2014, although, during 2015 and 2016, it decreased to $\sim 7,300$ million tons/y (34). In 2016, China accounted for $\sim 50\%$ of the global coal production (3,550 million tons/y), followed by India (922 million tons/y) and the United States (661 million tons/y), while all other countries combined accounted for less than 30% of total global production (35).

Measured V concentrations in coals worldwide vary from 7 mg/kg to 100 mg/kg, with an estimated global mean of 25 mg/kg (36–39). Archival data on coals from the United States also show a mean V value of 25 mg/kg (median = 20 mg/kg; $n = 6,593$; ref. 40). The 25-fold increase in the V concentration of coal, compared with the plant tissue from which it forms, likely results from the affinity of V for organic material under reducing conditions and its retention as these materials are compacted and lithified to form coal (e.g., ref. 41). Using this average V concentration in coal, and estimates of global increases in coal production, we estimate that V extraction associated with coal mining has increased from $\sim 100 \times 10^9$ g V/y at the end of the 20th century to 180×10^9 g V/y to 190×10^9 g V/y in 2014–2016 (Fig. 1).

During coal combustion, V volatilization is followed by its rapid condensation from flue gas and retention by high-surface-area fly ash particles (42, 43). V is almost completely accumulated on fly ash and other coal combustion residues (CCRs), with little or no V loss due to volatilization (e.g., ref. 44). The V composition in CCRs reflects the V content of the parent coal. The ratio between the volume of CCRs and the volume of utilized coal is about 0.10 (45). Combined with efficient uptake of V in CCRs, this suggests an approximate 10-fold V enrichment in the residual ash compared with coal, averaging ~ 250 mg/kg based on the global average V in coal. This estimate is within the range of values (150 mg/kg to 700 mg/kg) reported for V in CCRs (e.g., refs. 37 and 46).

In recent decades, installation of high-efficiency cold-side electrostatic precipitators, fabric filters, and wet flue gas desulphurization systems has reduced particulate matter (PM) emissions, especially from coal-fired plants. It has been shown that such "scrubber" systems can eliminate $\sim 99\%$ of particulate emissions (42). In the United States, most coal-fired plants installed these systems during the 1980s and 1990s (47), while, in China, installation of scrubbers in major power plants increased from almost zero in the early 2000s to about 80% of coal plants in 2010 (48). The dramatic rise in worldwide coal production since the early 2000s due to the accelerated coal mining in China and India suggests higher rates of V mobilization. On the other hand, the transition to modern coal plant technologies with more efficient capturing of PM would restrict the atmospheric emission of V, although the actual effectiveness is still unknown in countries like India or the industrial sector in China. For comparison, atmosphere emissions of Cu and Zn from coal combustion in China increased 1.9% and 1.33% per year, respectively, from 1995 to 2014 (49).

In the United States, about half of CCR is used by the cement industry and other beneficial uses (50), and the other half is disposed of in landfills and surface impoundments. Similarly, a large fraction of CCR in China is used by the cement industry (45). The effluent discharged from coal ash ponds has a wide range of V concentrations; a study of effluent in North Carolina showed values ranging from 0.3 µg/L to 53.3 µg/L with a mean value of 10 µg/L (51). Thus, a fraction of the V that is accumulated in CCRs is potentially mobilized to aquatic systems and released to the environment. In North Carolina, 857 million cubic meters of effluent was discharged through regulated outfalls during 2012. Assuming an average V concentration of 10 µg/L in effluent waters, we estimate the annual flux of V from coal ash ponds in North Carolina is 8.6×10^6 g V/y. Since the capacity of coal-powered units in North Carolina (10,430 MW) is equivalent to 3% of the US total capacity (338.7 GW), we estimate the overall V flux from coal ash effluents is about 0.28×10^9 g V/y for the United States, assuming similar effluent discharge practices throughout the country. Since US coal production is about 10% of the global coal production, we estimate that the global V flux to the hydrosphere through effluent release is about 2.8×10^9 g V/y. Recent studies have indicated
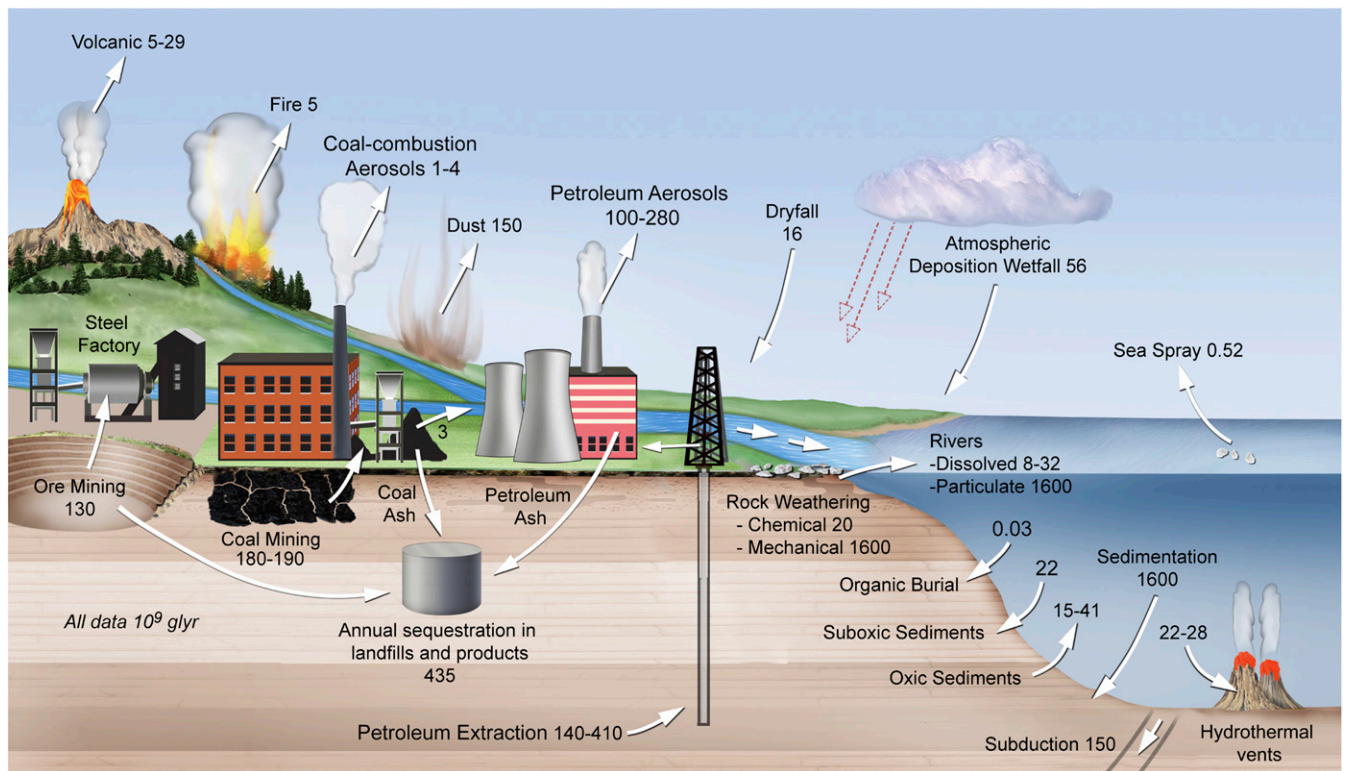
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Fig. 1. The global biogeochemical cycle of V as estimated for current conditions. All values are given in 10^9 grams per year and rounded to two significant figures from calculations throughout the text.

that coal ash ponds in the United States, and presumably elsewhere, are leaking (52), and thus this value may underestimate the full magnitude of V flux to the hydrosphere from disposal of CCRs in coal ponds and landfills (53).

Petroleum production. V and nickel are the two most abundant metals in petroleum, with concentrations up to 1,600 mg/kg and 340 mg/kg, respectively (54). In bitumen, the V level can reach 4,760 mg/kg (55). The V and Ni are associated with organic matter derived from algae that encounters suboxic conditions early in its depositional history (55). The transformation of organic molecules such as plant chlorophylls into organic metallic complexes, known as geoporphyrins, and chelation of Ni^{2+} and VO^{2+} to generate metalloporphyrins, preserves V compounds during petroleum diagenesis and catagenesis (56).

The differential incorporation of Ni and V into geoporphyrins results in different V and Ni abundances and V/Ni ratios in crude oils. Petroleum from marine environments (defined as Classes A and B) with high sulfur contents is known to contain higher V contents and V/Ni ratios relative to petroleum from mixed and terrestrial settings (Classes C, D, E) (54). V bonds to high molecular weight organic compounds (57), resulting in a positive correlation between V concentration and crude oil density. Consequently, heavy oils are enriched in V relative to light oils. A common unit to express oil density is the American Petroleum Institute gravity (API gravity), in which values above 10 reflect oils with densities lower than water, while oils less than 10 are heavier than water. Data from the US Geological Survey (58) shows greater V in oils with lower API gravity values and differences between conventional oil (average V =16 mg/kg; API gravity = 38), medium oil (V = 98 mg/kg; API gravity = 22), heavy oil (V = 177 mg/kg; API gravity = 16.3), and bitumen (V = 334 mg/kg; API gravity = 5). Similarly, crude oils from Venezuela show an inverse correlation between V concentration and API

gravity, with V concentrations up to 600 mg/kg in biodegradable oils (API gravity < 15), and up to 1,200 mg/kg in heavy (API gravity ~10) immature oils (59). Consequently, the mobilization of V by petroleum extraction depends strongly on the relative proportions of light and heavy oils.

Conventional oil production of light oils, which characterized much of the oil production during the 20th century, generates relatively low V fluxes. Due to increasing worldwide energy demands and technological developments, there has been a significant increase in the exploitation of heavy oils (e.g., Alaskan and Venezuelan oils) and unconventional petroleum resources (e.g., bitumen extraction from tar sands), resulting in significantly greater V mobilization. For example, the production of crude bitumen from Alberta tar sands has more than doubled since 2003, reaching an annual production of 841 million barrels in 2014 (60).

A first approximation of the current global V flux from the extraction of petroleum can be obtained using an estimate of the average quality of crude oil (API = 33.6; ref. 61) and an empirical correlation between API gravity and V concentration described by Barbooti (62). These assumptions result in an average V concentration of 28.9 mg/kg in crude oil and a global flux of V from petroleum production of 138×10^9 g/y, assuming 2015 world crude oil production of 34 billion barrels (34, 63). This calculated average V concentration in crude oil does not seem to reflect the increasing worldwide emphasis on heavier grades of crude oil, and the empirical correlation between API gravity and V concentration is based on a limited number of samples (62). Furthermore, V has been shown to be difficult to accurately measure in crude oils (62).

As a second approximation, we used recent estimates of the types of petroleum exploited in 2015, finding that about 31% was light sweet crude (averaging 16.2 mg/kg V), 48% was light sour (averaging 98.3 mg/kg V), 13% was heavy sour (averaging

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177 mg/kg V), and 4% was natural bitumen (averaging 334 mg/kg V) (34, 58, 63). From these estimates, we calculate a current mobilization of about 410×10^9 g V/y by extraction of petroleum from Earth's crust, a value about threefold that estimated above. Using this second approach, we also estimate that this flux has approximately doubled over the past two decades, roughly consistent with the annual flux (165×10^9 g V/y) calculated by Monakhov et al. (64) for the year 2000. The increasing V flux over this time is due to both the 1.5-fold increase in global oil production as well as the increasing proportion of high-V petroleum fuels in the mix. Together, these two approximations constrain the anthropogenic flux of V from petroleum extraction to lie between 138×10^9 g/y and 410×10^9 g/y.

While V is enriched in crude oils, limited data suggest that the V content in produced water generated during the production of oil is negligible. For example, oil-produced water from the Gulf of Mexico contains V up to 1 µg/L, and most water samples had values below detection limit (65). Consequently, unlike other elements that are enriched in the formation water associated with oil, and thus would contribute to anthropogenic fluxes, such as boron (66), cadmium (Cd), and lead (Pb) (65), it seems that the V flux through produced water is very small.

Mining and formation of V chemicals. V is produced by mining of vanadiferous titanomagnetite ores, and extracted as a byproduct in the processing of iron ore, phosphates, and uranium. Data presented by Monakhov et al. (64) suggest that the purposeful mining of V-bearing ores mobilized about 130×10^9 g V/y in 2000, with about 43% from virgin V ores and 56% produced as a byproduct. Analyses by the US Geological Survey show that world V production, primarily from mining, has more than doubled over the past two decades (from 34×10^9 g V/y in 1994 to 82×10^9 g V/y in 2014), with China, South Africa, and Russia as the major producers (67, 68).

We suggest that the total mobilization of V from Earth's crust by human activities is currently (2015–2016) 730×10^9 g/y, with 18% from direct and byproduct mining activities and, as described above, 56% from petroleum production, and 26% from coal.

Sinks for V Mobilized from Earth's Crust

Like other low-volatility elements, most V mobilized on land is transported to the oceans, where it is removed by a variety of processes. Removal of sedimentary V in subduction zones can account for 150×10^9 g V/y, calculated from estimates of the mass of subducted sediment (1.3×10^{15} g/y) multiplied by its average V concentration (116 mg/kg; refs. 69 and 70). For comparison, Hope (24) estimates 640×10^9 g of V is removed by subduction of ocean sediment each year. Both estimates are substantially lower than our estimate of the delivery of V to the oceans in suspended sediments ($1,625 \times 10^9$ g/y; *Mobilization of V from Earth's Crust*). The vast majority of suspended sediment delivered to the oceans is not subducted, however, but is instead deposited on passive continental margins and other areas of the ocean floor not currently subject to subduction (71). We estimate the mass of this sequestered ocean sediment as 11.3×10^{15} g/y, following the approach of Rae and Ruff (71) and substituting the recent estimates of sediment supply and subduction noted above (12.6×10^{15} g/y and 1.3×10^{15} g/y, respectively). Multiplying the mass of sediment sequestered by the mean concentration of V in sediment (129 mg V/kg; ref. 26), we calculate that about $1,460 \times 10^9$ g V/y is sequestered in oceanic sediment.

V is widely recognized for its retention on organic materials, especially under reducing conditions (72, 73). Assuming a concentration of 100 mg V/kg in organic deposits (16), the sequestration of V by the burial of organic matter (of 50% C) in the oceans (0.157×10^{12} g/y; ref. 74) is only about 0.03×10^9 g V/y. Thus, despite its affinity for organic matter, V is largely deposited in inorganic sediments in the marine environment. Oxic sediments

tend to release V to seawater, while suboxic (including buried) sediments adsorb and retain dissolved V (75).

The mean concentration of V dissolved in seawater, 1.8 µg/L, is higher than that in river waters (0.7 µg/L), implying additional sources of V in seawater. Some V is likely released from suspended or accumulating sediments as they experience the higher pH of seawater and from sedimentary environments with oxic conditions (72, 76). In contrast, hydrothermal vent systems appear to be a net sink rather than a source for V to seawater, with hydrothermal sediment accumulations ranging from 7.1×10^9 g V/y (75, 77) to 22×10^9 g V/y to 28×10^9 g V/y (32, 75). Further, while undersea volcanic eruptions at midocean ridges and oceanic volcanoes can influence the seawater composition of various volatile trace elements, V mobilized during such eruptions appears to be rapidly deposited on surrounding seafloor (78, 79). The sum of the dissolved V in rivers ($\sim21 \times 10^9$ g V/y to 30×10^9 g V/y) and the release from oxic sediments ($\sim15 \times 10^9$ g V/y to 41×10^9 g V/y; ref. 75) can accommodate the estimated uptake by hydrothermal deposits ($22 \cdot 10^9$ g V/y to 28×10^9 g V/y) and suboxic marine sediments (22×10^9 g V/y; ref. 75), so that the budget for dissolved V in the ocean is reasonably well balanced.

The mean residence time for dissolved V in the oceans is about 130,000 y, with respect to river inputs [i.e., 2.7×10^{15} g of V dissolved in seawater (13) divided by 21×10^9 g dissolved V in rivers (this paper)]. The estimated mean residence time decreases to about 42,000 y if the influx includes rivers, atmospheric deposition, and release from oxic sediments (Fig. 1). For comparison, Whitfield and Turner (80) estimate a mean residence time of about 100,000 y, based on the partitioning of V between seawater and marine sediments.

Exchange of V with Earth's Atmosphere

Natural Sources in the Atmosphere. V is delivered to the atmosphere as aerosols derived from various natural processes, each of which represents a small source relative to rock weathering, as discussed above. Current evidence suggests that the largest source of atmospheric V aerosols is wind erosion, with previous estimates ranging from 16×10^9 g V/y to 27×10^9 g V/y (15, 81). To this range, we provide a larger estimate of 155×10^9 g V/y, based on the eolian mobilization of crustal materials with particle sizes of <10 µm (i.e., PM_{10}; $1,600 \times 10^{12}$ g/y; ref. 82) multiplied by the mean concentration of V in Earth's crust (97 mg/kg; refs. 1 and 11).

The next largest source of atmospheric V is subaerial volcanic emissions. A common approach to calculate the global flux of trace metals from volcanic activity has been to estimate their metal/sulfur ratios and multiply by the relatively well-investigated volcanic sulfur emission. Previous estimates using this method suggest a global range for V emissions of 0.1×10^9 g/y to 5.5×10^9 g/y (ref. 15, adjusted for an error noted by ref. 83). While this approach and refinements upon it are logical for estimating the volcanic flux of volatile trace metals (e.g., Hg, Pb, Cd; ref. 84), it is likely less appropriate for estimating fluxes of low-volatility metals, such as V, which are emitted primarily in volcanic ash (e.g., refs. 78, 83, and 85–87). Therefore, building on the approach of Duce and Hoffman (81), we calculate V/Al ratios of volcanic particulates (using a range of upper crustal and andesitic values of 15.3 to 17 wt.% Al_2O_3; and 97 mg/kg V to 175 mg/kg V; ref. 1) and multiply by two estimates of global volcanic Al emissions [$4,500 \times 10^9$ g/y (88); $13,280 \times 10^9$ g/y (83)]. Using the lower Al emission value, we calculate global volcanic V fluxes ranging from 5×10^9 g V/y to 10×10^9 g V/y, similar to the estimate of Duce and Hoffman (81), while the higher Al value suggests a range of 14×10^9 g V/y to 29×10^9 g V/y.

Wildfires are also a source of V in the atmosphere, estimated between 1.8×10^9 g/y and 13×10^9 g/y (15, 24). We calculate wildfire emissions of V by assuming that 5×10^{15} g/y of biomass are burned annually (89), volatilizing V from tissues that have a mean

concentration of 1 mg/kg (10), and thus delivering 5×10^9 g V/y to the atmosphere.

Finally, while sea salt aerosols have been shown to be a significant atmospheric source for some elements (e.g., Na, B, Cl), little V is mobilized by this process. We calculate that production of sea salt aerosols at the ocean's surface (10.1×10^{15} g/y; ref. 82) multiplied by the ratio of V to total dissolved solids in seawater (5.14×10^{-8}) would inject 0.52×10^9 g V/y into the marine atmosphere—a trivial flux in its global cycle. Zoller et al. (14) indicate an even smaller value, 0.012×10^9 g V/y.

Anthropogenic Additions of V to Atmosphere.

Coal combustion. To provide a first estimate of the atmospheric emission of V from coal combustion, we use US Environmental Protection Agency data (90) that quantifies the masses PM_{10} and $PM_{2.5}$ that are annually emitted from electric utilities in the United States, combined with our estimate of the average V concentration in CCRs (250 mg/kg). Our calculations indicate that, despite the doubling in national coal production in the United States from 500 million tons/y to 600 million tons/y during the early 1970s to ~1,000 million tons/y in the mid-2000s, the atmospheric flux of V as determined by the PM mass flux declined from 0.4×10^9 g V/y in the early 1970s to 0.1×10^9 g V/y in the late 2000s and recent years, representing a fourfold reduction. This trend reflects improvements in the use and efficiency of ESP and other scrubber systems in reducing PM emissions to the atmosphere. Since global PM emission from coal plants is unknown, we use the US dataset to approximate the global flux under two different scenarios. In the first scenario, we assume that the reduction of PM emission that was achieved in the US is valid for the rest of the world; in the second scenario we assume that the conditions that characterize high PM emission in the US in the early 1970s apply to the rest of the world today. In recent years, US coal production represents about 10% of global coal production and thus we can assume that V fugitive emissions in the US are also equivalent to 10% of the global V emission. Under Scenario 1 (global reduction of PM emission), the global V atmospheric flux from coal combustion is about 1.1×10^9 g V/y (i.e., 10 times the current US emission). According to Scenario 2 (global emission mimics the US emission during early 1970s), the global V atmospheric flux from coal combustion is about 4.4×10^9 g V/y (i.e., 10 times the US emission during early 1970s normalized to the current global coal production).

Petroleum Sources of V to the Atmosphere.
Monakhov et al. (64) estimated that the annual V flux to the atmosphere from petroleum combustion during the year 2000 was 113×10^9 g/y, which represented about 69% of the V contained in petroleum extracted from the ground (165×10^9 g V/y). Since then, global oil production has increased, and the V content in extracted petroleum may lie between 138×10^9 g V/y and 410×10^9 g V/y (see above). While improvements have been made in developed countries to capture a greater proportion of the particulate flux from all forms of fossil fuel combustion (e.g., ref. 91), this is offset by increased emissions in developing countries and the absence of emissions regulations for various types of fuel in some developed countries. Visschedijk et al. (92) report that 69% of the emissions of V are not subject to scrubbing in Europe. If we assume that 69% of the V content from petroleum combustion is emitted to the atmosphere, we calculate that the current flux may be as high as 283×10^9 g V/y. This flux now dominates the emission of V to the atmosphere. The anthropogenic additions of V to the atmosphere may now exceed natural sources by a factor of 1.7 (Table 1)—larger than the similar ratios for Hg and Pb, but somewhat lower than estimated by previous workers (24, 93).

An increasing fraction of V atmospheric emissions estimated above derives from combustion of unconventional petroleum products, such as residual/heavy oils and petroleum coke. The selective incorporation of V into high molecular weight organic compounds (57) controls the preservation and accumulation of V in residual organic materials during distillation and refining. As a result, V is enriched in the residues during the conversion and refinement of oil and bitumen. Global production of residual/heavy oil was about 467 million metric tons per year in 2014, although, in recent years, demand has decreased in most sectors (94). Other notable residue products include petroleum coke, a solid carbon-rich material increasingly used as a combustion fuel due to its high carbon content, low cost, and growing abundance (95). V enrichment in these residues is often marked; for example, petroleum coke produced during distillation of bitumen from the Athabasca Oil Sands Region in Canada shows a mean V concentration of 1,280 ± 120 mg/kg (96), while bitumen from this region ranges from 60 mg/kg to 640 mg/kg (97).

The global production of petroleum coke rose to about 124 million metric tons per year in 2014, with the United States producing about 47% (94). Approximately 70% of worldwide production is used as a source of combustible fuel (94). In some cases, petroleum coke substitutes for coal; for example, in 2002, about 10% of power plants in Kentucky utilized petroleum coke instead of coal (98). Fly ash originating from combustion of petroleum coke is highly enriched in V, with reported concentrations between 2,000 mg/kg and 40,000 mg/kg (99, 100). Consequently, fugitive emission of fly ash particles from petroleum coke combustion would result in high atmospheric emission of V.

In the absence of effective scrubber systems, combustion of heavy oils and petroleum coke can dominate regional atmospheric V emissions. For example, a study of 2005 emissions in northwestern Europe showed that combustion of residual oil (e.g., ships and petroleum refineries) and petroleum coke (power plants and refineries) contributed 80% and 18%, respectively, of the total atmospheric emission of V in that region (1.57×10^9 g V/y; ref. 92). Studies in Spain (101) and in the United States (14, 102) show similar findings. Based on estimates of the current mix of petroleum products exploited (described above), we estimate that unconventional fuels, with their higher V concentrations, represent about 40.5% (166×10^9 g V/y) of the total V mobilized to the atmosphere from the extraction of petroleum (410×10^9 g V/y). If we also assume that, of the V emitted to the atmosphere from burning petroleum products (283×10^9 g V/y), 40.5% originates from unconventional fuels, we calculate that 115×10^9 g V/y are released to the atmosphere from the combustion of residual/heavy oil, petroleum coke, and other unconventional fuels.

Sinks of V from the Atmosphere

Measurements of the concentration of V in rainfall collected in remote areas and in continental areas subject to human activities range over four orders of magnitude (Table 2). Whenever possible, we provide the ratio of V to Al in these samples to provide an estimate of the "enrichment factor" of V in rainwater versus the V in Earth's crust. Most of the data from remote areas have enrichment factors of <10, whereas those from areas of human activities have factors ranging up to 1,000. For remote sites, the median concentration of V in rainfall, 0.03 µg/L and global precipitation of 5×10^{17} L/y yields an estimate of global atmospheric deposition in rainfall of ~15×10^9 g V/y in preindustrial times. This atmospheric deposition of V might have accounted for a small portion of the dissolved V in rivers. For modern conditions, we assume that the wet deposition over the oceans has not been affected by human activities and thus could be 11×10^9 g V/y. For the land, the median of all concentration values for V in modern precipitation, ~0.4 µg/L, would imply deposition of 45×10^9 g V/y. The median of samples with enrichment factors of <10 would imply deposition of 35×10^9 g V/y from the atmosphere and a

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Table 2. Concentrations of V in precipitation collected in various locations

Location	n	Volume-weighted concentration, μg/L	Enrichment factor*	Ref.
Remote areas				
East Antarctica		0.00046		109
Coats Land, East Antarctica		0.00056		110
East Antarctica	12	0.003	5 to 10	105
Greenland	9	0.015	1.0 to 2.1	Herron et al. 1975 as cited by ref. 81
Enewetak Atoll	14	0.018		111
Tibetan Plateau, China	79	0.033	1.0 to 3.5	112
Bermuda		0.096	14	113
Hawai'i (volcano quiescent)	3	0.13		85
Korea (rural)	87	0.14	10	114
Alps, Switzerland		0.14		115
Hong Kong, China	32	0.18		116
Alps, Switzerland		0.223		115
Continental areas with moderate human activities				
Hiroshima, Japan	152	0.23		117
Newark, New Jersey, USA	46	0.24	42.8	118
Pensacola, Florida	225	0.274		119
Lamto, Ivory Coast	50	0.29	~2.0	120
Lhasa, Tibet, China	157	0.31	1.0 to 5.0	121
Japan (four sites)		0.38		122
Tibetan Plateau, China	103	0.43		123
Culpepper, Virginia	58	0.43	~1 to 10	124
Reston, Virginia	26	0.47		125
Tokyo, Japan	20	~0.5	1 to 20	126
Delaware		0.67	18	113
Montreal, Canada	65	0.75	35	127
Oleiros A Coruna, Spain	18	0.83	113	128
South China	37	1.08	~10 to 50	129
Massachusetts,	12	1.1	16	130
Rhode Island	269	1.27		131
Northern China		1.4		Li et al. 2012 as cited by ref. 121
Ankara, Turkey	76	2.22	0.5 to 10	132
Kollo, Niger	22	2.29	~2.0	120
Southern Jordan	27	4.21	~20	133
Singapore, Malaysia	84	3.54	~1,000	134
Nanjing, China		4.6		Tang 2007 as cited by ref. 121
Mexico City, Mexico	81	5.13	~500	135

*Versus Al; namely, $EF = (V/Al)_{rain}/(V/Al)_{crust}$.

substantial enhancement (~9.0×) due to human activities. The latter amounts to slightly more than 20% of estimated gross sources of V in the atmosphere, suggesting that a substantial amount of dry deposition must occur near sources of human emissions (7, 103, 104). However, some V is carried long distances in the atmosphere. For example, dissolved and particulate phases are roughly equally represented in Antarctic snow (105), and V in Greenland snow shows a strong relation to crustal dusts, which are the largest natural source of V in the atmosphere (106).

In the remote atmosphere, concentrations of V are typically about 1×10^{-9} g/m^3, which would result in a global dry deposition of 16×10^9 g/y, assuming a nominal dry deposition velocity of 0.1 cm/s for small particles. Our calculation of the sum of wet and dry deposition (72×10^9 g/y) is less than the estimated sources to the atmosphere, leaving us with an unbalanced budget for V in the atmosphere. In urban areas, airborne concentrations can exceed 10×10^{-9} g/m^3 (14, 92, 101, 102), so the atmospheric budget may be balanced by dry deposition near emission sources.

Conclusions

Overall, our data provide insights on the current anthropogenic V fluxes from coal mining and combustion; crude oil exploration, processing, and combustion; and ore mining and industrial processing. Since the beginning of the 21st century, the increasing use of V-rich heavy oil, bitumen, and petroleum coke from unconventional petroleum resources and production residues has changed the V fluxes, such that the V derived from petroleum products is now the largest global flux (56%), followed by coal (26%) and V mining (18%). Data on atmospheric V emissions are limited, but the accumulation of V in heavy oils and bitumen residuals, such as petroleum coke, poses a risk associated fugitive emission of V-rich PM, with unknown impacts on human health.

Fig. 1 summarizes the salient points for the global biogeochemical cycle of V:

i) Humans have potentially increased the total mobilization of V from Earth's crust by a factor of >1.45, as a result of mining of V ores and the extraction and combustion of fossil fuels. The dissolved flux to the seas has likely increased by ~15%.

ii) Human emissions of V to the atmosphere now exceed background levels by as much as a factor of 1.7, and we are likely to have increased the deposition of V from the atmosphere by a similar amount since preindustrial times. Much of this is probably derived from airborne emissions during the combustion of fossil fuels, and this flux is likely to increase in the near future as humans pursue sources of petroleum from heavy oils and bitumen.

iii) The human impact on the atmospheric flux of V may exceed that for Hg and Pb (Table 1), primarily due to the significant

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enrichment of V in heavy crude oil and byproducts. While future air pollution control could mitigate atmospheric V emission from combusted fossil fuels, the expected increasing utilization of unconventional petroleum resources could further exacerbate the anthropogenic V flux in the future.

iv) The budget of dissolved V in the oceans is remarkably well balanced—with about 40×10^9 g V/y to 50×10^9 g V/y inputs and outputs, and a mean residence time for dissolved V in seawater of about 130,000 y with respect to inputs from rivers.

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