WRC WATER RESEARCH CENTRE

228/2

DETERMINATION OF POLLUTANTS IN EFFLUENTS
(PLC 4332CD)

PROPOSED ENVIRONMENTAL QUALITY STANDARDS FOR VANADIUM IN WATER AND ASSOCIATED MATERIALS

Project Leader: A R Agg

Authors: R Norton
A R O'Donnell

With Annexes prepared by
J Fawell and T R Robertson, WRC

and

J C Sherlock
Food Science Division
MAFF

October 1984

520-M/1
(Revised following consideration by the EQO Sub-Group of TACDS)

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SUMMARY

Under the EEC Dangerous Substances Directive, Member States are required to reduce pollution of both fresh and salt waters, resulting from the discharge of List II substances, by the Environmental Quality Objectives (EQO) approach. DOE have contracted WRC to recommend Environmental Quality Standards (EQSs) for selected List II substances. This report is one of a series of nine produced in fulfilment of the contract.

Common uses of vanadium are discussed and the chemistry of vanadium in water reviewed. Information is presented on the concentration of vanadium in the environment, with emphasis on UK and European waters and biota.

Because of the paucity of the available data EQSs have only been proposed for the protection of fish and other aquatic organisms in both fresh and salt waters and for the irrigation of crops. Even for these EQSs suitable information is limited.

The recommended EQS values are summarised in an annotated Table.

It is concluded that the recommended EQS values are consistent with measured concentrations in fresh and salt waters in the UK. Vanadium is not a cause of water pollution in the UK and it is therefore unlikely that these proposals will cause an increase in the cost of monitoring the quality of UK Waters.

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ANNEX A QUALITY STANDARDS FOR VANADIUM IN POTABLE ABSTRACTION

CONTRIBUTED BY J FAWELL AND T R ROBERTSON OF WRC

ANNEX B QUALITY STANDARDS IN FISH AND SHELLFISH FOR LIST II SUBSTANCES

CONTRIBUTED BY DR J C SHERLOCK, FOOD SCIENCE DIVISION, MINISTRY OF AGRICULTURE, FISHERIES AND FOOD

1. INTRODUCTION

This report is one of a series on the selection of environmental quality standards for List II substances in connection with the EC Directive on Dangerous Substances(1), and is produced in fulfilment of a contract placed by the Department of the Environment (DOE) with the Water Research Centre (WRC).

A general introduction to this series of reports has been prepared (2). This discusses the environmental quality objective (EQO) approach, the methods used to derive environmental quality standards (EQS) and the uncertainties in EQS values resulting from inadequacies in the data available. The principal uses of water for which EQS values may need to be set have also been listed.

All of the water uses listed in reference 2 are considered below. Information on the chemistry and behaviour of vanadium in aquatic environments, its effects on organisms, and concentrations of vanadium reported in waters and associated materials has been summarised. This information has been used to derive the EQS values proposed in Table 1.

2. VANADIUM IN THE ENVIRONMENT

The origins, chemistry and applications of vanadium, and its distribution and behaviour in the environment have been reviewed. The principal facts required for an understanding of the behaviour and effects of vanadium in UK waters, and the setting of the EQS values, are summarised below.

2.1. ORIGIN

Vanadium is widely distributed and constitutes approximately 0.025% of the earth's crust. It is very seldom found as a free metal, the main commercial ores being patronite, roscolite, vanadinite and carnolite. It is commonly present in fossil fuels at high concentrations, e.g. 30 mg/kg in American bituminous coals and up to 1400 mg/l in petroleum crude oils. Ash from oil-fired power stations may contain up to 70% vanadium pentoxide (V_2O_5), and recovery of this from smoke stacks can be a commercial source. Clearly combustion of fossil fuels represents a significant source of vanadium release to the environment.

2.2. USES

The pure metal has little commercial use. The major use is as ferrovanadium in the manufacture of high-speed tool steels, engineering and high-strength structural steels and wear-resistant cast iron. Vanadium (commonly as ammonium metavanadate and vanadium pentoxide) is also an important industrial catalyst, e.g. in the oxidation of sulphur dioxide to sulphur trioxide during the synthesis of sulphuric acid. Vanadium compounds are also

important catalysts in the polymerisation of propene and ethene and in the production of certain dyestuffs, e.g. Aniline Black. Vanadium is used in the manufacture of glasses and ceramic glazes.

Vanadium has been shown to be an essential trace element for all vertebrates and some plants, micro-organisms and tunicates. Its exact physiological role has not been defined, except in tunicates where it is believed to form an essential blood compound.

2.3. CHEMISTRY

Pure vanadium is a soft, ductile metal. A member of group V, it can exist in a wide range of oxidation states from -1 to +5 of which +5 and +4 are the most important. Vanadium (5+) oxide is slightly soluble in water and dissolves in acids. Although mainly acidic in character, it is readily soluble in bases. The vanadium (5+) species formed are moderately strong oxidising agents. Mono-, di- and tri-nuclear species may be formed depending on pH. Complex solutions containing a range of species are also formed when the pentoxide is dissolved in acid.

The only pentahalide known is the fluoride which is unstable to water. Other halides are found only as oxy-anions.

Vanadium (4+) is the most important oxidation state under ordinary conditions. Vanadium (3+) is oxidisd to vanadium (4+) by atmospheric oxygen and vanadium (5+) is readily reduced by mild reducing agents. The oxide, VO_2, is amphoteric. In strongly basic solutions the simple vanadate (4+) ions probably do not exist, various hypovanadates being formed. In acid solution, the bright blue vanadyl (VO^{2+}) species which dominates the chemistry of vanadium (4+) is produced. Almost all vanadium (4+) complexes are vanadyl complexes.

2.4. BEHAVIOUR OF VANADIUM IN AQUEOUS ENVIRONMENTS

Information on the behaviour of vanadium in aqueous environments is scarce. However, Orvini et al (3) have reviewed this area and much of the following information is taken from their paper. The aqueous chemistry of vanadium has also been reviewed (4).

The concentration of vanadium in fresh-water rivers is normally in the range 0.1 to 1.0 µg V/l (5) while the concentration in sea water is typically 2.0 µg V/l (6). Levels of 0.1 to 1.5 µg/l in lakes and groundwaters have been reported (7). The species present will depend upon many factors including pH, ionic strength, and vanadium concentration. The presence of vanadium (5+) has been reported in well-aerated water (8) and vanadyl (4+) ions may be present

under reducing conditions (9). Information on the stabilities of synthesised organically-bound vanadium compounds in water suggests that these may be unimportant (9). However, vanadium will bind strongly with soil humus (10).

Orvini et al have applied neutron activation and radiotracer analysis to filtered river-water samples which were subsequently separated into tetravalent, pentavalent and complexed vanadium fractions. They concluded that, in the six different fresh waters analysed, vanadium could be present in all three fractions. They observed anionic vanadium (5+) in all waters but were unable to define the exact chemical nature. However, HVO_4^{2-} and VO_3^- have been reported earlier (8). The presence of polyanions seems to be excluded since these are formed only at vanadium concentrations greater than 10^{-4}M while the levels reported were 10^{-7}M. Orvini et al (3) discounted the possibility of the presence of the vanadyl ion VO^{2+} because this species is characteristic of acid solutions below pH 4. Not unexpectedly, in view of its stability, they also reported the presence of vanadium (4+). They were unable to identify the nature of the complexed vanadium but, since this was absent from water of natural origin (from the inner Alps), they suggested that it may be indicative of long term contamination of fresh water.

It would therefore appear that the chemistry of vanadium in the aqueous environment is relatively simple. Vanadium may be present as organic complexes or as ions in oxidation states 5+ and 4+, of which the latter is the more stable. Vanadium 4+ may be present as the hydrated vanadyl ion. Vanadium 5+ occurs only as mononuclear anions below a concentration of 10^{-4}M, so that the pH-dependent formation of polyanions is likely to be important only in grossly polluted systems. In the pH range of natural waters (pH 4 to 8), $VO_2(OH)_2^-$ predominates, with $VO_3(OH)^{2-}$ at higher pH values and $VO(OH)_3aq$ and VO_2^+ under more acidic conditions.

2.5. CONCENTRATIONS OF VANADIUM REPORTED IN UK AND EUROPEAN WATERS

Information on the concentration of vanadium in inland waters is very limited (Table 2). Vanadium concentrations are not regularly monitored by water authorities (WAs) in the UK. Data for dissolved and total vanadium are available for 7 sites within Northumbrian WA region for 1979 to 1981. At only two sites did the observed concentrations of total vanadium exceed the limit of detection of 10 µg/l. At these two sites (the R Coquet at Warkworth and the R Wear at Lambridge) maximum concentrations of 20 and 40 µg/l respectively were recorded. Both rivers support good game fisheries. Data for European rivers

are again scarce. From these limited data and those available for N America (Table 2), it appears that vanadium concentrations (in either soluble or particulate phases) are generally low and seldom exceed 20 µg/l in freshwater. The only data currently available for European tidal waters are for 15 stations in the eastern North Atlantic (mean concentration of 1.19 µg/l dissolved vanadium for all depths, with an observed range of 0.83-1.57 µg/l) (20).

The concentration of vanadium found in rainwater can be high and comprehensive studies in the UK indicate annual mean concentrations in rainwater ranging from 0.98 µg/l at Plynlimon in mid-Wales to 38 µg/l at Styrrup in Nottinghamshire (21). The latter site is situated within a few kilometers of an active coal mine and is 25 km to the east of Sheffield. It should also be noted that the samples analysed included dry-weather deposits and would therefore give an overestimate of the true vanadium concentrations in rainwater. No information has been published for the concentration of vanadium in urban runoff. It has been estimated that the normal concentration of vanadium in sewage sludge is 15 mg/kg dry weight (22).

3. LIMITATION OF THE PRESENCE OF VANADIUM ON USES OF WATER

3.1. POTABLE WATER

Vanadium is not one of the parameters covered by the EC Surface Water Abstraction Directive (75/440/EEC) (23). J Fawell and T R Robertson of the WRC have reviewed the available information (Annex A) and conclude that there are insufficient data for an EQS to be recommended.

3.2. FOOD FOR HUMAN CONSUMPTION

In the absence of legislation governing the levels of vanadium in food sold for human consumption, guidance was requested from the Food Science Division of MAFF.

Following consultation with the Department of Health and Social Security, Dr J C Sherlock produced comment on behalf of MAFF and DHSS and this is reproduced in Annex B.

It is concluded that the highest estimated intake of vanadium from fish and shellfish is unlikely to cause risk to human health, and consequently no EQS value is proposed.

There is no requirement for water authorities or purification boards to monitor levels of vanadium in fish or shellfish sold for human consumption, this responsibility being with MAFF, DAFS and the public health authorities.

3.3. PROTECTION OF FRESHWATER FISH

Information on the toxicity of vanadium to freshwater fish is summarised in Table 3.

In deriving an EQS for freshwater fish the objective is to provide protection for fish populations that are continuously exposed to metal concentrations which are generally very low relative to acutely toxic concentrations. It is not intended that these standards will provide full protection against the occasional exceptionally high concentration of short duration. For this reason, the approach preferred has been to reduce the lowest (non-lethal) adverse effect concentration reported in the literature by a suitable margin and to recommend this value as the EQS.

Most of the data for vanadium are derived from LC50 tests of relatively short duration. There are only two exceptions(26), a 28-d LC50 and a 96-d no-effect exposure. For only two of these tests are the toxicity values reported as the concentrations measured in the test chambers. In all other cases the reported concentrations are notional values based on the quantity of vanadium added and are therefore likely to be over-estimates of the true exposure concentration as vanadium may be removed from solution by adsorption onto particulates and container walls. All the reported data are for total vanadium.

The data indicate that the form of vanadium tested may affect the value of the 6-d LC50 by as much as a factor of three(27). Toxicity appears to decrease with increasing water hardness, although it is not possible to detail this relationship. The few data for salmonid fish are restricted to a single species, rainbow trout, and do not indicate a clear difference in susceptibility to vanadium when compared with non-salmonid species.

Objective derivation of an EQS for freshwater fish is not possible on the basis of the limited toxicity data. The lowest LC50 value (for 6-day exposure) (24) has therefore been reduced by an arbitrary factor of approximately 20 to give a tentative EQS value of 20 µg/l as an annual average concentration of total vanadium. This value is based on data for relatively soft water (total hardness 65 mg/l as $CaCO_3$) and it is suggested that it should apply to freshwaters with a total hardness that is less than 200 mg/l as $CaCO_3$. In harder waters it is recommended that the EQS should be a factor of 3 greater, this being the smallest ratio of 96-h LC50 values reported for soft and hard waters for the same species (27)(see use a(iv) in Table 1). Because of the paucity of data it has not been possible to recommend an EQS for dissolved vanadium.

Also it has not been possible to propose a standard for waters through which anadromous fish migrate. The proposed EQS has been developed for resident populations and may be too stringent for such waters. It is recommended that the standard for the passage of such migratory fish should be based on local judgement as other factors such as low flows or dissolved oxygen concentration are normally the critical constraint.

3.4. PROTECTION OF OTHER FRESHWATER LIFE

The available toxicity data for invertebrates and plants are summarised in Table 4. These are so limited that it is not possible to propose an EQS for the protection of other freshwater life and it is therefore recommended that the EQS for freshwater fish should apply (see use a(v) in Table 1).

3.5. PROTECTION OF MARINE FISH, OTHER MARINE LIFE AND ASSOCIATED NON-AQUATIC ORGANISMS

The toxicity of vanadium to marine organisms is very poorly documented and the limited information available, summarised in Table 5, all refers to short-term lethal concentrations; no data are available for long-term exposures. Objective derivation of the EQS is not possible on the basis of these data. As the toxicity data are limited to one species of fish and three invertebrates, and to adult stages in all cases, it is considered that, should the EQS be based on application of an arbitrary factor to the lowest LC50 value, then this factor should be sufficiently large to allow for the current lack of knowledge. It is therefore proposed that the lowest LC50 value (10 mg/l)(38) should be reduced by an arbitrary factor of 100 to provide a tentative EQS value of 100 µg/l as the annual mean concentration of total vanadium. This value should be revised as and when adequate toxicity information for marine organisms becomes available.

3.6. BIOACCUMULATION OF VANADIUM

The few data reported for the bioaccumulation of vanadium are summarised in Table 6 and are concerned exclusively with marine organisms. Unfortunately differences in species tested and methods employed prevent meaningful comparison of the bioconcentration factors.

3.6.1. Tissue levels in freshwater organisms

Data are limited to two studies of fish populations in N America (42,43) and these are summarised in Table 7. Concentrations are generally less than 1 mg/kg wet weight, with a maximum of 2.9 mg/kg wet weight. No data are available for freshwater invertebrates.

3.6.2. Tissue levels in marine organisms

The majority of the available data are summarised in Table 8 and concern molluscs and tunicates. Some species of tunicates are able to accumulate

vanadium to exceptionally high concentrations (eg 9 mg/g dry weight in Perophora annectens (55)) whereas other species may only accumulate 10-50 µg/g (dry weight). In those tunicate species which preferentially accumulate vanadium, the element is bound up in the blood and it has been suggested that vanadium may be a vital constituent of the tunic (54).

The data for marine organisms belonging to other taxa indicate tissue concentrations which are normally below 20 mg/kg unless the organisms come from a polluted habitat when concentrations may be more than an order of magnitude higher.

3.7. AGRICULTURAL USES

Vanadium is not mentioned in the recent ADAS leaflet (No 776) concerning the quality of irrigation water and the following comment has been provided on behalf of MAFF by J H Williams:-

> "Vanadium is generally present in plant tissue in only very small amounts, usually less than 0.1 ppm but can accumulate in roots in toxic amounts. In culture solution, vanadium in concentrations of 0.5 ppm or greater has been found to be toxic to plants. In a sandy soil, 10 ppm vanadium can be phytotoxic to crops. On this meagre evidence and based on the assumption made in Leaflet 776 (Water usage of 500 mm/annum over a period of 50 years) a suggested maximum concentration of 0.08 mg/litre would be recommended. The recommendation from the United States is 0.10 mg/litre for continued use on all soils."

This standard is aimed at limiting the accumulation of vanadium in agricultural soils to acceptable levels. It is based upon an assumed application rate of 500 mm of water annually for 50 years. This would be appropriate for glasshouse crops. For field crops application rates would be much lower and the EQS would allow application to continue for a longer period. Where water is directly abstracted, water authorities will not necessarily be aware of the detailed requirements of the user. It is therefore incumbent on the user to ensure that the water is suitable for individual applications, i.e. specific crops.

Following consultation with Miss G Lewis of the ADAS Central Veterinary Laboratory it has been concluded that insufficient data exist on which to base a standard for livestock watering.

3.8. INDUSTRIAL USES

In the absence of an EQS value for water abstracted for potable supply it is not possible to recommend an EQS for the food processing industry. It may be necessary to impose local EQS values for vanadium to protect certain industrial

uses of water, but it is expected that such special needs would usually be met by treatment within the industrial plant.

Saline water is only likely to be required for cooling purposes, which are unaffected by the presence of vanadium. Consequently no EQS value is proposed for this use.

3.9. RECREATIONAL AND AESTHETIC CONSIDERATIONS

EQS values have not been proposed for bathing waters and waters used for contact water sports as there are insufficient data on health effects (see Annex A).

No standard is proposed for elimination of public nuisance. The presence of vanadium does not affect odour, nor is it likely to affect the appearance of the water, unless particulates or coloured vanadium compounds are discharged or formed. Such problems are usually best dealt with locally by restricting discharges of particulate material or coloured compounds as a whole, and not by dealing with each element individually.

4. RECOMMENDED ENVIRONMENTAL QUALITY STANDARDS

Environmental quality standards recommended by WRC are given in Table 1. These values are based on existing knowledge of the chemistry and behaviour of vanadium in the environment and the effects of vanadium on human consumers, fish, other biota, agricultural crops etc. as summarised in Sections 2 and 3 and in the Annexes, and on advice received from national experts, as acknowledged below. Values for similar water uses have not been proposed by other national or international pollution control organisations.

It is recognised that existing knowledge of the behaviour and effects of vanadium is inadequate in many respects. As this knowledge improves, the standards proposed in Table 1 will need to be reviewed and possibly updated.

Table 1. EQS values recommended by WRC. See note 1

Use		EQS value (µg V/l except where stated) Average concentration	95-percentile concentration	Maximum allowable concentration	Dissolved (D) or total (T)	Note
FRESHWATER						
(ai)	Direct abstraction to potable supply	–	–	–	–	2
(aiv)	Protection of freshwater fish					
	Total hardness less than 200 mg $CaCO_3$/l	20	–	–	T	3
	Total hardness greater than 200 mg $CaCO_3$/l	60	–	–	T	3
(av)	Protection of other freshwater life and associated non-aquatic organisms					
	Total hardness <200 mg $CaCO_3$/l	20	–	–	T	4
	Total hardness >200 mg $CaCO_3$/l	60	–	–	T	4
(avi)	Irrigation of crops	80	–	–	T	5
(aviii)	Abstraction for food processing industry	–	–	–	–	
(aix)	Bathing and contact water sports	–	–	–	–	
SALTWATER						
(bii)	Protection of saltwater fish and shellfish	100	–	–	T	5
(biii)	Protection of other saltwater life and associated non-aquatic organisms	100	–	–	T	5
(bv)	Bathing and contact	–	–	–		
(aiii) and (bi)	Food for human consumption derived from fresh or salt waters		–	–	–	6

NOTES ON TABLE 1

1. The numbering of each water use follows the numbering system in reference 2. None of these values is mandatory.
2. Vanadium is not one of the parameters for which standards are set by the EC Council Directive concerning the quality of water intended for the abstraction of drinking water in the Member States (OJ L 194/26, 25 July 1975).
3. Vanadium is not one of the parameters covered by the EC Council Directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life. Official Journal L 222/21, 4 August 1978.
4. See Section 3.6 and Annex B of this report. Other values may be appropriate to local situations, e.g: for the protection of particularly sensitive species.
5. Information supplied by J H Williams, Regional Soil Scientist, ADAS, and based on the same assumptions as ADAS Leaflet No 776. The value given is the suggested maximum average concentration for the normal irrigation period (i.e. the summer months). If exceeded, soil levels should be monitored.
6. The maximum estimated intake from fish and shellfish is not thought to present a risk to human health. The considered response of MAFF following consultation with DHSS is reproduced in Annex B.

5. CONCLUSIONS

The environmental quality objective approach is intended to provide a rational system for the control of discharges of contaminants to waters. Having identified the uses to which water is to be put, standards can be defined restricting levels of contaminants in the water so that the intended uses are protected. Standards for vanadium are proposed in this report for various uses of water, and justification for the values chosen has also been given. As far as is known, the standards proposed are consistent with levels measured in fresh and saline waters in the UK and the uses to which those waters are being put.

The responsible authorities can make use of the standards by setting consents to discharges so that levels of vanadium in water do not exceed the standards, except within the immediate mixing zone. Monitoring is required to ensure that the standards are being met, and the detection limit of the analytical method used should ideally be a tenth or less of the standards. Consequently, for soft waters supporting fish, 2 µg V/l is required, and for saline waters supporting fish and other life 10 µg V/l is required. In practice vanadium is not known to be a cause of water pollution in the UK at present and it seems unlikely that these proposals will cause an increase in the cost of monitoring the quality of UK waters.

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TABLES OF DATA ON TOXICITY AND ENVIRONMENTAL LEVELS

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TABLE 2. Concentrations of VANADIUM Reported in Fresh Waters

Water Body	Site	Concentration of Vanadium (ug/l)	Reference
EUROPE			
River Wear	U.K.	<10 - 40 T	11
" Coquet	U.K.	<10 - 20 T	11
" South Tyne	U.K.	<10 T	11
" Derwent	U.K.	<10 T	11
" North Tyne	U.K.	<10 T	11
" Tees	U.K.	<10 T	11
" Tyne	U.K.	<10 T	11
Saar River	W.Germany	<1 - 5.T F	12
" "	" "	<0.5 - 14.6 S	12
River Ruhr	" "	<5	13
River	N.Stockholm	2.6 D	14
River Ticino	Italy	0.64 T	15
River Tana	Norway	0.36	16
" Namsen	"	0.45	16
" Forra	"	<0.20	16
" Gaula	"	0.53	16
" Rauma	"	0.18	16
" Jostedals	"	0.78	16
" Glomma	"	0.27	16
" Drammens	"	0.14	16
" Aulielva	"	0.30	16
" Skienselva	"	0.12	16
" Mandalselva	"	0.13	16
CANADA			
Lake Ontario	Canada	6.0-6.6 D	17
" St. George	"	3.5-3.8 D	17
" Simcoe	"	6.8 D	17
" Scugog	"	6.1 D	17
Rice Lake	"	4.2 D	17
U.S.A.			
Sacromento River	California	3.93 T (3.44-4.31)	19
Supply Well	Fresno, Calif.	20.50 T (19.4-21.6)	19
Green River	Flaming Gorge, Utah	0.9 T (0.2-1.8)	19
Colorado River	Page, Arizona	3.4 T (1.5-5.2)	19
" "	Hoover Dam, Arizona	3.0 T (1.8-4.1)	19
" "	Parker Dam,	3.0 T (1.7-4.3)	19
San Joachim River	Vernalis, California	6.87 T (6.75-7.01)	19
Animas River	New Mexico	0.30 T (0.2-0.5)	19
San Juan River	Shiprock, New Mexico	7.5 T (0.5-49.2)	19
Colorado River	Loma,Colorado	4.6 (1.9-11.5)	19

KEY : T = Total, D = Dissolved, F = Filtered, S = Suspended.

TABLE 3. Summary of VANADIUM Toxicity Data for Freshwater Fish

SPECIES	WATER HARDNESS (mg/l $CaCO_3$)	VANADIUM CONCENTRATION (mg/l)	TOXIC EFFECT	VANADIUM SOURCE	REFERENCE
Carassius auratus	65	8.08 ET	6-day LC50	V205	24
" "	"	2.95 ET	" "	VOS04	24
" "	"	3.82 ET	" "	NH4V03	24
" "	"	2.45 ET	" "	NaV03	24
Gobio gobio	-	4.80 ET	Lethal after 96 hours	VOS04	25
Jordanella floridae (adult)	347	11.20 MT	96-hr LC50	V205	26
Jordanella floridae (larvae)	"	1.13 MT	28-day LC50	"	26
Pimephales promelas	20	4.80 ET	96-hr LC50	VOS04	27
" "	400	30.00 ET	" "	"	27
" "	20	13.00 ET	" "	V205	27
" "	400	55.00 ET	" "	"	27
Lepomis macrochirus	20	6.00 ET	" "	VOS04	27
" "	400	55.00 ET	" "	"	27
Lebistos reticulatus	65	1.50 ET	6-day LC50	V205	24
" "	"	0.37 ET	" "	VOS04	24
" "	"	1.49 ET	" "	NH4V03	24
" "	"	0.49 ET	" "	NaV03	24
Salmo gairdneri (embryos and alevins)	"soft"	118.0 ET	96-hr LC50	V205	28
	90	11.4 ET	" "	-	29
(juvenile 4-10 g wt)	-	2.0-5.6 ET	7-day LC50	-	30
(juvenile)					
" "	230	14.0 ET	24-hr LC50	Na3V04	31
" "	"	50.0 ET	" "	NaV03	31
" "	100	5.2-11.7 MD	96-hr LC50	V205	31
" "	368	13.2 MD	" "	"	31
" "	100	2.6-4.3 MD	8-day LC50	"	31
" "	368	3.4 MD	" "	"	31
" "	100	2.5 MD	20-day LC50	"	31

KEY: E = estimated concentration. M = measured concentration. T = total vanadium. D = dissolved vanadium

TABLE 4. Summary of VANADIUM Toxicity Data for Freshwater Plants and Invertebrates

Species	Toxic Effect	Vanadium Concentration (ug/l)	Vanadium Source	Reference
PLANTS				
Chlorella pyrenoidosa	Growth slightly retarded	100	–	17
" "	Growth inhibition	25000	NH4VO3	32
" "	Complete inhibition of cell division after 3 days	20	V(+5)	33
" "	Optimal stimulation of chlorophyll photosynthesis	500	"	33
" vulgaris	" "	300000	VOSO4	34
" "	" "	1000000	NaVO3	34
Navicula pelliculosa	Growth slightly retarded	100	–	17
INVERTEBRATES				
Daphnia magna	Toxic threshold	100	–	35
FISH				
Jordanella floridae (larvae)	No deleterious sub-lethal effects after 96 days exposure	41	V2O5	26

TABLE 5. Summary of VANADIUM Toxicity Data for Marine Life

SPECIES	VANADIUM CONCENTRATION (mg/l)	TOXIC EFFECT	VANADIUM SOURCE	REFERENCE
PHYTOPLANKTON				
Gymnodium splendens	10 - 25	Minimum total mortality level	NH4VO3	36
Isochrysis galbana	50	"	"	
Thalassoria pseudonana	20 - 40	"	"	
Glenodinium halli	50 - 100	"	"	
Dunaliella marina	0.5	96-hour LC50	NaVO3	37
Prorocentrum micans	3.0	"	"	
Asterionella japonica	2.0	"	"	
INVERTEBRATES				
Carcinus maenas	35.0	9-day LC50	"	37
Mytilus provincialis	65.0	"	"	
Nereis diversicolor	10.0	"	"	
FISH				
Limanda limanda	44.00	24-hr LC50	NH4VO3	38
" "	30.70	48-hr LC50	"	
" "	27.80	72-hr LC50	"	
" "	27.80	96-hr LC50	"	

TABLE 6. Summary of Bioaccumulation Data for VANADIUM

ORGANISM	SOURCE OF VANADIUM	CONCENTRATION OF VANADIUM DURING EXPOSURE (mg/l)	DURATION OF EXPOSURE	TISSUE INVOLVED	BIOCONCENTRATION FACTOR	REFERENCE
PHYTOPLANKTON						
Dunaliella marina	Water	0.5	7 days	Whole cell	360.1	39
MOLLUSCA						
Mytilus edulis	Contaminated bacteria	-	24 hrs	Soft tissue	0.080	40
" "	Water	-	19 days	Muscle	0.001	40
Mytilus galloprovincialis	"	-	3 weeks	Whole	40*	41
Mytilus adulis	"	0.1	19 days	Whole	2.0	40
" "	"	10.0	19 days	Soft tissue	0.5	40
" "	"	50.0	19 days	Soft tissue	4.0	40
" "	"	0.1	19 days	Soft tissue	80.0	40
" "	"	1.0	19 days	Shell	8.0	40
" "	"	10.0	19 days	Shell	3.5	40
" "	"	50.0	19 days	Shell	0.5	40
ANNELIDA						
Nereis diversicolor	"	-	3 weeks	Whole	35*	41
CRUSTACEA						
Lysmata seticaudata	"	-	3 weeks	Whole	10*	41
Penaeus kerathurus	"	-	19 days	Mixed soft tissue	0.004	40
Carcinua maenas	"	-	3 weeks	Whole	10*	41
FISH						
Solea solea	Contaminated Mussels	-	19 days	Liver	0.012	40

* Bioconcentration factor in these studies defined as: C.P.M. V 48/g animal/C.P.M. V 48/ml of sea water

TABLE 7. Reported Levels of VANADIUM in Freshwater Fish

Common Name	Site	Vanadium Concentration [Fresh Weight] (ug/g)	Reference
Lake Trout	Lake Cayuga	2.02 (1.1-3.4)	42
" "	Fourth Lake	0.08-0.55	
Chain Pickerel	Lake Cayuga	0.13-0.32	
Largemouth Bass	" "	0.18-0.95	
" "	" Champlain	0.13	
" "	" Chautauqua	0.65	
Northern Pike	" "	0.25-0.45	
" "	Lake Delta	0.07	
" "	" Erie	2.40	
" "	" Ontario	0.55	43
" "	" Saratoga	0.07	
Walleye	Lake Delta	0.14-0.24	
"	Sacandaga Resevoir	0.10-0.33	
"	Lake Saratoga	0.19	
"	St. Lawrence River	0.05-0.08	
Black Crappie	Lake Delta	0.10	
Muskellunge	" "	0.65	
Smallmouth Bass	" "	0.80	
" "	Lake Delta	0.80	
Whitesucker	Fourth Lake	2.90	
Striped Bass	Hudson River	0.09	

Table 8. Reported levels of vanadium in marine organisms
(D = Dry weight; W = Wet weight; ? = not stated)

Species	Life stage	Organ	V concn (µg/g)	Site	Ref.
CRUSTACEANS					
Centropages typicus	larvae	whole	16.0 D		44
Centropages hammatus	"	"	16.0 D		44
Calanus finmarchicus	"	"	21.0 D		44
Carcinus maenas	-	"	0.4 ?		45
Euphasia krohnii	-	"	13.0 D		44
Lepas anatifera	-	"	1.2 ?		45
CHAETOGNATHA					
Sagitta elegans	-	"	7.0 ?		44
ANNELIDA					
Eudistylia vancouveri	-	"	786.1 D	Near sewage outfall Vancouver Bay	46
" "	-	"	94.0 D	Far from sewage outfall Vancouver Bay	46
Perinereis cultifera	-	"	0.7 ?		45
Arenicola marina	-	"	1.8 ?		45
COELENTERATA					
Anemonia sulcata	-	"	2.3 ?		45
Cyanea capillata	-	"	5.0 D		44
CTENOPHORA					
Beroe cucumis	-	"	8.0 D		44

Table 8 (contd)

Species	Common name	Organ	V concn (µg/g)	Site	Ref.
MOLLUSCA					
Cellana stearnsii		soft tissue	0.496 W	Osaka, Jpn	47
" "		"	0.584 W	Wakayama, Jpn	47
" "		"	0.243 W	Oita	47
Liolophura japonica		"	0.136 W	Osaka	47
" "		"	0.359 W	Wakayama	47
" "		"	0.072 W	Oita	47
" "		viscera	0.991 W	Osaka	47
" "		"	1.363 W	Wakayama	47
" "		"	0.103 W	Oita	47
Collisella heroldi		soft parts	0.446 W	Osaka	47
Mytilus edulis	Mussel	"	0.213 W	"	47
" "	"	"	0.156 W	California	47
" "	"	"	0.67-2.75 D	Yaquina Bay	48
" "	"	gonads	0.49 D	Oregon	48
" galloprovicialis	"	viscera	3.0 D	Monaco	49
" "	"	muscle	0.3 D	"	49
Crassotrea virginica	Oyster	soft parts	0.084-0.187 W	Hiroshima	47
" "	"	"	0.097-0.134 W	Osaka	47
" "	"		0.174 W	Oita	47
" rhizoporae	Mangrove oyster	"	139.2 D	Nr sewage outfall Guadaloupe	50
" "	"	"	20.0 D	Clean mangrove Guadaloupe	50
Placeopectan magellanicus	Scallop	whole	11.4-45.7 D	N Jersey	51
"	"	soft tissue	0.094-0.328W	Aomori	47
Limacina retroversa		whole	85.0 D		44
Clione limacina		"	16.0 D		44
Ommestrephes illicebrosa		"	4.0 D		44
Diacria trispinosa		shell	50-60 D		52
Sycillium cabriculata		"	4.0?		41
Patella vulgata		soft tissue	0.1?		45
ECHINODERMATA					
Asterias glacialis		body wall	2.8?		45
Cucumaria lefevrei		whole	1.0?		45
PORIFERA					
Ficulina fucus		whole	1.7?		45

Table 8 (contd)

Species	Life stage	Organ	V concn (μg/g)	Site	Ref.
TUNICATA					
Amaroucium pellucidum	-	whole	320-410 D	Bermuda and Naples	54
Clavelina picta	-	"	150 D		
Eustidoma olivaceum	-	"	200 D		
Diazona violacea	-	"	120-240 D		
Rhopalea neapolitana	-	"	1700-2000 D		
" abdominalis	-	"	1800 D	-	55
Ciona intestinalis	-	siphon tips	40 D		54
" "	-	stomach	510 W	-	56
" "	-	gut	257 W	-	
" "	-	mantle	11 W	-	
" "	-	whole	29 W	-	
" "	-	blood	160 D	N California	55
Ecteinascidia conklini	-	whole	1800 D		54
" turbinata	-	"	600-1300 D	-	
Perophora viridis	-	"	470-1150 D	-	
" annectens	-	"	8-9000 D	N California	55
Ascidia correlloides	-	"	1130 D		54
" nigra	-	without tunic	3300-5200 D		
" "	-	tunic only	100-600 D		
" mentula		"	170 D		
" "		without tunic	1200-1900 D		
" "		whole	470-1400 D		
Ascidiella aspersa		"	690-790 D		
" "		without tunic	920-960 D		
Phallusia mamillata		dried ova	180 D		
Salpa fusiformis	larvae	whole	7 D	-	44
Ascidia ceratodes		"	1300 D	N California	55
" "		blood	6200 D	"	
Amaroucium californicum		whole	<10 D	"	
" solidum		"	<10 D	"	
Clavelina huntsmani		"	30 D	"	
Cystodytes lobatus		"	50 D	"	
Eudistoma diaphenes		whole colony	25 D	"	
" psammion		"	80 D	"	
" ritteri		"	320 D	"	

Table 8 (contd)

Species	Common name	Organ	V concn (μg/g)	Site	R
FISH					
Sphyraene barracuda	Barracuda	dorsal muscle	171.5 D	Nr sewage outfall Guadeloupe	
" "	"	"	18.9 D	"Clean" area Guadeloupe	
Centropomus ensiferus		-	14.4 D	"	
Gadus merlangus		-	14.0 ?	"	
	Dogfish	whole	0.04 ?		
	Gurnet Red	"	0.10 ?		
Trachurus mediterraneus		flesh	0.071-0.15 D	Aegean Sea	
Scomber japonicas colias		flesh	0.014 D	"	
" " "		liver	0.024 D	"	

ANNEX A

QUALITY STANDARDS FOR VANADIUM IN POTABLE WATER

Contributed by J K Fawell and T B Robertson of WRC

INTAKE

Food is thought to be the main route of vanadium intake for man, though the information available is very limited. Most studies indicate that the vanadium content of foods is 1ng/g or less. Recent studies (1, 2, 3) indicate that the average daily intake of vanadium by man is likely to be about 20 µg.

Information on vanadium in water is limited, but data from 3 surveys undertaken in the USA (3, 4, 5) indicate concentrations of 0-100 µg/l. However, the mean of each of the three sets of data was about 5 µg/l which indicates that very few waters contained more than a few micrograms. In a survey carried out in 25 towns in the UK (6), 40 samples being taken from each town, 73% of the fully flushed water samples taken at domestic taps contained vanadium at a concentration of less than 11 µg/l; 27% of the samples contained less than 2 µg/l. Water consumption of each subject was estimated by questionnaire and 65% of the estimated total intake values from all sources of water were below 15 ug per day (6).

A report on Drinking Water and Health (4) by the U.S. National Academy of Sciences, discusses the contribution of drinking water to vanadium nutrition, and states:

"Assuming a daily intake of 2 litres of water, data indicate that typical drinking water sources would contribute between negligible amounts and 140 ug of vanadium daily. The average contribution is probably near 8 µg of vanadium daily which would be 40% of the amount of vanadium derived from usual dietary sources. In some instances, the contribution of drinking water to the daily intake of vanadium may be much greater than the contribution of the diet. For example, if the drinking water contained 33 µg of vanadium per litre, it would contribute 3 times as much vanadium as a typical diet".

ABSORPTION, DISTRIBUTION, EXCRETION

Data on the absorption of vanadium is extremely limited. Soluble vanadium compounds probably vary in the extent to which they are absorbed but it has been estimated that about 25% of inhaled vanadium is absorbed from the lung. Even soluble vanadium compounds appear to be poorly absorbed from the gastro-intestinal tract. For example, only about 0.1-1.0% of oxytartarovanadate was absorbed of an experimental dose in man. In addition, Vouk (3) states that the International Commission on Radiological Protection (ICRP) estimate that gastrointestinal absorption of the soluble vanadium compounds is 2%. Only one

very early report indicates a higher level of absorption at about 12-13% however, analytical techniques were by no means as accurate as they are today (7).

Vanadium which is absorbed is widely distributed in body tissues, but the prime site for short term localisation appears to be bone (3,4,5). Talvite and Vagner (3,8) reported a 75% retention in the bones of rabbits, with a small amount retained in the kidneys, liver, spleen, lungs, adrenals, bone marrow, skin and muscle.

Twelve per cent of the ingested dose was retained for two weeks. Retention in the endocrine glands and gonads has also been reported (3).

Scott, Hamilton and Wallace (3, 8) found a similar widespread distribution in rats 4 days after an intramuscular dose of radio labelled metavanadate in isotonic saline. The highest percentages of the absorbed dose were found in the bone (9.9%), liver (6.2%), muscle (5.0%), kidney (4.4%) and blood (1.5%). Sixty-four days after dosing, 10% of the injected vanadium remained in the body with 4-6% remaining in the skeleton.

Vanadium compounds are rapidly excreted, primarily in urine (4). In studies in rabbit and rat with intravenous and intraperitoneal injections of sodium tetravanadate, it was found that most of the vanadium was excreted via the kidneys in a ratio of 5.1 to faecal elimination. Sixty-one per cent of the injected vanadium was eliminated via the kidneys within 24 h. Similar results were obtained in dogs and rabbits. Data in man support the contention that almost all the absorbed dose of vanadium is excreted through the kidneys (3, 8, 9).

The excretion of vanadium appears to be rapid though kinetic data is sparse. The ICRP, however, estimate a whole-body retention in man of 42 days (3,8).

There is evidence that vanadium is an essential element in the rat and chick though there is less evidence to support this contention for other species. Suggested beneficial effects of vanadium in protectng against dental caries have not been substantiated and there are contrary findings in the literature (3). Similarly, findings with regard to effects on lipid metabolism of chicks and rabbits need to be further investigated (10). It has been suggested (11,12) that the very potent natural diuretic effect of vanadium linked with inhibition of the sodium pump in the kidney tubules, resulting in excretion of sodium ions, is of benefit in relation to cardiovascular disease. Golden and Golden (13) suggested that nutritional oedema may result from vanadium deficiency.

There is, however, considerable doubt (14) over suggestions that vanadium may be involved in some neural disorders.

TOXICITY

Most data on the toxicity of vanadium are derived from inhalation studies and examination of subjects occupationally exposed to vanadium in air (3, 4, 5, 8). However, since vanadium appears to be absorbed more readily from the lung than gastrointestinal tract, the occurrence of systemic effects indicates the target organs in vanadium toxicity.

The acute toxicity of vanadium varies widely with different compounds presumably due to differences in solubility and valence. Oral LD50's of vanadium trioxide, vanadium pentoxide and vanadium trichloride to albino mice were determined to be 130, 23 and 23 mg/kg respectively (15).

Long-term exposure, by inhalation, of rats and rabbits to high levels of various vanadium compounds resulted in fatty changes and cell necrosis in the liver and fatty changes in the kidney (16). Fatty changes in liver of rats were also observed (17) following sub-cutaneous injections of vanadium (1 µg/kg/day) for 30 days. Effects have been shown on the nervous (16, 18, 19), haemopoietic (20, 21, 22) and cardiovascular systems (16, 23), but no recent well-controlled studies with the advantages of modern techniques are available.

Vanadium certainly can exert metabolic effects at relatively low doses and is a potent inhibitor of Na+K+ATPase (24, 11) and also appears to inhibit biosynthesis of coenzyme A (25, 26). How these and other metabolic effects relate to mammalian toxicity is not clear but they do complicate the issue of essentiality or beneficial effects of the element. The effects demonstrated in rat kidney to induce natriuresis appear to be a function of the ability of vanadium to inhibit sodium/potassium-ATPase (11, 27, 28) which could be a toxic effect or the mechanism of action as an essential trace element in the modulation of renal sodium excretion.

Vanadium appears to be of relatively high toxicity when administered parenterally, of moderate toxicity by inhalation and of low toxicity when taken orally, reflecting the extent to which it is absorbed.

CARCINOGENICITY, TERATOGENICITY, MUTAGENICITY

There appear to be no data regarding the carcinogenicity, teratogenicity or mutagenicity of vanadium compounds.

CONCLUSIONS

1. Vanadium may be a beneficial element but the importance of the contribution from drinking water is not clear.

2. The intake of vanadium from food is thought to be about 20 µg/day. The contribution from drinking water in the U.K. would appear to be less than 20 µg/day on the whole but may be more than 50 µg in extreme cases.
3. The toxicity of vanadium has been poorly studied but "the evidence does not indicate that vanadium in drinking water is a problem" (4).
4. There is insufficient information available at present to recommend a standard for vanadium in drinking water.

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ANNEX B

QUALITY STANDARDS IN FISH AND SHELLFISH FOR LIST II SUBSTANCES

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HUMAN HEALTH ASPECTS

Introduction

1. The Ministry of Agriculture, Fisheries and Food (MAFF) has prepared estimates of the intakes from fish and shellfish of tin, boron and vanadium. These estimates have been considered by officials at the Department of Health and Social Security (DHSS) who have made judgements about the risks to health arising from these intakes.

Basis of the Estimates of Intake

2. In the first instance it was necessary to make estimates of the quantities of fish and shellfish consumed by people who regularly eat these foods. For the purposes of these calculations MAFF has used the 97.5th percentile of consumption in one week by people who eat fish or shellfish; this is likely to produce an overestimate of extreme consumption in the long term. In addition the intakes have been calculated by assuming that a person consumes fish and shellfish both at the 97.5th percentile level, again this is likely to produce an overestimate of what happens in practice.

3. The intakes have been calculated by multiplying the extreme consumption data by, as appropriate, the highest observed concentration of tin or boron or vanadium in a particular species of fish or shellfish. This will tend to overestimate the long term intakes which would be observed in practice.

Results of the Consideration

4. The estimates of intake produced by MAFF have been considered by officials at DHSS and their judgement about the risks to health arising from the estimated intakes are given below. The judgements are subject to certain caveats, in particular the paucity of data about the toxicology and speciation of vanadium in food.

(1) Tin: the estimated intakes are acceptable.
(the data on the concentration of tin in fish and shellfish were derived from the Total Diet Study. In this study analyses are made on a composite of fresh and canned fish. The major source of dietary tin is canned food, this source of dietary tin is unaffected by environmental pollution. The judgement on risks to health assumes that the tin is not present as organotin compounds. If this assumption is incorrect then the judgement may be changed.)

(2) Boron: the estimated intakes are acceptable.

(3) Vanadium: the estimated intakes are only just acceptable. However actual measurements on the intakes of vanadium from fish duplicate diets indicate that in practice there is a greater margin of safety between DHSS estimated tolerable intake and observed intakes. In ivew of the lack of data about the speciation of vanadium in fish and shellfish and the relatively few toxicological data bout vanadium, it may be considered desirable that there should be monitoring of the effects of fish and shellfish of pollution of the marine environment by vanadium.

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