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An assessment of the global impact of anthropogenic vanadium

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Abstract. Evidence that environmental levels of vanadium are increasing has raised concern over the injection of vanadium into the environment from anthropogenic sources. Two simple global mass balance models (simulating current and pre-industrial conditions) were developed to demonstrate the influence of anthropogenic vanadium on the global distribution of this trace metal. Current vanadium emissions owing to man's current industrial activities were estimated to comprise ≈30% of total atmosphere loading, ≈3% of total ocean loading, and ≈6% of total land loading. These loadings were always considerably less than those resulting from non-anthropogenic sources or events. Differences noted between the pre-industrial and current models were not sufficiently great to suggest that injection of anthropogenic vanadium constitutes a significant environmental threat on a global scale.

Introduction

Vanadium is a major trace metal in fossil fuels and combustion of these materials provides a significant source of vanadium in the environment (Duce & Hoffman 1976). Little vanadium is retained in refined oil products, and vanadium contamination occurs as fallout from refining operations and burning of residual oils. These are the major environmental vanadium fluxes resulting from human activity; other sources are products of coal combustion, leachates, and effluents from mining and milling of uranium and titanium (Nrigau & Pacyna 1988). There is evidence that environmental levels of vanadium are increasing (Sato & Okabe 1978). To better understand the global impact of anthropogenic vanadium, a first approximation biogeochemical cycle was constructed for this element. Principle goals were: (1) description of major components (reservoirs and fluxes) of the global vanadium cycle and (2) estimation of the extent to which anthropogenic inputs have affected the global cycling of this element.

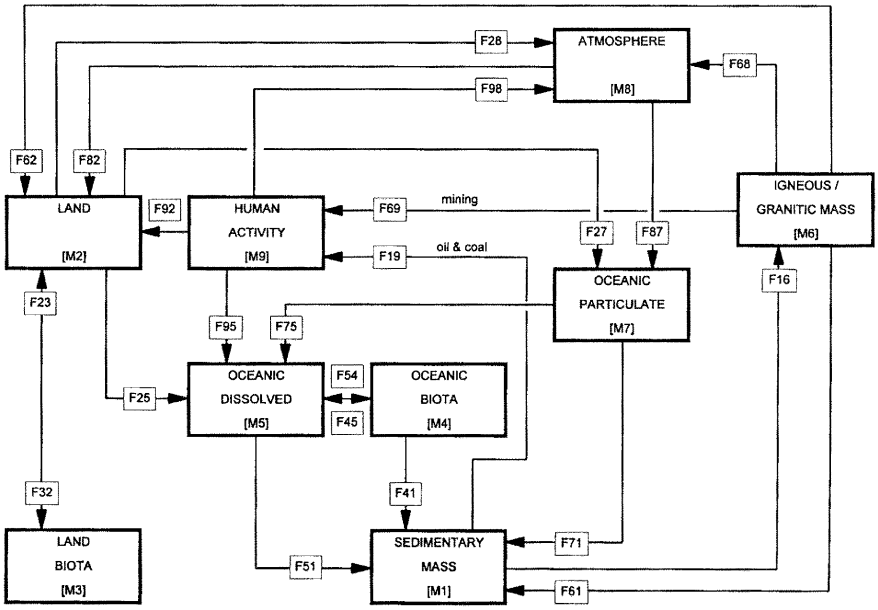

Figure 1. Schematic diagram showing relationships between reservoirs and fluxes.

Methods

Two models were constructed to represent "current" and "pre-industrial" (defined as prior to 1800 AD) conditions, respectively. For each model, nine reservoirs (sedimentary mass, land, land biota, oceanic biota, oceanic dissolved, igneous/granitic mass, oceanic particulate, atmosphere, and human activity) and twenty-two fluxes were defined to provide the resolution required to evaluate the movement of natural and anthropogenically derived vanadium on a global scale. The mass of each reservoir was represented by M_i, where i = 1, 2, . . . 9. Each flux between reservoirs was represented by F_{ij}, where i = the source reservoir, j = the receiving reservoir, i, j = 1, 2, 3 . . . 9, and $i \neq j$. Figure 1 provides a schematic diagram of relationships between fluxes and reservoirs. All reservoir mass values are in units of kilograms (kg); all flux rates are in units of kilograms per year (kg/yr); all residence times are in units of years (yr).

Several values were derived for each mass and flux value, using data taken from an extensive literature review of existing data on the distribution, sources, and geochemical behavior of vanadium. Data used to estimate initial reservoir mass values are summarized in Table 1, while data used to derive initial flux values are summarized in Table 2. The arithmetic mean of these values was used as the initial mass and flux values for the current model. The

pre-industrial model was then derived from the current model by assuming an absence of all industrial, mining, or fossil fuel extraction or combustion activities and associated emissions.

For F32, a simplifying assumption was made wherein loss of vanadium from land biota was assumed equal to uptake of vanadium by land biota, so that F32 = F23. Calculation of F45 was based on the hypothesis that a near equilibrium condition exists between uptake of dissolved vanadium by oceanic biota (F54) and its subsequent release (F45) through decomposition of dead, decaying biota, adjusted for vanadium lost through biogenous sedimentation (F41) (Lisitzin 1972). A flux (F51) for removal of dissolved vanadium, other than through biotic uptake (F54), was also considered possible. Presumably, before the emergence of significant anthropogenic inputs, a steady state condition would have prevailed, causing natural river and biota inputs to be balanced by other natural removal processes as defined by F51. Adsorption to particles reaching sediments, interactions with the sediment surface, and other chemical processes for removal are possible. The value of F51 was taken as that flux rate which brought each model into balance. For the current model, removal of vanadium from igneous and granitic masses by human activity was considered equal to the vanadium mineral extraction rate (1975 production data) (NAS 1974; Turekian & Wedepohl 1961). For the pre-industrial model, this value was set to zero.

For F71, it was assumed that all of particulate-bound vanadium in the river suspended load (F27) and the majority of vanadium from atmospheric deposition (F87) would remain attached to particles, not react with seawater, and precipitate into the sediment. Because particulate-bound vanadium, particularly that resulting from fossil fuel emissions, can move rapidly into solution in seawater (Duce & Hoffman 1976; Hoffman et al. 1974; Walsh & Duce 1976), it was assumed that some fraction of the material resulting from atmospheric deposition would partition into seawater; as defined by a soil-water partition coefficient (K_d), so that $F71 = F27 + (F87 - F87/K_d)$ and $F75 = F87/K_d$, where $K_d = 1000$ (Baes et al. 1984).

The two models were constructed within a Microsoft Excel® Version 5.0 spreadsheet environment. Mean values obtained from range estimates for F19, F23, F25, F27, F28, F32, F41, F54, F61, F62, F68, F69, F92, F95, and F98, as shown in Table 2, were entered as initial values for the current model. Mean values for F16, F45, F51, F71, F75, F82, and F87 were then computed for the current model using the algorithms shown in Table 2. The MS-Excel® version 5 Solver numerical approximation routine was then used to derive final mean values for F51, F62, or F92 that brought the model into balance. For the pre-industrial model, mean values for F19, F69, F92, F95, and F98

Table 1. Range of reservoir mass estimates used to develop mean values for use in the pre-industrial and current models.

Reservoir	Mass estimates (kg)	Sources of data used in estimation calculations
Sedimentary mass (M1)	8.03×10^{16}	Garrels & Mackenzie 1971; Turekian & Wedepohl 1961; Mackenzie & Wollast 1977
	1.71×10^{17}	Dobrovolsky 1994
	7.70×10^{16}	Garrels & Mackenzie 1971; Turekian & Wedepohl 1961; Mackenzie & Wollast 1977
Land (M2)	2.77×10^{13}	HCP 1992; Bertrand 1950; Bowen 1966; Kabata-Pendias & Pendias 1984; NAS 1974
	2.13×10^{13}	HCP 1992; Kabata-Pendias & Pendias 1984
	1.81×10^{13}	HCP 1992; Kabata-Pendias & Pendias 1984
Land biota (M3)	4.68×10^{9}	Yockstick 1987
	3.75×10^{9}	Dobrovolsky 1994
	1.00×10^{10}	Dobrovolsky 1994; Bertrand 1950; Cannon 1963; Landergren 1974; NAS 1974; Schroeder 1970
Oceanic biota (M4)	2.00×10^{7}	Bolin 1970; Bowen 1966
	1.00×10^{7}	Dobrovolsky 1994
Oceanic dissolved (M5)	2.06×10^{12}	HCP 1992; Morris 1975; Riley & Taylor 1971; Sugawara et al. 1956
	2.74×10^{12}	HCP 1992; Bowen 1966
Igneous/granitic mass (M6)	1.11×10^{18}	Dobrovolsky 1994; Kabata-Pendias & Pendias 1984
	6.23×10^{17}	Dobrovolsky 1994
Oceanic particulate (M7)	2.19×10^{10}	Dobrovolsky 1994; Bowen 1966
	6.85×10^{9}	HCP 1992; Lisitzin 1972; Mackenzie & Wollast 1977; Bowen 1966
	2.74×10^{10}	HCP 1992; Lisitzin 1972; Mackenzie & Wollast 1977; Turekian & Wedepohl 1961
Atmosphere (M8)	2.35×10^{6}	HCP 1992; Chester & Stoner 1974; Duce & Hoffman 1976; Hoffman et al. 1972; NAS 1974; Zoller et al. 1973
	4.34×10^{6}	Dobrovolsky 1994; HCP 1992
	1.28×10^{6}	HCP 1992; Goldberg 1971; Kabata-Pendias & Pendias 1984

Table 2. Range of flux estimates used to develop mean values for use in the pre-industrial and current models.

Flux	Flux estimates (kg/yr)	Sources of data used in estimation calculations
Sedimentary mass ⇒ igneous/ granitic mass (F16)		F16 = F61 + F62 + F68 + F69
Sedimentary mass ⇒ human activity (F19)	2.20×10^8	Dobrovolsky 1994; Fishbein 1981
Land ⇒ land biota (F23)	8.14×10^7	Bowen 1966
	2.58×10^8	Dobrovolsky 1994
Land ⇒ oceanic dissolved (F25)	3.20×10^7	Garrels & Mackenzie 1971; Holeman 1968; Bertrand 1950; Riley & Chester 1971
	4.00×10^7	Dobrovolsky 1994
	3.20×10^7	Bertine & Goldberg 1971
Land ⇒ oceanic particulate (F27)	3.49×10^9	Dobrovolsky 1994
	2.30×10^9	Dobrovolsky 1994
	2.88×10^9	Mackenzie & Wollast 1977
	5.18×10^8	NAS 1978
	1.52×10^9	Lisitzin 1972
Land ⇒ atmosphere (F28)	1.85×10^8	Dobrovolsky 1994; Kabata-Pendias & Pendias 1984; Mackenzie & Wollast 1977
	2.55×10^8	Dobrovolsky 1994
	5.00×10^7	Fishbein 1981
Land biota ⇒ land (F32)		F32 = F23
Oceanic biota ⇒ sedimentary mass (F41)	8.78×10^6	Garrels & Mackenzie 1971 1972; Wollast 1974; Martin & Knauer 1973; 1973; Nicholls et al. 1959; Riley & Roth 1971
	1.00×10^7	Dobrovolsky 1994; Bowen 1966
	3.75×10^5	Dobrovolsky 1994; Mackenzie & Wollast 1977
Oceanic biota ⇒ oceanic dissolved (F45)		F45 = F54 – F41
Oceanic dissolved ⇒ sedimentary sedimentary mass (F51)		Calculated to balance model

Table 2. Continued.

Flux	Flux estimates (kg/yr)	Sources of data used in estimation calculations
Oceanic dissolved ⇒ oceanic biota (F54)	7.50×10^7	Ryther 1969
	3.84×10^8	Martin & Knauer 1973; Nicholls et al. 1959; Riley & Roth 1971; Lisitzin 1972; Pytkowicz 1973
	2.20×10^8	Dobrovolsky 1994; Bowen 1966
	3.30×10^8	Dobrovolsky 1994
Igneous/granitic mass ⇒ sedimentary mass (F61)	4.20×10^8	NAS 1974; DOI 1977
	2.29×10^9	Garrels & Mackenzie 1971; Kabata-Pendias & Pendias 1984; HCP 1992
Igneous/granitic mass ⇒ land (F62)	3.24×10^9	HCP 1992; Kabata-Pendias & Pendias 1984
	4.05×10^8	Kabata-Pendias & Pendias 1984; Dobrovolsky 1994
	9.46×10^8	HCP 1992; Dobrovolsky 1994
Igneous/granitic mass ⇒ atmosphere (F68)	2.03×10^7	Goldberg 1971; Kabata-Pendias & Pendias 1984
	1.22×10^8	Kabata-Pendias & Pendias 1984; Dobrovolsky 1994
	2.00×10^7	Dobrovolsky 1994; Fishbein 1981
Igneous/granitic mass ⇒ human activity (F69)	3.00×10^7	NAS 1978
Oceanic particulate ⇒ sedimentary mass (F71)		$F71 = F27 + (F87 - F87/K_d)$, where $K_d = 1000$
Oceanic particulate ⇒ oceanic dissolved (F75)		F75 = F87/Kd
Atmosphere ⇒ land (F82)		$F82 = (F28 + F68 + F98) \times 0.292$
Atmosphere ⇒ oceanic particulate (F87)		$F87 = (F28 + F68 + F98) \times 0.708$
Human activity ⇒ land (F92)	1.32×10^8	Nriagu & Pacyna 1988
Human activity ⇒ oceanic dissolved (F95)	1.16×10^7	Nriagu & Pacyna 1988
Human activity ⇒ atmosphere (F98)	8.60×10^7	Nriagu & Pacyna 1988

were set to zero and final model balancing mean values were derived only for F51 and F62.

Uncertainty in estimates of mass transfers at the global level undoubtedly arises from two primary sources: stochastic variability (uncertainty that can be reduced through additional measurement) and knowledge uncertainty (uncertainty that is unknown and/or difficult to measure). While this analysis did not attempt to distinguish between these sources, it did consider uncertainty in the aggragate by providing, whenever sufficient data were available, a credible range of estimates for all reservoir masses and certain flux rates, as shown in Tables 1 and 2. The minimum and maximum of these ranges were used to define the boundaries of uniform distributions for M1, M2, M3, M4, M5, M6, M7, M8, F23, F25, F27, F28, F41, F54, F61, F62, and F68; distributions then sampled 5000 times using the Latin hypercube strategy implemented with Crystal Ball® version 3.01 Monte Carlo simulator software (added into MS-Excel® version 5). Uncertainty in mass, flux, and residence time estimates were then expressed in terms of the standard error of the mean (S.E.).

Results and discussion

Results for reservoir masses and residence times are summarized in Table 3 and those for flux rates in Table 4. Percentage contributions by each flux to the total flux for each reservoir and differences in flux contributions to each reservoir estimated for pre-industrial versus currrent conditions are detailed in Table 5.

Based on a comparison of the pre-industrial and current contributions as shown in Table 5, human industrial activities have had no or only minimal effects on the sedimentary mass (M1), land biota (M3), oceanic biota (M4), and igneous/granitic mass (M6) reservoirs, their associated fluxes and residence times. Current direct anthropogenic releases (F92) to surficial soils constitute only a small fraction (6.07% $\pm$ 0.004 mean standard error (S.E.)) of total vanadium loading to the land reservoir (M2). Deposition (F82) of vanadium in fallout from the atmosphere constitutes an even smaller fraction (3.60 $\pm$ 0.03%) of total current loading. Comparison of current and pre-industrial results suggests that anthropogenic sources contribute only 1.00% $\pm$ 0.03 S.E. to current loading, as opposed to $\approx$2.5% from natural (continental and volcanic dust) sources.

Direct anthropogenic releases (F95) constitute only a small fraction (4.83% $\pm$ 0.06 S.E.) of total vanadium loading to the oceanic dissolved reservoir (M5). Additional contributions (F75) from the particulate reservoir, through desorption of vanadium adhering to particles resulting from atmospheric

Table 3. Mean and mean standard error of masses and residence times for each reservoir estimated by the pre-industrial and current models.

Reservoir	Mean mass (kg $\pm$ 1 S.E.)	Pre-industrial model Mean residence time (years $\pm$ 1 S.E.)	Current model Mean residence time (years $\pm$ 1 S.E.)
Sedimentary mass (M1)	$1.24 \times 10^{17} \pm 8.58 \times 10^{14}$	$3.43 \times 10^{7} \pm 2.91 \times 10^{5}$	$3.36 \times 10^{7} \pm 2.89 \times 10^{5}$
Land (M2)	$2.29 \times 10^{13} \pm 8.77 \times 10^{10}$	$1.15 \times 10^{4} \pm 1.70 \times 10^{2}$	$1.14 \times 10^{4} \pm 1.66 \times 10^{2}$
Land biota (M3)	$6.87 \times 10^{9} \pm 5.71 \times 10^{7}$	44.90 ± 0.61	45.10 ± 0.63
Oceanic biota (M4)	$1.50 \times 10^{7} \pm 9.13 \times 10^{4}$	0.07 ± 0.001	0.07 ± 0.001
Oceanic dissolved (M5)	$2.40 \times 10^{12} \pm 6.21 \times 10^{9}$	$1.07 \times 10^{4} \pm 1.44 \times 10^{2}$	$1.01 \times 10^{4} \pm 1.26 \times 10^{2}$
Igneous/granitic mass (M6)	$8.67 \times 10^{17} \pm 4.45 \times 10^{15}$	$2.39 \times 10^{8} \pm 1.67 \times 10^{6}$	$2.50 \times 10^{8} \pm 1.79 \times 10^{6}$
Oceanic particulate (M7)	$1.71 \times 10^{10} \pm 1.88 \times 10^{8}$	9.80 ± 0.20	9.25 ± 0.17
Atmosphere (M8)	$2.81 \times 10^{6} \pm 2.80 \times 10^{4}$	$1.39 \times 10^{-2} \pm 2.07 \times 10^{-4}$	$9.53 \times 10^{-3} \pm 1.20 \times 10^{-4}$

Table 4. Mean and mean standard error of flux rates estimated by the pre-industrial and current models.

Flux	Pre-Industrial model Mean flux rate (kg/year ± 1 S.E.)	Current model Mean flux rate (kg/year ± 1 S.E.)
Sedimentary mass ⇒ igneous/granitic mass (F16)	$3.70 \times 10^{9} \pm 1.71 \times 10^{7}$	$3.55 \times 10^{9} \pm 1.71 \times 10^{7}$
Sedimentary mass ⇒ human activity (F19)	0.00	Table 2
Land ⇒ land biota (F23)	$1.70 \times 10^{8} \pm 1.61 \times 10^{6}$	$1.70 \times 10^{8} \pm 1.61 \times 10^{6}$
Land ⇒ oceanic dissolved (F25)	$3.60 \times 10^{7} \pm 7.31 \times 10^{4}$	$3.60 \times 10^{7} \pm 7.31 \times 10^{4}$
Land ⇒ oceanic particulate (F27)	$2.00 \times 10^{9} \pm 2.72 \times 10^{7}$	$2.00 \times 10^{9} \pm 2.72 \times 10^{7}$
Land ⇒ atmosphere (F28)	$1.53 \times 10^{8} \pm 1.87 \times 10^{6}$	$1.52 \times 10^{8} \pm 1.87 \times 10^{6}$
Land biota ⇒ land (F32)	$1.70 \times 10^{8} \pm 1.61 \times 10^{6}$	$1.70 \times 10^{8} \pm 1.61 \times 10^{6}$
Oceanic biota ⇒ sedimentary mass (F41)	$5.19 \times 10^{6} \pm 8.79 \times 10^{4}$	$5.19 \times 10^{6} \pm 8.79 \times 10^{4}$
Oceanic biota ⇒ oceanic dissolved (F45)	$2.24 \times 10^{8} \pm 2.83 \times 10^{6}$	$2.24 \times 10^{8} \pm 2.82 \times 10^{6}$
Oceanic dissolved ⇒ sedimentary mass (F51)	$2.85 \times 10^{7} \pm 2.15 \times 10^{-3}$	$4.01 \times 10^{7} \pm 2.87 \times 10^{-3}$
Oceanic dissolved ⇒ oceanic biota (F54)	$2.29 \times 10^{8} \pm 2.82 \times 10^{6}$	$2.29 \times 10^{8} \pm 2.82 \times 10^{6}$
Igneous/granitic mass ⇒ sedimentary mass (F61)	$1.36 \times 10^{9} \times 1.71 \times 10^{7}$	$1.35 \times 10^{9} \pm 1.71 \times 10^{7}$
Igneous/granitic mass ⇒ land (F62)	$2.27 \times 10^{9} \pm 1.50 \times 10^{-1}$	2.10×10^{9}
Igneous/granitic mass ⇒ atmosphere (F68)	$7.10 \times 10^{7} \pm 9.32 \times 10^{5}$	$7.10 \times 10^{7} \pm 9.32 \times 10^{5}$
Igneous/granitic mass ⇒ human activity (F69)	0.00	Table 2
Oceanic particulate ⇒ sedimentary mass (F71)	$2.16 \times 10^{9} \pm 2.72 \times 10^{7}$	$2.22 \times 10^{9} \pm 2.72 \times 10^{7}$
Oceanic particulate ⇒ oceanic dissolved (F75)	$1.58 \times 10^{5} \pm 1.47 \times 10^{3}$	$2.19 \times 10^{5} \pm 1.43 \times 10^{3}$
Atmosphere ⇒ land (F82)	$6.53 \times 10^{7} \pm 6.06 \times 10^{5}$	$9.04 \times 10^{7} \pm 5.98 \times 10^{5}$
Atmosphere ⇒ oceanic particulate (F87)	$1.58 \times 10^{8} \pm 1.47 \times 10^{6}$	$2.19 \times 10^{8} \pm 1.45 \times 10^{6}$
Human activity ⇒ land (F92)	0.00	Table 2
Human activity ⇒ oceanic dissolved (F95)	0.00	Table 2
Human activity ⇒ atmosphere (F98)	0.00	Table 2

Table 5. Mean and mean standard error for percentage contributions to total flux by each flux and percentage differences (current minus pre-industrial model results) in contributions to each reservoir.

Reservoir	Contributions by fluxes in				Contribution by fluxes out			
	Flux	Pre-industrial (% ± 1 S.E.)	Current (% ± 1 S.E.)	Difference (% ± 1 S.E.)	Flux	Pre-industrial (% ± 1 S.E.)	Current (% × 1 S.E.)	Difference (% × 1 S.E.)
Sedimentary mass (M1)	F41	0.16 ± 0.005	0.16 ± 0.005	0	F16	100	94.04 ± 0.04	−5.96 ± 0.02
	F51	0.88 ± 0.01	1.22 ± 0.02	0.34 ± 0.02	F19	0	5.96 ± 0.04	5.96 ± 0.02
	F61	39.05 ± 0.63	38.14 ± 0.60	−0.91 ± 0.63				
	F71	59.90 ± 0.64	60.49 ± 0.61	0.59 ± 0.63				
Land (M2)	F32	6.78	6.78	0	F23	8.49 ± 0.21	8.41 ± 0.20	0.08 ± 0.19
	F62	90.68 ± 0.09	83.60 ± 0.08	−7.75 ± 0.08	F25	1.80 ± 0.04	1.80 ± 0.04	0
	F82	2.60 ± 0.03	3.60 ± 0.03	1.00 ± 0.03	F27	82.26 ± 0.39	82.27 ± 0.38	0.01 ± 0.37
	F92	0	6.07 ± 0.004	6.07 ± 0.004	F28	7.45 ± 0.19	7.52 ± 0.20	0.07 ± 0.19
Land biota (M3)	F23	100	100	0	F32	100	100	0
Oceanic biota (M4)	F54	100	100	0	F41	2.75 ± 0.09	2.69 ± 0.09	−0.06 ± 0.09
					F45	97.25 ± 0.09	97.31 ± 0.09	0.06 ± 0.09
Oceanic dissolved (M5)	F25	15.88 ± 0.29	14.99 ± 0.26	−0.89 ± 0.28	F51	12.74 ± 0.24	16.94 ± 0.29	4.20 ± 0.27
	F45	84.05 ± 0.29	80.08 ± 0.34	−3.97 ± 0.32	F54	87.26 ± 0.24	83.06 ± 0.29	−4.20 ± 0.27
	F75	0.07 ± 0.002	0.09 ± 0.002	0.02 ± 0.002				
	F95	0	4.83 ± 0.06	4.83 ± 0.06				
Igneous/granitic mass (M6)	F16	100	100	0	F61	35.22 ± 0.43	36.65 ± 0.44	1.43 ± 0.45
					F62	62.83 ± 0.42	60.46 ± 0.43	−2.37 ± 0.43
					F68	1.96 ± 0.04	2.03 ± 0.04	0.07 ± 0.04
					F69	0	0.86 ± 0.004	0.86 ± 0.004
Oceanic particulate (M7)	F27	91.11 ± 0.23	88.13 ± 0.28	−2.98 ± 0.24	F71	99.99	99.99	0
	F87	8.89 ± 0.23	11.87 ± 0.28	2.98 ± 0.24	F75	0.01	0.01	0
Atmosphere (M8)	F28	67.09 ± 0.58	47.74 ± 0.52	−19.35 ± 0.57	F82	29.20	29.20	0
	F68	32.91 ± 0.58	23.15 ± 0.41	−9.76 ± 0.52	F87	70.80	70.80	0
	F98	0	29.16 ± 0.21	29.16 ± 0.21				
Human activity (M9)	F19	0	88.00	88.00	F92	0	60.96	60.96
	F69	0	12.00	12.00	F95	0	4.64	4.64
					F98	0	34.40	34.40

deposition, are of minimal (0.02% $\pm$ 0.002 S.E.) significance to total vanadium loading to this reservoir, with inputs from natural sources (F25 and F45) contributing >94%. Anthropogenic inputs have increased cycling in this reservoir by about 5%, as indicated by a $\approx$600 yr (from 1.07×10^4 yr pre-industrial to 1.01×10^4 yr current) reduction in residence time. However, this very long (>10,000 yr) residence time suggests that much of the vanadium in solution in seawater is either not available to, or not required by, a majority of biologic or sedimentary processes.

Deposition (F87) of vanadium in fallout from the atmosphere constitutes a small fraction (11.87% $\pm$ 0.28 S.E.) of total current loading to the oceanic particulate (M7) reservoir. Comparison of current and pre-industrial results shows that anthropogenic sources contribute only 2.98% $\pm$ 0.24 S.E. to current loading. The terrigenous suspended load of rivers (F27) contributes the majority ($\approx$88%) of particulate-bound vanadium to the world ocean. Anthropogenic inputs have minimally enhanced cycling in this reservoir, as indicated by a $\approx$0.2 yr (from 9.80 yr $\pm$ 0.20 SE pre-industrial to 9.53 yr $\pm$ 0.17 SE current) reduction in residence time.

The impact of anthropogenic releases are most notable in the atmosphere (M8) reservoir. Comparison of current and pre-industrial results indicates that anthropogenic sources (F98) contribute 29.16% $\pm$ 0.21 S.E. of total atmospheric vanadium loading, overshadowing contributions (23.15 $\pm$ 0.41%) from volcanogenic sources (F68) but considerably less than those (47.74% $\pm$ 0.52 S.E.) from continental dust sources (F28). The extremely short current atmospheric vanadium residence time (9.53×10^{-3} yr) and very low concentrations of vanadium in air samples taken at the South Pole (Zoller et al. 1974) argue against an assumption of uniform global distribution of all vanadium injected (Chester & Stoner 1974; Hoffman et al. 1972). Direct impacts to human or ecological health from fallout of anthropogenic vanadium are therefore more likely to occur in the vicinity of emission sources (NAS 1974; Sugimae & Hasegawa 1973), and be most apparent on a local, rather than a global, scale.

In summary, the differences noted between the pre-industrial and current models were not sufficiently large, given the uncertainties inherent in estimates of masses and fluxes on a global scale, to suggest that injection of anthropogenic vanadium constitutes a significant environmental threat on a global scale. It is entirely possible, however, that given a more restricted geographic area and a specific set of unfavorable circumstances, vanadium could create an adverse environmental impact.

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