Vanadium in the Environment

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PREFACE

There is general agreement internationally on a priority list of chemical substances which at present constitute the main potential risks when released into the environment. In nearly every instance, this knowledge has come from actual experiences, where harm to wildlife, crops or livestock and in some cases to man himself, has ensued from uncontrolled chemical usage.

It goes without saying that it would be much more satisfactory if we did not have to wait for such harmful events to appear before we could identify potentially toxic chemicals. It is obvious that a continual reviewing and updating of our knowledge of a whole range of chemicals would be prudent in order to identify beforehand the likelihood of meeting again the kind of problems encountered from using certain organochlorine pesticides and heavy metals.

Any chemical that tends to be biochemically active, especially to the point of toxicity, is suspect, and a candidate for careful scrutiny, particularly if it is also bioaccumulative, and in addition mobile, persistent and increasingly released in the biosphere. It is for reasons such as these that several expert groups have somewhat tentatively added the element vanadium to their priority lists. There is in fact no history of overt vanadium problems but at the same time there is an absence of any thorough reviews of the behaviour of vanadium in the environment. However, there is recent evidence that vanadium from fuel burning, deposited from the atmosphere in trace amounts, appears to be a powerful inhibitor of soil enzyme activity, thus reducing the mineralization processes which release plant nutrients.

The above considerations have led to the present Technical Report which describes current knowledge about vanadium and its behaviour in the environment. The Report draws attention to the gaps in present knowledge and also helps to characterize which variables it will in future be most informative to monitor. Although vanadium cannot at present be regarded as posing anything like the potential hazard of certain other elements, notably cadmium, lead and mercury, the Report clearly indicates that vanadium should be regularly reviewed as a potential priority chemical.

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1.0 Introduction
The purpose of this paper is to review the published literature on vanadium insofar as it relates to environmental problems. A summary is given of vanadium concentrations in soil, water, air, fossil fuels and biological materials. This is followed by a discussion of biological functions and toxicity of vanadium. Finally, an estimate of the biogeochemical cycle for vanadium is given in Figure 1, and the need for further research studies is emphasized.

2.0 Chemistry, general occurrence and commercial use of vanadium
Vanadium, atomic number 23, molecular weight 50.94, is a metallic element, naturally present in the earth's crust at a mean concentration of ca. 100ppm. At least fifty different minerals are known to contain vanadium. The most economically important sources are carnotite, roscoelite, vanadinite and patronite. Substantial amounts of vanadium are also present in certain crude oils while commercial production from petroleum ash is of some importance. The element is also found in phosphate rocks, in certain iron ores and in oil shales.

Vanadium can exist in four different oxidation states, *i.e.*, 2, 3, 4 and 5. Its tendency to form various oxoanions is a property which it has in common with molybdenum, tungsten, arsenic and phosphorous. In nature it is known to exist as vanadates of varying composition as well as in organically complexed forms. Metallic vanadium of any degree of purity was not produced until the 1920's. It has a high melting point, 1890°C, and is used to produce steel alloys for making rust-resistant springs and high-speed tools. Information on the total world production of vanadium is inadequate. Vanadium is also of importance (as the pentoxide) as a catalyst in several chemical processes and is used in ceramics and in dyes and paints.

3.0 Concentrations of vanadium in the environment
The following survey of vanadium concentrations in environmental material is based on figures from the literature given in the accompanying tables. In some cases, secondary statements in literature surveys have been used.

As is the case with several other minor elements and trace substances in environmental samples, different analytical methods do not produce quite comparable results at very low concentrations of the element. Therefore, data given in the tables should be interpreted with great care. As no thorough comparative evaluation of the reliabil-

ity of various analytical methods for the low concentrations of vanadium is available, data obtained by any one particular method have largely not been considered too unreliable for inclusion. Many different techniques have been used for determining vanadium concentrations in environmental samples. In older work, colorimetric, spectrometric and spectrographic methods dominate; in more recent work, atomic absorption spectrophotometry (ASS, often using a graphite furnace) and neutron activation analysis are used more commonly.

Although the data included in the tables below should be regarded as examples of concentrations encountered in environmental samples, their representativeness cannot always be guaranteed. But in certain environmental media, available data are scanty and when included they have had to be accepted at face value. Vanadium levels in certain environmental media, *e.g.* in water and air, have been in the forefront of investigations in recent years, whereas most vanadium data for plants and animals date back to the 1930's and 1940's. The reasons for biological data being scanty in recent years are probably the low sensitivity of the AAS flame method and the fact that vanadium has been considered a less "interesting" element in environmental studies than *e.g.,* lead, cadmium and mercury. However, rapid increase of the amounts of high-vanadium fossil fuels being burned during the last decades and the resulting high concentrations of the element in urban industrial air are motivating research on vanadium in biological material. In addition, vanadium is now recognized as metabolically essential in certain instances. In particular, its properties of influencing certain enzyme systems, its capability of accepting electrons biochemically as well as its environmental persistence all confer upon it the status of a biologically active element.

3.1 Concentrations in soil, water and air

The concentration of vanadium in bedrock is usually fairly high; ca. 125 ppm is considered the mean for the earth's crust, ca. 140 ppm for the earth's interior (11, 34, 35). Figures stated for soils are usually somewhat lower (6, 24, 72), probably because more vanadium may be leached in weathering of the minerals than occurs with silica, iron and aluminium. Podsols in the U.S.S.R. were found to be lower in total vanadium than tundra and chernozem soil profiles (72). The biological availability of soil vanadium is poorly understood. A few organisms have been found which make vanadium soluble and take it up very easily, but most plants take up very little, considering the compara-

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tively high total concentration in soils. Soil organic matter is usually low in vanadium. Purely organic mor in the coniferous woodland of central Sweden has a total concentration of only 4-11 ppm (70) and it is not likely that this level represents a wholly unpolluted condition.

Soils of urban and industrial areas are usually higher in vanadium. Topsoils from the vicinity of highways may contain three to four times as much vanadium as comparable soils from sites without local sources of pollution (24) and urban topsoils are probably most often higher in vanadium than rural soils but available data on this point are still rather few. Soils from the vicinity of metallurgical industry may contain several hundred parts per million (ppm) of vanadium, in some cases probably even more. However, the scantiness of available data in this field makes evaluations of the frequency and degree of soil pollution difficult.

A great deal of information is available on vanadium in water, particularly drinking water (19, 54) and sea water (34, 39). Data given in the literature are, however, very variable and seem to represent not only real differences but also differences in the accuracy of various analytical methods.

It appears reasonable to regard vanadium concentrations of 0.1-1 ppb (ng/g) as a normal range in present-day freshwater, and concentrations above 2 ppb as representing a polluted state or as indicating a specially high vanadium content in the bedrock of the catchment system. The figures for seawater are usually within the same order of magnitude as those given for freshwater. Concentrations of 0.1-0.3 ppb are reported from the open sea, 0.5-2 ppb from coastal areas of industrialized countries. Even higher concentrations may be found in littoral surface waters near polluting industry.

The vanadium concentration in the air, especially urban air, is rather well documented by many recent studies. According to recent reports (76), the concentration of vanadium in the air at the South Pole *i.e.,* far away from continents and human sources of pollution, is as low as 0.001-0.002 ng/m³. Concentrations in ocean air of the middle latitudes is about two orders of magnitude higher (22, 32) and non-urban continental air two to three orders of magnitude higher (75) than the air of the South Pole. A concentration of 0.5-2 ng/m³ is a reasonable estimate of the average for continental air far from urban areas.

Higher (sometimes much higher) concentrations are characteristic of urban air, particularly in the winter half of the year in areas with a cold climate (28, 31, 38, 63, 73, 75). Figures as high as 2000 ng/m³ have

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been reported from several cities in north-eastern U.S.A., *i.e.*, a vanadium concentration at least one million times higher than was measured in south polar air. Annual means of ≥100 ng/m³ have been calculated for certain cities. Concentrations tend to be lower in cities with warmer climates than in comparable cities with colder climates. For Los Angeles, 2.2-28 ng/m³ has been reported, and for San Francisco, 1.5-11 ng/m³. There is a close relationship between vanadium in the air and the estimated combustion of oil for domestic heating and other purposes, per unit of time and unit of area.

As regards the concentration of vanadium in air particulates, figures for the lower troposphere of various ocean areas do not usually deviate much from the concentrations found in mineral soils. Only in coastal areas adjacent to densely inhabited and industrialized land are particulate concentrations much higher, 300-400 ppm, reflecting the polluting influence of human activity (11).

3.2 Concentrations in fossil fuels

One of the main sources of anthropogenic vanadium in the environment is fossil fuel, mainly certain types of fuel oils. Crude oils, particularly those from Venezuela, may contain hundreds of ppm and figures as high as 1400 ppm have been reported (1, 12, 34, 41, 59). This means that vanadium constitutes a major inorganic component of these oils. However, there are also many types of crude oil which are very low in vanadium (<1 ppm has been measured in several types of different origin) but most types fall within the concentration range of 10-100 ppm.

High vanadium concentrations are also found in certain types of coal and lignite; 50-200 ppm have been reported from several areas in the world (34). In most cases concentrations are lower but sometimes high enough to be of importance as a source of pollution.

The great variability of the vanadium content of fossil fuels probably reflects differences in biological origin. It is quite probable that ascidians (sea-squirts), known to be very high in vanadium (cf. concentration in animals below), were important constitutents of the organic matter out of which the high-vanadium oils were generated. However, the vanadium content of some terrestrial coals is more difficult to explain, as most plants nowadays probably are very low in this element. The possibility exists that certain species of the carboniferous floras were vanadium accumulators.

3.3 Concentrations in plants

In spite of the comparatively high content of total vanadium in soils, vascular plants are not known to absorb the element to any greater degree. However, rather few detailed analyses of vanadium concentrations in plants from natural soils are available in the literature (6, 37, 56, 62). The average concentration in plants from unpolluted sites can be estimated to fall within the range of 0.5-2 ppm dry weight. Both higher and lower concentrations have been reported for several species or plant tissues. Concentrations in vegetable crops often seem to be lower than 0.5 ppm but the variability of data is great and fresh weight is often used as the basis of calculation, which makes comparisons difficult. The concentrations in fungi are usually on the same general level as in vascular plants; as a mean of several genera of basidiomycetes, 0.66 ppm dry weight was reported (6). One case of specific bioaccumulation in fungi is known: *Amanita muscaria* has proved to accumulate as much as 61-181 ppm dry weight (6). The general validity of this observation geographically has probably not been tested. In algae, high figures have also been reported but only from polluted waters. The vanadium concentration in macroscopic species is usually similar to that in vascular plants (5).

Mosses are known to accumulate metals easily from dry and wet deposition. *Hypnum cupressiforme* samples from forest areas in south-central Sweden and from the outer archipelago of Stockholm have a vanadium concentration of ca. 10 ppm, much higher than common vascular species from similar sites (50, 68). In city areas of Sweden, 50-250 ppm are the present-day concentrations in mosses (50, 68); and still higher levels are sometimes encountered in areas with iron and ferro-alloy industry or in the vicinity of large, oil-fired power stations.

3.4 Concentrations in animal and human tissues

Comparatively good information is available on vanadium in animals. The early discovery of the bioaccumulation of vanadium by some species of the marine tunicates has led to a search for accumulators in other animal groups that has been unsuccessful so far. However, certain tunicates, particularly species of the families Ascidiidae and Cionidae, proved to be outstanding accumulators of vanadium with body concentrations often exceeding 1000 ppm dry weight (6, 65). The element is concentrated in blood vanadocytes, which are sites of the respiratory functions of these animals.

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In most invertebrates studied so far, vanadium concentrations of 0.5-2 ppm dry weight seem to be the rule (6). Many insects are very low in vanadium — in the honey bee a mean of 0.16 ppm dry weight is reported. The body concentration in vertebrates is also very low, often only 0.1-0.2 ppm dry weight or sometimes even less (6). In mammals (including man), considerable differences have been measured between various organs but any distinct accumulation pattern of general validity is difficult to ascertain. Maxima may be recorded in the liver, kidney, lung or spleen (47, 56). High vanadium concentrations, a mean of 3.2 ppm dry weight, have been recorded in the lungs of coal miners and workers in vanadium industry (64). The total body burden of human adults is reported to be 17-43 mg, which corresponds to an approximate mean of 0.4 ppm wet weight (56, 57). The mean daily intake is 1.1-1.2 mg; according to other studies 0.4-0.6 mg (55, 56). An excretion rate of 0.2-0.3 mg/day has been reported.

4.0 Biological function and toxicity

Vanadium is, as far as we know, an essential element for some, but not for all, organisms. Thus, it is worth noting (Annex 2), that some kind of requirement or stimulatory influence of vanadium is rather well documented in organisms as different as bacteria, algae, vascular plants, tunicates and vertebrates. Much work has been performed on the role of vanadium in biological nitrogen fixation. It has been demonstrated by many studies that vanadium is able, or partly able, to replace molybdenum as the activator of nitrogenase in *Azotobacter* and *Clostridium butyricum* (7, 8, 9, 10, 23, 26, 33). Additionally, in the blue-green alga *Anabaena circinalis* a stimulation of the nitrogen fixation has been demonstrated at low concentrations of vanadium in the medium (52). However, several of these studies on the role of vanadium in nitrogen fixation have shown that molybdenum is often a better activator than vanadium. An elevated level of vanadium may in certain instances actually decrease the fixation rate, probably by competing with molybdenum. The problem is of great ecological significance, as the vanadium : molybdenum ratio of soils must be considered to increase due to pollution from human activity.

It is possible but far from certain that vanadium at low levels stimulates growth in algae. Concentrations to an upper limit of 100 ppm in solution may increase the growth rate in *Scenedesmus obliquus* (2). However, high concentrations have proved toxic to both bacteria and algae (2, 52). Acid phosphatases of conifer forest soil, probably mainly

of fungal origin, are significantly inhibited (20-30%) by addition to the soil of V_2O_5, $VOSO_4$, $NaVO_3$ or Na_3VO_4 at a rate of 50-100 ppm as vanadium of the dry weight of the soil (71).

Low concentrations of vanadium seem to be able to stimulate growth and increase the yield in various kinds of vascular plants (7, 53). However, the dose is often critical and higher concentrations may cause development disturbances and may decrease the yield. The nitrogen metabolism of the plant is easily affected due to inhibition of nitrate reductase. The activity of this enzyme was completely inhibited by 100 μm $VOCl_2$ or $NaVO_3$ in cell free extracts of tomato leaves (9). This enzymatic effect may cause an accumulation of nitrate in the tissues, an undesirable consequence in crops. The biochemical changes induced in sugar beet by spraying the foliage of young plants with 0.01 M $VOSO_4$ solution have been studied closely (61). The growth of the leaves was markedly retarded though the net CO_2 assimilation rate increased. The activity of nitrate reductase, phosphatase, glutamic-pyruvic transaminase and invertase was partly inhibited, whereas the activity of "sucrose synthetase" increased. This resulted in a higher content of sucrose and nitrate in the storage root, but in a lower content of reducing sugar, amino acids and protein. This metabolic change was probably favourable to the economic production of sugar but would probably not have favoured the survival of the plant in a natural site, *i.e.,* under non-agricultural conditions.

The biological function of vanadium in invertebrate animals is little studied and understood, except in the case of tunicates. It was mentioned above that certain groups of tunicates accumulate vanadium to high concentrations. The site of accumulation is the vanadocytes of the blood, where the element is concentrated as haemovanadium and evidently exerts a function not identical but in several respects similar to that of iron in the erythrocytes of the blood of other animal groups (37). It is interesting that many tunicates are high in iron but very low in vanadium and, conversely, that some vanadium is usually present in erythrocytes of vertebrates studied. Considering these findings, the biochemical adjustment to vanadium instead of iron seems less surprising but it is still a question how these animals can find enough vanadium in their surroundings for such intensive accumulation.

In addition to this, in many — perhaps in all — vertebrates, small amounts of vanadium are favourable or even essential for normal development. Vanadium deficiency in domestic fowls causes abnormal bone development, body growth reduction and reduced growth

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of wing and tail feathers (74). In rats, vanadium deficient food reduces growth rate, increases the iron content of blood and bone tissue, induces abnormal bone development, impairs the reproduction and evokes a high blood cholesterol level (49). The minimum demand of vanadium for a normal development in rat is reported as 1-2 μg per day and 0.25 ppm in the food is considered optimal for growth, although 20-30 ppm $NaVO_3$ in the food can be tolerated without severe damage (35, 57). Even higher concentrations may be tolerated, if the diet is rich in casein, which evidently counteracts vanadium toxicity. Prolonged exposure to vanadium in the air is reported to increase mortality from heart diseases and certain forms of cancer in rats and mice (18).

A need for vanadium for the normal development of man has not been clearly documented but is probable (42). That modern civilized man is suffering from vanadium deficiency is, however, improbable. On the contrary, many cases of vanadium poisoning have been described, mainly of workers in the vanadium industry. Symptoms reported are nervous depressions, cough due to bronchial spasm, vomiting, diarrhoea and anaemia. Death may follow in serious cases after paralysis of the respiratory organs (37, 67). Most cases of poisoning have been caused by high concentrations of vanadium, *e.g.,* vanadium pentoxide, in the air. Biochemical reasons for the toxicity in man (as in other vertebrates) are the inhibiting effects of vanadium on certain enzymes, *e.g.,* on cholinesterase and amino-oxidase (3). Both cationic and anionic forms of vanadium are active but the anions are the more toxic. According to recent findings, vanadium influences the formation of dental caries in man but its function is neither obvious nor clearly understood (49).

5.0 A tentative environmental flow chart for vanadium

As is evident from the preceding paragraphs, our knowledge of vanadium concentrations in the environment is still scanty. The total amounts present in the soil may be stated with a fair degree of accuracy, but we know very little of how much of this is actually biologically available. The amounts of vanadium present in other main compartments of the global environment can only be stated with an accuracy of about one order of magnitude, which is insufficient as a reliable base for monitoring and control of environmental pollution. More research is needed which takes into consideration the problem of representative sampling as well as the analytical problem. At pres-

ent, the lack of data which can be used in an environmental model is obvious.

A tentative environmental flow chart for vanadium is shown in Figure 1. The main pathways and compartments are indicated and, wherever possible, rough estimates are given of the amounts of vanadium present in the compartments and the annual exchange between them. In many instances it has not been possible to give any values. It seems, as for most other elements, that the ocean floor is the main long-term sink of vanadium in the global circulation, the annual input to the oceans being about 10^6t* contained in sediment particles and about 10^5t in more or less water-soluble forms. For the input of vanadium to the atmosphere due to human activity (mainly from fossil fuels), 10^5t/yr is the estimated order of magnitude, similar to the estimated amount annually circulated by organisms.

*t=metric ton

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RIVERS & LAKES
10^5 - 10^6 t

RELEASE

UPTAKE

LEACHING

EROSION

SEDIMENT TRANSPORT 10^6 t/yr

SALT TRANSPORT 10^4 t/yr

RELEASE

ORGANISMS 10^6 t

RELEASE
10^5 t/yr

RELEASE

UPTAKE
10^5 t/yr

UPTAKE

SOIL* 2×10^{10} t

ORES &
FOSSIL FUELS
10^8 t

WATER POLLUTION

DRY & WET
DEPOSITION

OCEAN 10^8 - 10^9 t
(water soluble)

SEDIMENTATION

MARINE SEDIMENTS
?

RELEASE?

INHALATION OR DIRECT SORPTION

DRY & WET DEPOSITION 0·5-1x10^5 t/yr

WIND EROSION

HUMAN
ACTIVITY

AIR
POLLUTION
10^5 t/yr

SPRAY

DRY & WET DEPOSITION 0·5 – 1 x 10^5 t/yr
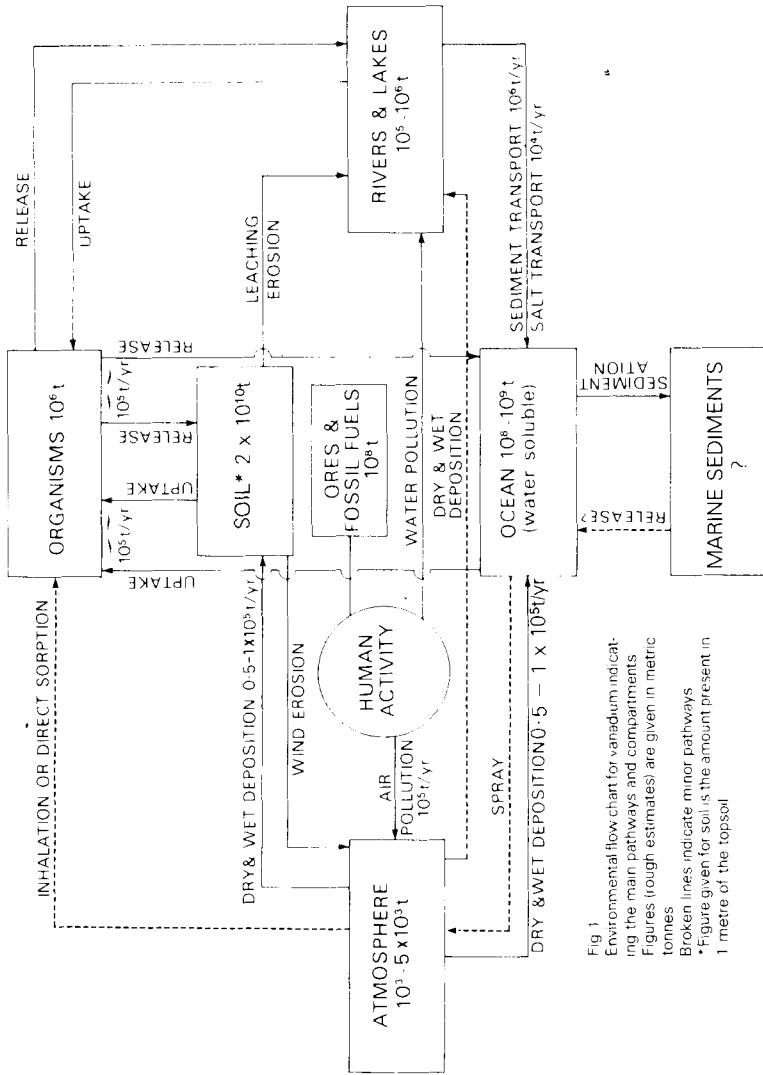
ATMOSPHERE
10^3 - 5×10^3 t

Fig 1
Environmental flow chart for vanadium indicat-
ing the main pathways and compartments
Figures (rough estimates) are given in metric
tonnes
Broken lines indicate minor pathways
*Figure given for soil is the amount present in
1 metre of the topsoil

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6.0 Conclusions

Vanadium is a biologically active element, the role of which is only partly understood. It intervenes and sometimes interferes in the biological fixation of nitrogen, which is of supreme importance to the productivity of ecosystems. In low concentrations it promotes growth and development of plants and animals belonging to many different groups and it is probably an essential micronutrient in many organisms. A requirement for vanadium in large amounts has been documented only in certain forms of the marine tunicates, where it replaces iron in the blood pigment. Otherwise, most organisms exposed to high levels of vanadium display poisoning symptoms. Severe poisoning leads to death or to irreversible damage. The inhibition of several enzymatic functions is a general property of many chemical forms of the element and a main reason why it is biologically active.

Many types of fossil fuels, particularly fuel oils, have high concentrations of vanadium. The increased combustion of oil in recent decades has, in all probability, increased the deposition rate, hence the degree of vanadium pollution in most inhabited parts of the world. The documentation is still very scanty, but the concentration of vanadium in city air may be several orders of magnitude greater than in the countryside.

Considering this, we should be aware of the possible risks for man and the environment of an increasing degree of vanadium exposure, particularly any long-term effects on natural or agricultural productivity which may result from reduced mineralization rates in the soil.

More research is needed both on concentrations encountered in polluted and "unpolluted" environments and on biological effects of vanadium.

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ANNEX I

Table 1, Vanadium concentrations in soils

Reference	Type of soil	Analytical Method	Conc. ppm dry wt. (total V)			Comment
72	Tundra soil		110	110	95	USSR, A, B and C-horizon, resp. (n=3)
	Podsol		83	65	50	''
	Chernozem		140	94	88	''
	Forest soil		69	70	80	''
14	Surface soil polluted by flyash		30-429			USSR
6 (survey)	Surface soils (0-20 cm)	AAS	(3.1-68) 22.5			Various locations, probably not total vanadium
24			15	9	11	Toronto, Canada, rural site, 0-½, 2-3 and 5-6 inch depth, resp., mean of 6 profiles
			56	33	33	Same as above but close to highway

34, 11	Upper 16 km of the earth's crust.		117 (25-200)	mean (and range) from 11 different sources
35	Earth's crust		135	
	Earth's interior		140	
70	Spruce mor, purely organic topsoil	AAS	4-11	South-Central Sweden, Conifer forest area
51	''	AAS	40-80 7-10	Vicinity of metal alloy industry, Sweden, and "background" area, resp.

Table 2, Vanadium concentrations in water

Reference	Water type	Analytical Method	Conc. ppb (ng/g)	Comment
34 (survey)	Freshwater, rivers		ca 1 0.-1.1 ca 8 20	Japanese rivers USSR, Ob Brook in metalliferous area Seine, Paris
74	Freshwater, rivers	Mass spectroscopy	0.3-7.1	Tributary to Lake Michigan Varying degrees of eutrophication (n=30)
55 (survey)	Drinking water	Colorimetric	0.0-0.8	Switzerland
	"	"	0.0-6.6	Poland
	"	Neutron activation	0.50 0.11	Stockholm, Sweden Boston, USA
	"	Spectrochemical	3-9	Wyoming, USA
19	"	Emission spectroscopy	<5	100 largest cities in USA

Ref	Sample	Method	Concentration	Location
39	Seawater		0.52-0.71	Italian Coast
34 (survey)	"	AAS, graphite furnace	<0.3 0.24-7	in general "
	"		1.8	Western Pacific; Japanese bays and coast water
	"		2.4-7	North Atlantic
	"		0.1-0.2	North Sea and North Atlantic
	"		0.2-0.3	North Sea
	"		1.8	Irish Sea, surface water
36	"		0.9	Pacific Ocean at Pasadena

Table 3, Vanadium concentrations in air

Reference	Type of air	Analytical method	Conc ng/m³	Comment
32, 22	Non-urban air	AAS	0.17±0.13	Pacific Ocean (n=9)
			0.16±0.11	
			0.34 (0.14-1.0)	Windward, Hawaii (n=9)
75	"		0.72 (0.21-1.9)	Canada (n=24)
76	"		0.0015±0.006	South Pole (n=10)
16	"	AAS and neutron activation	0.06-14	The Atlantic, 30°N (298°K, 1 atm) (n=13)
75 (survey)	Urban air		4.5 (1.2-16)	Niles, Michigan (n=25)
			12 (2.2-28)	Los Angeles (n=12)
			6.2 (1.5-11)	San Francisco (n=9)
			7.4 (5-18)	N/W Indiana (n=25)
			22 (2-120)	Chicago (n=22)
			800 (500-2000)	Buffalo, NY (=6)
			170 (90-320)	New York City (n=270)
			160 (70-230)	Boston
			600 (400-2000)	Boston (n=10)
			940 (89-2400)	Boston (n=10)

28	"	Neutron activation and gamma spectroscopy	21 (6-59)	Chilton, Milford Haven and Salford, England (winter)
73	"	Neutron activation	1.5-2.5	Karlsruhe, Germany (autumn)
31	"	Emission spectrography	60 140 90	Chicago, annual mean Philadelphia, annual mean Washington, annual mean
38	"	Neutron activation	490 (80-1320)	Cambridge, Mass., Sept. 1969; (n=11)
63	"	Emission spectrography	160 (50-550)	Cities in Japan 1969 (n=11)

Table 4, Vanadium concentrations in air particulates

Reference		Analytical method	Conc. ppm	Comment
11	Particulates of the lower troposphere	Spectrographic	80-386	Range: various marine areas of the world
			80	Southern Indian Ocean
			386	Inland Sea, Japan

Table 5, Vanadium concentrations in fossil fuels

Reference	Type of fuel	Analytical method	Conc. ppm	Comment
34 (survey)	**Coal**		740-980 (ash)	Niederschlesien
			1460-3360 (ash)	Italy
			32000 (ash)	Durham, England
			19	USSR, Donez
			<1-110 (ash)	Japan
			470 (ash)	Argentina
	Lignite		10-150	Sachsen
			20-160	USSR (Ukraine, Tataria)
			30	USSR (Tula)
29	**Oil** High sulfur oil		150	
1	Crude oils		Traces	Louisiana
			1.8	East Texas
			23 30	Kuwait, two places
			95 114	Iraq, Iran
			0.6 370 1400	Venezuela, three places
	Fuel oil	AAS	49	mean and range for
			(3-143)	24 samples of varying
				origin

Table 5, *contd.*

Reference	Type of fuel	Analytical method	Conc. ppm	Comment
59	Crude oils	Neutron activation	(4-168)	California,
			82	Libya (n=7)
			21	
34 (survey)	"Rock oil"		2.0-14.8% in the ash	Western USA
			171	Venezuela, mean of 44 tests
12	"Mineral oil"	Flameless AAS	227	Venezuela
			22	Middle East
			<0.2	Nigeria
41	"Petroleum"		262	Venezuela, 7 tests
			29	Middle East, 3 tests
			60	California, 7 tests

Table 6, Vanadium concentrations in plants

Reference	Plant group (species)	Analytical method	Conc. ppm dry wt.	Comment
5	**Algae** Fucus vesiculosus Ulva latissima	Col	0.79 2.4	France
6 (survey)	**Fungi** Species of Aspergillus, Russula, Lactarius, Cantarellus, Amanitopsis, Amanita, Amanitina	Col	0.66 0.15-2.4	mean range
7	Amanitina citrina Amanita muscaria	Col	0.06 116 61-181	mean; n=203 mean range
68	**Mosses** Hypnum cupressiforme	AAS	75-125 8-12	City of Norrköping, 110,000 inhab., Sweden; n=53 Forest area, south central Sweden; n=5

Table 6, *contd.*

Reference	Plant group (species)	Analytical method	Conc. ppm dry wt.	Comment
50	Hypnum cupressiforme, Bryum argenteum	AAS	100-260 25-100 8-20	City area of Stockholm, Sweden (n=100) Surburban area of Stockholm (n=80) Outer archipelago of Stockholm (n=20)
37	**Vascular plants** In general	—	Ca. 1	Typical concentration level
5 (survey)	Species of Leguminosae (beans, soya, lupin)	Col	2.5 0.2-12	mean total range
62	Species of Acer, Quercus, Taxus, Tsuga, Picea	AAS	Below detection in most samples	City of New Haven and rural Vermont
56 (survey)	Leaves of deciduous trees (9 species) Leaves of conifers Leaves of Berberis vulgaris Trifolium repens Medicago sativa		0.0-0.93 0.0-0.27 1.25 0.70 4.00	wet wt wet wt wet wt wet wt wet wt

Table 7, Vanadium concentrations in animals

Reference	Animal group (species)	Analytical method	Conc. ppm dry wt.	Comment
5 (survey)	**Invertebrates**			
	Porifera:			
	Ficulina		1.7	
	Coelenterata:			
	Anemonia		1.7	
	Echinodermata		2.3	3 species
			1.9	
	Bryozoa:			
	Plumatella		16.8	
	Annelida		1.2	2 species
	Mollusca		0.7	5 genera
	Arthropoda:			
	Apis		0.16	
	Carcinus		0.4	
	Tunicata:			
	Ascidiidae		740-6520	Ascidia, Phallusia
	Polyclinidae		0.0-8.3	7 species
	Pyuridae		0.0-7.1	4 species
	Cionidae		166-1300	Cionia intestinalis
65	Tunicata:	Spectrographical		
	Perophoridae		700-9000	California
	Diazonidae		1800	California
	Synoicidae		< 10	California

Table 7, *contd.*

Reference	Animal group (species)	Analytical method	Conc. ppm dry wt.	Comment
5 (survey)	**Vertebrates**			
	Fish		0.04-0.22	5 species
	Bufo bufo		0.20	
	Bird, pectoral muscle		0.03-0.04	2 species
	liver		0.02	1 species
	Dog, kidney		<0.02	
	pancreas		0.008	
	blood		0.086	
	liver		0.20	
	Mouse		<0.02	
	Rat		0.15	
56 (survey)	Rat, liver	Col	ca. 2.0 (0.39 net wt.)	Fed on diet containing 3.2 ppm. Calculated from wet weight
	Deer, kidney		ca. 8	
	liver		ca. 0.35	
	heart		ca. 0.5	
	hoof		ca. 3	
17	Domestic animals, teeth	Spectrographical	34 (ash wt)	

Table 8, Vanadium concentrations in human tissues

Reference	Type of tissue	Analytical method	Conc. ppm	Comment
13	Hair, children	Emmission spectography	0.20;0.40	New York City (n=264) Low and high degree of pollution, resp.
	Hair, adult		0.12;0.35	
64	Lung	Spectrographic	3.2 (dry wt.)	West Virginia coal miners (n=129)
			0.8 (dry wt.)	West Virginia non-miners (n=15)
47	Lung	Col	0.304 (wet wt.)	Germany
	Liver		0.162 (wet wt.)	
	Kidney		0.174 (wet wt.)	
	Blood		0.061 (wet wt.)	polluted environment
	Spleen		0.520 (wet wt.)	polluted environment
56, 57	Total body adult	—	0.23-0.57 (wet wt.)	Calculated from an estimated total body burden of 17-43 mg.

Table 9, Vanadium concentrations in human food

Reference	Type of food	Analytical method	Conc. ppm in edible parts	Comment
5	Cabbage, Spinach	Col	1.1-1.9	France, calculated on dry wt.
	Orange		0.4-1.1	
	Oats (whole grain)		0.35	
66	Fruits	neutron activation	0.0011-0.0086	Samples from USA, Sweden and Portugal
	Radish		0.056	
	Milk		$0.74\text{-}1.1 \times 10^{-4}$	wet wt.
	Fish and meat		$4\text{-}13 \times 10^{-4}$	wet wt.
	Gelatine		440×10^{-4}	wet wt.
	Lobster		430×10^{-4}	wet wt.
56	Milk and dairy products		0.0-0.62	USA calculated on wet wt.
	Fish and meat		0.0-2.25	
	Vegetables		0.0-1.49	
	Fruits		0.0-0.18	
	Grain and cereal		0.0-6.03	

Daily intake
Institutional diet
—

mg
1.17
0.41-0.57

56
54

ANNEX 2

Biological effects of Vanadium

Reference	Species	Comment
4, 8, 10, 23, 33 (and several others)	**Bacteria** Azobacter (different species, many strains)	Vanadium is able, or partly able, to replace molybdenum as a catalyst of the nitrogen fixation (activator of nitrogenase) Stimulates growth.
26, 9	Clostridium butyricum (five strains)	Is able to replace molybdenum as a catalyst of the nitrogen fixation.
21	Salmonella gallinarum (chicken)	Is able to reduce growth rate
52	**Algae** Anabaena circinalis	0.5 ppm in the medium increased nitrogen fixation, 1.0 ppm decreased it.
2	Scenedesmus obliquus	Initial growth rates increased when V was added (upper limit 100 μg per L)

Ref.	Material	Effect
70, 71	**Soil enzymes** Acid phosphatase probably fungal origin	The activity in mor soil is partly inhibited by addition of V_2O_5, $VOSO_4$, $NaVO_3$ or Na_3VO_4, but not by Na_2SO_4
7	**Vascular plants** Beet	Some increase in yield is obtained on adding V to soils low in this element.
7	Wheat, rye, oats, barley, maize, peas.	Some increase in yield is often obtained when V is added at low concentrations.
53		Higher concentrations cause development disturbances and decrease of yield.
9	Flax, soya bean, peas.	Growth and development disturbances
	Wheat (germs)	Inhibition of nitrate reductase activity.
	Tomato (cell free extract of leaves)	Activity of nitrate reductase is completely inhibited by 100μm $NaVO_3$, $VOCl_2$.
43	Bean (seeds)	Some increase in P concentration of seeds of the following generation on addition of sodium vanadate.
46	Bean (seeds) Lentil (seeds)	Spraying with V increased the tryptophane content of seeds more than their content of crude protein.

ANNEX 2, *contd.*

Reference	Species	Comment
45	Spinach	Addtion of V to sand culture caused accumulation roots.
25	Alfalfa	High concentrations of added V reduced growth particularly.
61	Sugar beet	Spraying with 0.01m $VOSO_4$ of the foliage of young plants resulted in: (a) significantly less growth of the leaves (b) increase in sucrose content of storage root. (c) higher net CO_2-assimilation rate. (d) decreased rate of nitrate reductase, glutamic-pyruvic transaminase, phosphatase, and invertase activity. (e) increased rate of sucrose synthetase (f) lower content of reducing sugar, amino acids and protein, higher content of nitrate.
37 (survey)	**Invertebrate animals** Tunicata: several groups	Present as haemovanadium of particular vanadocytes in the blood. Respiratory pigment.

	Vertebrate animals	
42	Chicken	Vanadium deficiency: Abnormal bone development, body growth reduction, high plasma concentration of cholesterol, reduced growth of wing and tail feathers.
49 (survey)	Rat	Vanadium deficiency: Growth reduction, increase in blood and bone iron impaired reproductive performance, high cholesterol conc. in plasma, abnormal bone development.
57	Rat	Minimum demand for normal development 1-2 μg per day. 0.25 ppm in food is optimum for growth.
49 (survey)	Rat	Toxic effects : 0.05 mmol/l (4 or 5 valent V) inhibits cholesterol synthesis.
35 (survey)		20-30 ppm $NaVO_3$ in food causes small loss of weight, 360 ppm causes severe damage. Casein diet counteracts toxicity.
27		1.25-2.5 ppm body weight causes diarrhoea and loss of weight. Toxic effects related to degree of accumulation in liver.
60		V_2O_5 in air: pulmonary irritant
18		Prolonged exposure to vanadium in air: mortality from heart diseases and certain cancers.
35	Mouse	LD_{50}: 10mg V/Kg body weight
	Dog	LD_{50}: 4mg V/kg body weight

ANNEX 2, *contd.*

Reference	Species	Comment
56	**Man**	Vanadium is a normal component of the erythrocytes, biochemically active but not essential. Takes part in the metabolism of the sulphur-containing amino acids.
42		Essentiality for man not yet demonstrated but possible.
3 (survey)		Toxicity: inhibits cholinesterase and amino-oxidase.
18		Inhalation of high concentrations ($>1\,mg/m^3$) affects the gastro-intestinal and respiratory tracts.
37		Symptoms of V poisoning: nervous depressions, cough due to bronchial spasm, vomiting and diarrhoea, anaemia. Death follows after paralysis of respiratory organs.
67 (survey)		Anion forms of V are more toxic than cation forms
44 (survey)		Promotes cardiovascular disease and carcinogenesis
49		Has both caries preventing and caries provoking action.