POTENTIAL TRANSFORMATIONS OF CHROMIUM IN NATURAL WATERS

DAVID C. SCHROEDER* and G. FRED LEE**
Institute for Environmental Sciences, University of Texas-Dallas, Richardson, Tex. 75080, U.S.A.

(Received 13 June, 1974; in revised form 29 October, 1974)

Abstract. A study has been conducted on the transformation of Cr(III) and Cr(VI) in simulated natural water conditions. It has been found that these forms are readily interconvertible under natural water conditions. The results of this study indicate that Cr(VI) is reduced by Fe(II), dissolved sulfides, and certain organic compounds with sulfhydryl groups, while Cr(III) is oxidized by a large excess of MnO_2 and at a slow rate by O_2 under conditions approximating those in natural waters. Based on the results of these studies, water quality standards for Cr should be based on total Cr rather than on Cr(VI), as has been frequently done in the past.

1. Introduction

A frequently recommended limit for Cr in natural waters of 0.05 mg l^{-1} of Cr(VI) is based on toxicity to aquatic life and on possible harmful effects on man when present in drinking water (FWPCA, 1968; McKee and Wolf, 1963; USPHS, 1962). Little attention has been given to Cr(III) either in toxicity studies or in the establishment of standards, although McKee and Wolf (1963) accumulated evidence to conclude that Cr(III) is also hazardous to aquatic life.

The objectives of this study are to consider the possibilities for and evidence of reduction of Cr(VI) and oxidation of Cr(III) in natural waters. Such reactions, if they occur, will have an effect on the distribution of Cr in these waters, since Cr(III) is known to be sorbed to a much greater extent by naturally occurring solids than is Cr(VI) (Canter and Gloyna, 1967; Krauskopf, 1956; Chuecas and Riley, 1966) and is also restricted in solubility in the pH range of natural waters (Pourbaix, 1966; Sillen and Martell, 1964). When both direction and rate of these reactions are considered, if Cr(VI) is favored, then the available evidence indicates that Cr will accumulate as soluble forms in the water. If Cr(III) is favored, then the accumulation will likely occur in the sediments. If Cr(III) and Cr(VI) are interconvertible in natural waters, then water quality standards for Cr should be based on total Cr and not Cr(VI) as has frequently been done in the past.

At pH 6.5 to 8.5, the overall oxidation reaction is (Latimer, 1952; Pourbaix, 1966; Sillen and Martell, 1964)

$$2Cr(OH)_2^+ + 1.5O_2 + H_2O \rightarrow 2CrO_4^= + 6H^+ . \qquad (1)$$

---

* Graduate student, University of Wisconsin.
** Director, Institute for Environmental Sciences, University of Texas, Dallas.

Water, Air, and Soil Pollution 4 (1975) 355–365. *All Rights Reserved*

Given the standard free energy change for this reaction (Latimer, 1952) as +12.7 kcal mole^{-1}, at pH=7.0 and $P_{O_2}=0.21$ atm, at equilibrium,

$$\frac{\{CrO_4^{=}\}}{\{Cr(OH)_2^{+}\}} = 7 \times 10^{15}$$

indicating that under oxygenated natural water conditions Cr(VI) is the thermodynamically stable species. It is possible, however, that Cr(III) could be kinetically stable in natural water systems. The only previous study concerned with this reaction was that of Canter and Gloyna (1967) who found evidence of appreciable oxidation of ^{51}Cr(III) in five days at pH 8 to 10; however, they found that ^{51}Cr(III) is sorbed to a much greater extent by glassware than is ^{51}Cr(VI). These investigators used analytical procedures which measure soluble species only. When the sorption is considered, it is difficult to show that any oxidation occurred, since the results are reported as fractions of total activity rather than as actual concentrations.

2. Materials and Methods

2.1. MEASUREMENT OF Cr(VI) AND TOTAL Cr

Cr(VI) was measured by the diphenylcarbazide method and total Cr by the permanganate-azide method, both of which are described in Standard Methods (APHA *et al.*, 1971). The diphenylcarbazide method was evaluated and found to be specific for Cr(VI). Beer's Law was obeyed at concentrations up to 250 μg l^{-1} and the detection limit was found to be 1 to 2 μg l^{-1} with the apparatus used in this study.

The permanganate-azide method was also evaluated and found to be only marginally satisfactory with an average relative error of 21% and a relative standard deviation of 23% in a series of 22 determinations.

3. Results

3.1. OXIDATION OF Cr(III) BY O_2

The rate of formation of Cr(VI) was determined in buffered solutions containing 100 to 125 μg l^{-1} Cr(III) and DO. As a basis for comparison, a reference solution was used which contained 100 μg l^{-1} Cr(III), 10^{-2} M $KHCO_3$ buffer, and glass-distilled water maintained at room temperature (22 to 26 °C). This reference solution had an initial pH of 8.6.

To determine the effect of pH, the HCO_3^- buffer was replaced with $H_2PO_4^-$–$HPO_4^{=}$ buffer (pH 5.9) and with $CO_3^{=}$ (pH 9.9). To determine the effect of temperature, the reference solution was placed in water baths at 35 °C and 45 °C.

Figure 1 depicts the effect of temperature on the rate of oxidation of Cr(III) by DO in $KHCO_3$ buffer. At room temperature (22 to 26 °C), the rate was slow with about 3% of the added Cr(III) oxidizing in 30 days. At 35 °C, the same extent of oxidation occurred in 10 to 11 days, and, at 45 °C, in less than 3 days. This temperature effect

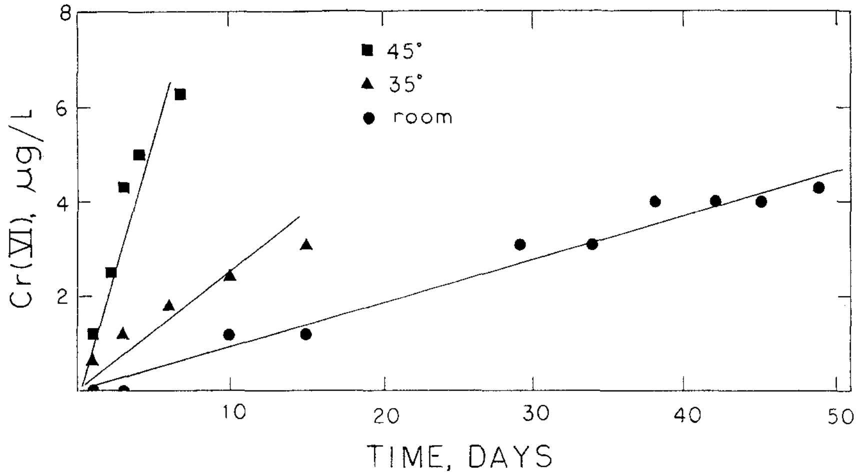

Fig. 1. Effect of temperature on the rate of oxidation of Cr(III) by O_2. Initial Cr(III) = μg l^{-1}. Room temperature = 22–26 °C.

indicates a high activation energy based on the rates at room temperature and 45 °C, $E_a = 22$ kcal $mole^{-1}$. In each case, approximately 20 to 25% of the Cr(III) was sorbed by glassware during the duration of the experiments and thus the true rate of oxidation was slightly higher than the apparent rate. Nevertheless, it appears that the rate of this reaction is sufficiently slow in natural waters that Cr(III) may be involved in other reactions, particularly sorption, before it can be oxidized by O_2.

In order to determine whether the materials in natural waters might influence the rate of oxidation of Cr(III) by DO, the rate was also measured in Lake Mendota, Wisconsin water, one sample of which was filtered through a 0.22 μ pore size filter, while another sample was left unfiltered except that aliquots were filtered just prior to CR(VI) measurement. Table I indicates that there was no evidence of such a catalyst in Lake Mendota water, since the rate in unfiltered lake water was essentially the same

TABLE I

Rate of oxidation of Cr(III) in Lake Mendota water, pH 8.3–8.7, room temperature, initial Cr(III) = 125 μg l^{-1}

Time, days	Cr(VI), μg l^{-1} [a]	Cr(VI), μg l^{-1} [b]
0	<1	1
1	<1	<1
4	<1	1.3
5	1.9	5.0
7	2.5	5.0
13	1.3	3.8

[a] Unfiltered.
[b] Filtered.

as the rate in $KHCO_3$ buffer. The slightly higher apparent rate in filtered lake water can be attributed to the formation of turbidity in the sample, since aliquots from this sample were not filtered immediately prior to Cr(VI) measurement.

To determine the effect of sorption of Cr(III) on the rate of oxidation, to the reference solution was added (a) sand, 50 g l^{-1} (b) bentonite, 10 g l^{-1} (c) MnO_2, 0.10 g l^{-1}, and (d) $Fe(OH)_3$, 0.2 g l^{-1}. These mixtures were stirred thoroughly once each day and allowed to settle overnight before aliquots were taken and filtered through medium-porosity glass fiber before Cr(VI) analysis.

TABLE II

Effect of solids in sorbing Cr(III) and on rate of oxidation of Cr(III) in $KHCO_3$ buffer. All figures are percentages of the original Cr(III)

	Sand	Bentonite	MnO_2	$Fe(OH)_3$
Sorbed in 1 day	46	93	11	89
Sorbed in 7 days	90	95	0	99
Oxidized in 1 day	1	2	89	1
Oxidized in 3 days	0	–	91	1
Oxidized in 7 days	2	–	100	–
Oxidized in 8 days	–	1	–	0

TABLE III

Rate of oxidation of Cr(III) by O_2 in three different buffers. Figures are percentages of the original Cr(III)

	pH range		
	5.9	8.3–8.9	9.5–9.9
Sorbed in 1 day	15	40	14
Sorbed in 7 days	22	21	21
Sorbed in 14 days	22	–	–
Oxidized in 1 day	1	1	1
Oxidized in 7 days	1	2	1
Oxidized in 14 days	1	1	1

Table II indicates that the naturally occurring solids studied all sorbed Cr(III) but that oxidation could only be detected with MnO_2. In the case of sand, bentonite, and $Fe(OH)_3$, there is no evidence to indicate that sorption of Cr(III) increases the rate of oxidation. MnO_2 appears to be a special case which will be discussed later.

Table III indicates that pH had no apparent effect on the rate of oxidation of Cr(III) by DO over the range of pH 5.9 to 9.9. Although there may well be a pH effect on this rate, the effect does not appear to be significant. In all cases, less than 2% of the added Cr(III) was oxidized in two weeks.

3.2. OXIDATION OF Cr(III) BY MnO_2

The rate of oxidation of Cr(III) in the presence of MnO_2 was determined by adding different amounts (25, 100, and 250 mg l^{-1}) of MnO_2 to reference solutions, stirring to keep the MnO_2 in uniform suspension, and filtering aliquots through medium-porosity glass fiber filters. The rate was also measured with Cr(III) and MnO_2 added to both filtered and unfiltered Lake Mendota water.

Figure 2 indicates that the rate of oxidation of Cr(III) in the presence of MnO_2 depends on the quantity of MnO_2, even when that quantity represents several hundred times the quantity required to oxidize all of the Cr(III) present. At 25 mg l^{-1} MnO_2, a weight ratio of MnO_2 : Cr of 200 : 1, half of the added Cr(III) was oxidized in 42 min, but, at 250 mg l^{-1} MnO_2, only 3 min were required.

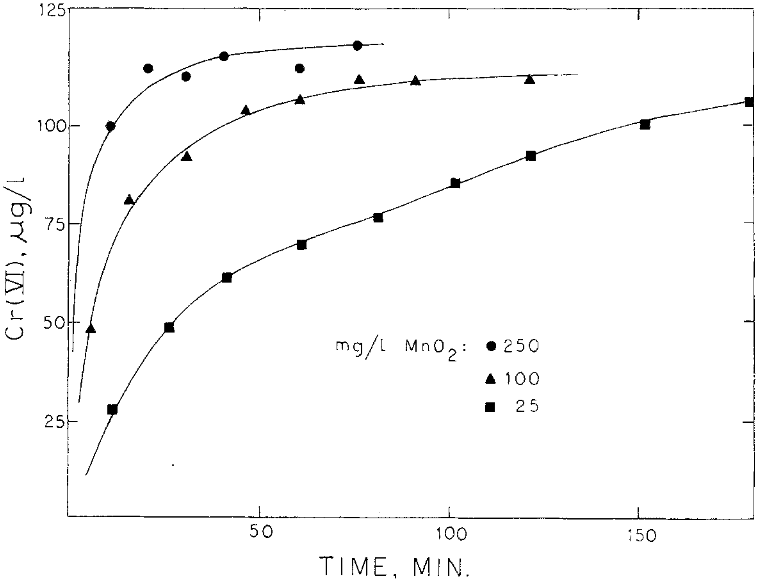

Fig. 2. Oxidation of Cr(III) by different amounts of MnO_2. Initial Cr(III) = 125 μg l^{-1}.

Figure 3 indicates that the reaction was strongly inhibited in Lake Mendota water. In filtered lake water, it is possible that other cations such as Ca^{++} and Mg^{++} occupied sorption sites on the MnO_2 particles such that the reaction ceased with 65% of the Cr(III) oxidized. In unfiltered lake water, even more inhibition was noted, probably because of sorption of some of the Cr(III) by other solids.

These results suggest that oxidation of Cr(III) by MnO_2 requires sorption of the Cr(III) onto sorption sites which are few in number in relation to the total surface area. The scarcity of these sites and the marked inhibition in Lake Mendota water imply that MnO_2 is not likely to have a significant effect on the distribution of Cr forms in natural waters.

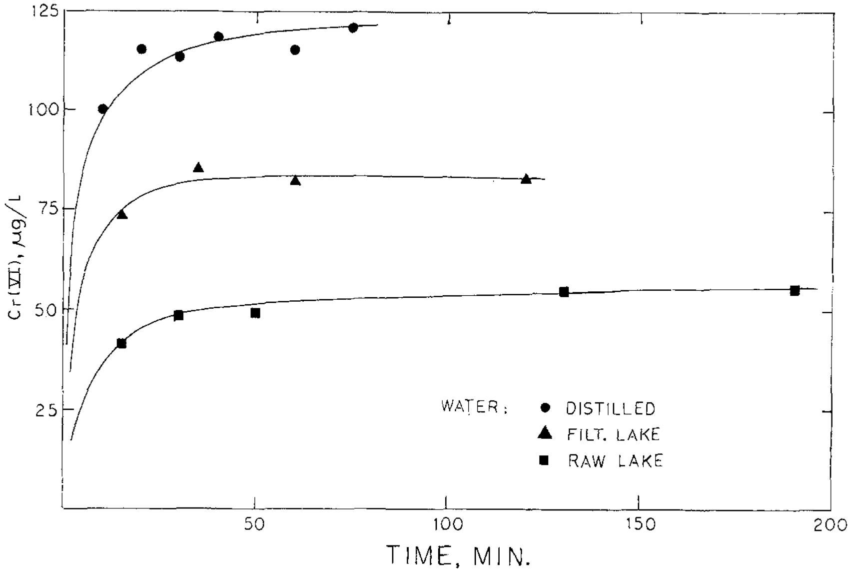

Fig. 3. Oxidation of Cr(III) by MnO_2 in buffered, distilled and in filtered and unfiltered Lake Mendota water. Initial Cr(III) = 125 $\mu g\ l^{-1}$, MnO_2 = 250 $mg\ l^{-1}$.

3.3. REDUCTION OF Cr(VI)

The rate of sorption of Cr(VI) was determined in buffered solutions to which selected reducing agents were added. To attempt to correct for sorption of Cr(VI) by glassware, no reducing agent was added to one solution. The reference buffer was 10^{-2} M $KHCO_3$. All solutions initially contained 100 $\mu g\ l^{-1}$ Cr(VI). Table IV indicates that the loss of Cr(VI) from the control sample proceeded at a rate of about 1 $\mu g\ l^{-1}$ week, a rate which is negligible in experiments lasting less than one day. The marked difference in rate and extent of sorption between Cr(III) and Cr(VI) is apparent.

TABLE IV

Loss of Cr(VI) from control sample

Time, days	Cr(VI), $\mu g\ l^{-1}$ [a]	Time, days	Cr(VI), $\mu g\ l^{-1}$ [a]
0	100	14	99
3	99	18	99
6	99	21	98
10	99	26	98

[a] In solution.

3.4. REDUCTION OF Cr(VI) BY Fe(II)

The effect of Fe(II) on Cr(VI) was determined by adding to the reference solution appropriate volumes of a $Fe(NH_4)_2(SO_4)_2$ stock solution prepared in dilute H_2SO_4.

In an additional reference solution, the pH was raised with 1N NaOH before Fe(II) was added. The initial reaction conditions were as follows: (a) 0.40 mg l^{-1} Fe(II), pH 7.5 (b) 1.20 mg l^{-1} Fe(II), pH 7.1, and (c) 0.40 mg l^{-1} Fe(II), pH 9.1.

Figure 4 indicates that Fe(II) will reduce Cr(VI) in the pH range of interest but that the extent of this reduction will depend on pH and Fe(II) concentration as well as

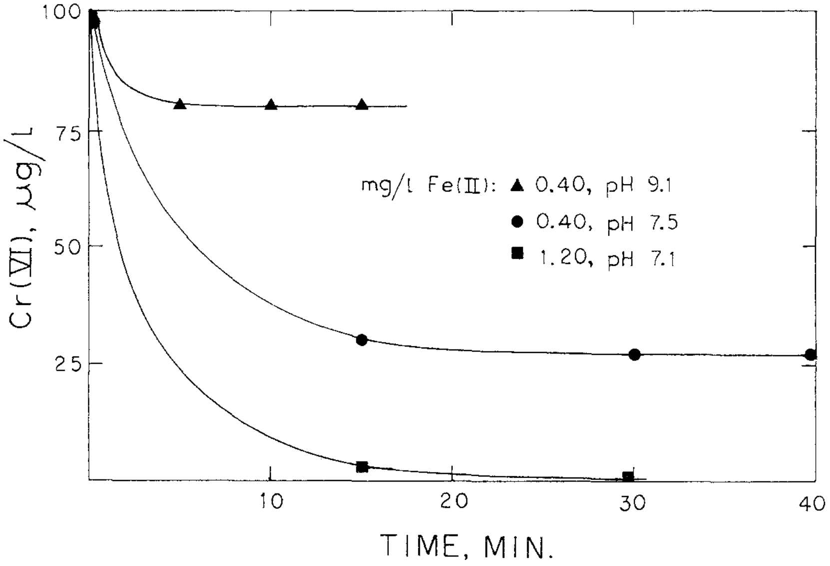

Fig. 4. Reduction of Cr(VI) by Fe(II).

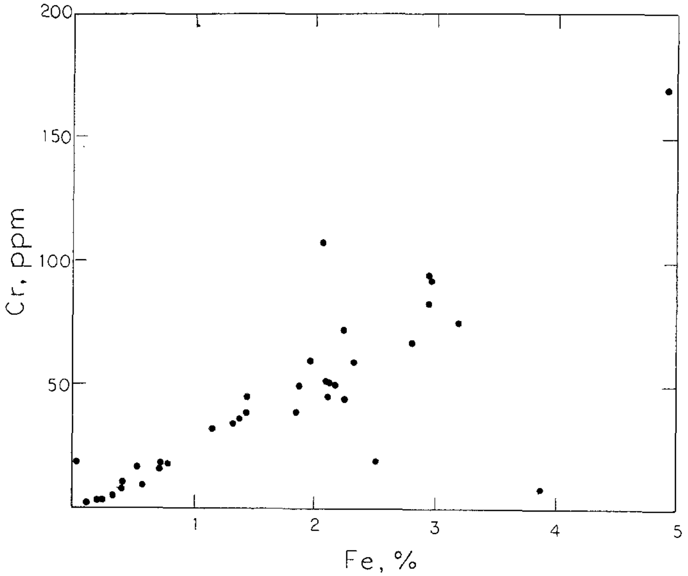

Fig. 5. The correlation between Cr and Fe content of Lake Michigan sediments using data from Copeland and Ayers (1972).

other factors. Fe(II) is, of course, also oxidized by O_2 in this pH range. At 0.40 mg l^{-1} Fe(II) and an initial pH of 7.5, approximately half of the original Fe(II) was oxidized by Cr(VI) and half by O_2, with 73% of the Cr(VI) being reduced. At an initial pH of 9.1, the Fe(II)-O_2 reaction was favored and only 20% of the Cr(VI) was reduced. At pH 6.5 to 8.5, the overall reaction between Cr(VI) and Fe(II) is

$$3Fe^{++} + CrO_4^{=} + 7H_2O \rightarrow 3Fe(OH)_3 + Cr(OH)_2^{+} + 3H^{+}. \qquad (2)$$

As previously noted, Cr(III) is sorbed very effectively by $Fe(OH)_3$. The result of the occurrence of reaction (2) in a natural water is likely to lead to the accumulation of Fe and Cr in the sediments and quite possibly a correlation between the two such as that seen in Figure 5 and Table V.

TABLE V

Correlation coefficients for Cr content of southern Lake Michigan sediments with other parameters, after Shimp *et al.* (1971)

Sediment interval	With organic carbon	With <2 μm clay	With water depth	With Fe_2O_3	With MnO_2
Top[a]	0.80	0.50	0.44	0.78	0.49
1–7 cm	0.72	0.49	0.20	0.76	0.47
4–12 cm	0.87	0.39	0.29	0.57	0.20
8–20 cm	0.94	0.79	0.66	0.79	0.42

[a] Variable, 2–4 cm.

Table V and Figure 5 are based on Shimp *et al.* (1971) and show a strong correlation between the Fe and Cr content of the sediments in Lake Michigan.

3.5. REDUCTION OF Cr(VI) BY SULFIDES

To determine the effect of dissolved sulfides on Cr(VI), a reference solution was made 10^{-3} M in Na_2S. The resultant pH was 9.0 and a faint H_2S odor could be detected throughout the experiment.

Figure 6 indicates that Cr(VI) was rapidly reduced by dissolved sulfides; 50% of the original Cr(VI) was reduced in less than five min in the presence of 10^{-3} M total sulfides. The reaction then slowed considerably but still went to essential completion after 27 h. The effect of pH on the rate of this reaction is not known. The predominant species of sulfide at this pH is HS^-. Like Fe(II), sulfides are also oxidized by O_2, but in this case the rate appears to be slower and the interference is not as great.

The significance of the reduction of Cr(VI) by sulfides lies in the fact that H_2S can be produced by decomposition of organic matter, by bacterial sulfate reduction, or by the discharge of certain industrial wastes. The Cr(III) produced by this reaction is then likely to be sorbed by suspended solids and removed from solution. The oxidation of sulfides by O_2 appears to be slow enough to allow their penetration for a short distance into aerobic waters, and it is in these boundary zones, such as at the thermocline, reduction of Cr(VI) is expected.

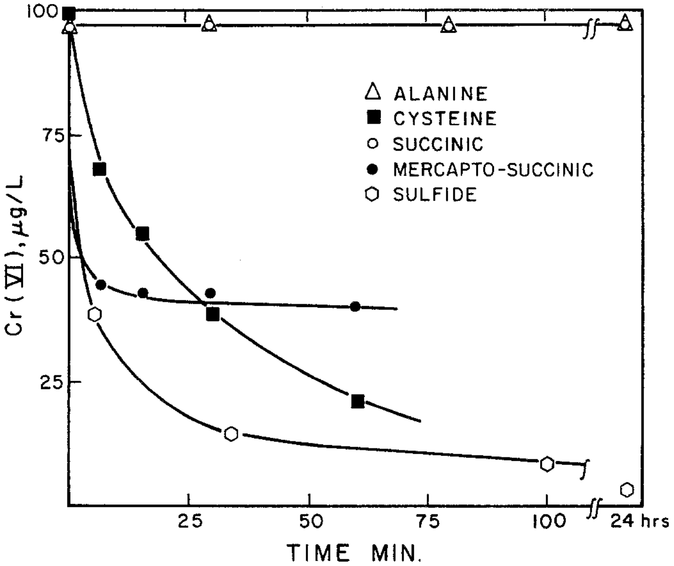

Fig. 6. Reduction of Cr(VI) by 10^{-3} M sulfides by pH 9.1, cysteine, alanine, and 10^{-3} M mercaptosuccinic acid.

3.6. Reduction of Cr(VI) by organic compounds with sulfhydryl groups

The effects of certain organic compounds on Cr(VI) were determined. The compounds chosen were the amino acid alanine, the sulfur-bearing amino acid cysteine, succinic acid, and mercaptosuccinic acid. In each case, the reference solution was made 10^{-3} M in the compound being tested.

Figure 6 indicates that cysteine and mercapto-succinic acid reduced Cr(VI) at a rapid rate while no reduction could be detected in solutions containing alanine or succinic acid. Mercaptosuccinic acid is apparently subject to oxidation by O_2 as well, since little or no reduction occurred after 10 min with 40% of the Cr(VI) remaining.

While it is unlikely that sulfhydryl-bearing compounds are abundant enough in natural waters to affect the distribution of Cr, a possibility exists that Cr(VI) taken up by aquatic organisms is reduced by, and inactivates, coenzymes bearing this group.

3.7. Reduction of Cr(VI) in natural water samples

Cr(VI) was added to natural water samples to determine the effects of natural organics and to detect any naturally occurring reducing agents. The sources of these samples were Lake Mendota, Madison, Wisconsin, with 5 units of true color, and Waunakee Marsh, located north of Lake Mendota, with 25 units of true color. Each sample was divided in half, with one portion initially filtered through 0.22 μpore size filters and the other left unfiltered with aliquots filtered before Cr(VI) analysis. Each sample had an initial Cr(VI) concentration of 100 $\mu g\,l^{-1}$.

The results presented in Table VI indicate that no significant reduction of Cr(VI) occurred in water from Lake Mendota or from Waunakee Marsh. The rate of loss of

TABLE VI

Reduction of Cr(VI) in Lake Mendota water and in Waunakee Marsh water. All figures are μg l^{-1} Cr(VI)

Time, days	Lake water Unfiltered	Filtered	Marsh water Unfiltered	Filtered
0	102	100	98	98
1	–	100	97	98
3	97	–	–	–
4	–	95	98	98
6	100	–	94	95
7	100	–	–	–
8	–	98	–	–
11	–	99	97	97
14	99	98	–	–
Average percent reduced per week:	0.5%	<0.1%	<0.1%	<0.1%

Cr(VI) in all samples was nearly identical with the rate in the control (Table V) after a period of 11 to 14 days. A temporary loss of Cr(VI) was noted in each sample after three to six days, apparently related to sorption or growth of micro-organisms, which does not appear due to reduction of Cr(VI).

4. Discussion

The results of this study indicate that under certain conditions the oxidation state of Cr may be altered in natural waters. Cr(III) is oxidized by O_2, but at a slow rate, and by MnO_2, although this reaction is inhibited by substances in natural waters. Cr(VI) is reduced by Fe(II), dissolved sulfides, and certain organic compounds with sulfhydryl groups, with the most significant interference in all cases being oxidation of these substances by O_2.

Because of the possibilities for oxidation of Cr(III) and reduction of Cr(VI), water quality standards should be based on total Cr rather than on Cr(VI). Recently the Environmental Protection Agency (EPA, 1973) has proposed water quality criteria based on total Cr, rather than the Cr(VI) frequently used in the past. The results of this investigation strongly support this approach.

Acknowledgments

This study was supported by Environmental Protection Agency Training Grant 5P2-WP-184-04. This investigation was conducted at the University of Wisconsin and received support from the University of Wisconsin's Department of Civil and Environmental Engineering. Also, support was given to this project by the Institute for Environmental Sciences, University of Texas at Dallas.

References

American Public Health Association, American Water Works Association and the Water Pollution Control Federation: 1971, *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, APHA, New York, N.Y., U.S.A.

Canter, L. W. and Gloyna, E. F.: 1967, *Radioactivity Transport in Water – Transport of Cr-51 in an Aqueous Environment*, Civil Engr. Dept., Univ. of Texas, Austin, Tex., U.S.A.

Chuecas, L. and Riley, J. P.: 1966, *Anal. Chim. Act.* **35**, 240.

Copeland, R. A. and Ayers, J. C.: 1972, 'Trace Element Distributions in Water, Sediment, Phytoplankton, Zooplankton, and Benthos of Lake Michigan', *Envir. Res. Group Spec. Rep.* **1**.

EPA Proposed Criteria for Water Quality: 1973, U.S. Envir. Prot. Agen., Washington, D.C., U.S.A.

Federal Water Pollution Control Administration: 1968, 'Report of the Committee on Water Quality Criteria', U.S. Dept. of the Int., Washington, D.C., U.S.A.

Krauskopf, K. B.: 1956, *Geochim. Cosmochim. Acta* **9**, 1.

Latimer, W. M.: 1952, *Oxidation Potentials*, 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., U.S.A.

McKee, J. E. and Wolf, H. W.: 1963, *Water Quality Criteria*, 2nd ed., State Water Qual. Control Bd., Sacramento, Calif., U.S.A.

Pourbaix, M.: 1966, *Atlas of Electrochemical Equilibria*, Pergamon Press, London.

Shimp, N. F., Scheicher, J. A., Ruch, R. R., Heck, D. B., and Leland, H. V.: 1971, 'Trace Element and Organic Carbon Accumulations in the Most Recent Sediments of Southern Lake Michigan', *Ill. State Geol. Surv. Environ. Geol. Notes* **41** (6).

Sillen, L. G. and Martell, A. E.: 1964, 'Stability Constants of Metal-Ion Complexes', *Special Pub. No. 17*, The Chem. Soc. (London).

U.S. Public Health Service: 1962, 'Public Health Service Drinking Water Standards', U.S. Pub. Health Ser.