Chapter 1

AN EVALUATION OF TOXIC METALS MONITORING IN THE CHEVRON REFINERY DISCHARGE

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The Chevron U.S.A. refinery in Richmond, California discharges a treated waste effluent averaging 48 million gallons per day into Castro Creek and the Castro Cove marshlands bordering San Pablo Bay (Figure 1) (RWQCB, 1985). Under a Regional Water Quality Control Board (RWQCB) permit, Chevron operates

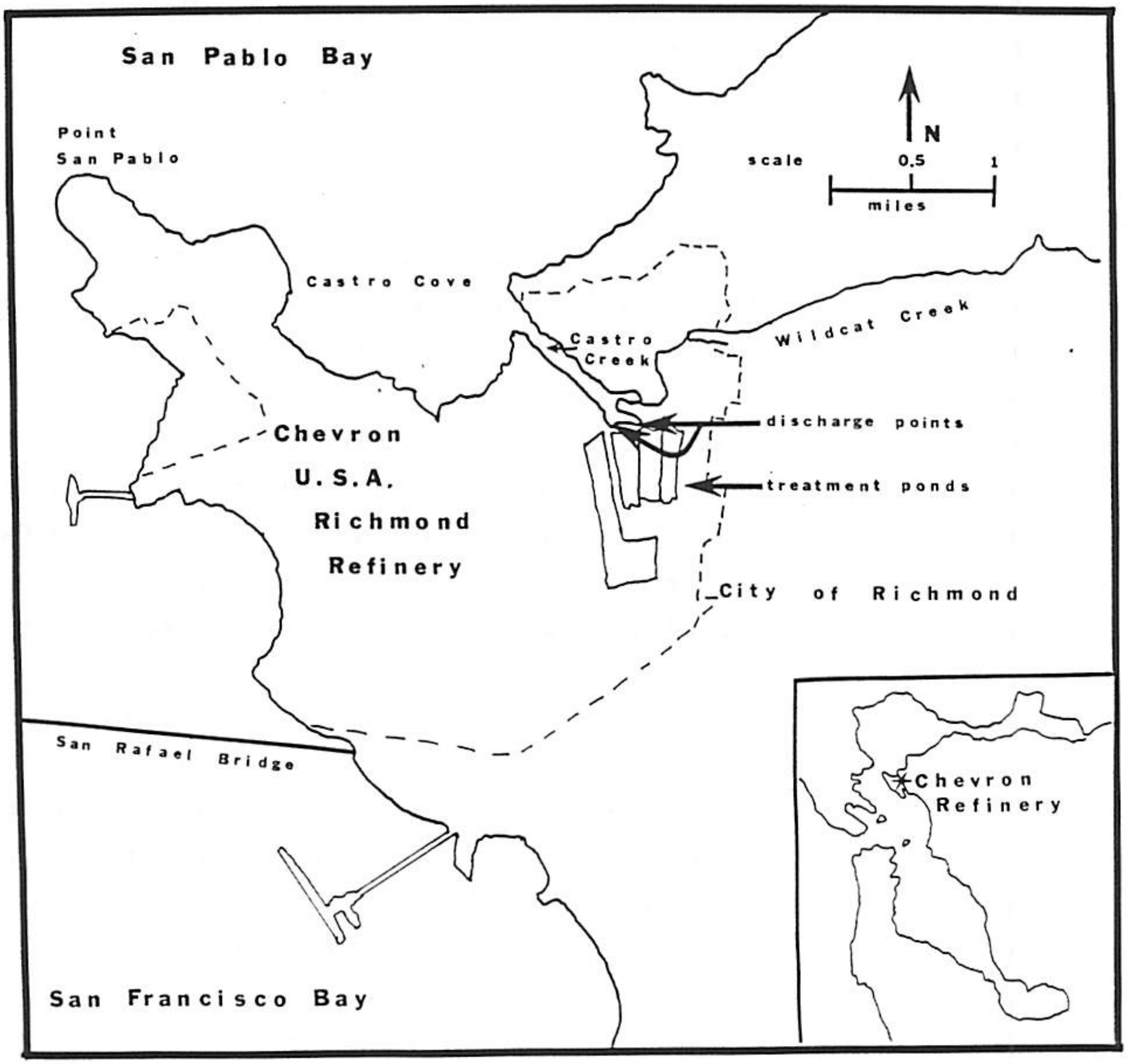

Figure 1: Chevron U.S.A. Inc. , Richmond Refinery

Source: After RWQCB, 1985

a self-monitoring program for the analysis of this wastewater's quality. Data from Chevron's analysis program indicate that the concentrations of several metals in the discharge reach levels that are regarded as toxic to organisms known to occur in the area of the effluent discharge (Ramo, 1985).

This report investigates Chevron's water quality analysis for several metals and researches the adequacy of the monitoring for estimating toxic effects on aquatic life in Castro Creek and Cove. An additional consideration is the applicability of toxicological data to this specific case. The discharge levels of chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) appear to pose the most serious problems to organisms in the Creek and Cove, such as polychaete worms (Capitella capitata), mussels (Mytilus edulis), rainbow trout (Salmo gairdneri) and striped bass (Morone saxatilis) (Ramo, 1985; CH_2M Hill, 1981). Investigation of the analytical techniques used in Chevron's water quality monitoring program will help to assess the adequacy of the program. Furthermore, evaluating the testing procedure may help to compare the reported concentrations of metals in the discharge with concentrations that are potentially harmful to aquatic life.

Background

The concentrations of metals in the Chevron discharge are within limits set by the Environmental Protection Agency (EPA) and do not themselves violate Chevron's waste discharge permit since the RWQCB has not specified limits for metals in discharges into San Francisco Bay. However, the permit (RWQCB, 1985), as well as the Clean Water Act (Karras, 1985, pers. comm.), prohibits any discharge which is harmful to aquatic biota in Castro Creek and Cove. Additionally, under summer conditions of low tide, the Chevron effluent is virtually the only water in Castro Cove, a direct violation of the State Water Resources Control Board's (SWRCB) Basin Plan which prohibits discharges into areas without an initial 10:1 dilution of effluent. For this reason, the RWQCB permit, approved in February 1985, prohibited the continuation of Chevron's discharge into Castro Cove after July 1, 1987 unless Chevron is granted an exemption by the RWQCB (RWQCB, 1985).

After several attempts to gain an exemption, Chevron presently plans to build a deep water outflow system which would dilute the effluent satisfactorily. Although a deep water discharge would benefit water quality in Castro Creek and Cove, it is likely to discharge wastewater into an area of San Pablo Bay that is a moulting region for Dungeness crab and that is in the migratory route of striped bass, two species already threatened by declining water quality in the Bay (Save S.F. Bay Assoc., 1985). At a February 1986 RWQCB hearing, Chevron agreed to build a deep water outflow as well as to upgrade some of its treatment system. Additionally, the RWQCB, which is in the process of developing metals and toxic pollutant standards specifically for discharges into the Bay, appeared willing to impose more restrictive limits on metals in Chevron's waste effluent (Karras, 1985, pers. comm.).

CBE Petition

The recent RWQCB action is largely the result of a petition filed with the SWRCB in May 1985 by Citizens for a Better Environment (CBE). The petition argued for a review of Chevron's discharge actions and RWQCB enforcement, including proposals for more stringent effluent standards (Ramo, 1985). Although there appears to be an agreed-upon problem with the levels of metals in the Chevron discharge, the complexity of metal interactions with the biological and physical environment makes the determination and application of appropriate standards a difficult task. In order to substantiate the validity of CBE's proposed standards, further study of the Chevron refinery discharge and its impact on the Bay ecosystem is necessary.

Much of the background research pertaining specifically to the Chevron discharge is summarized in the CBE petition. Elevated levels of metals in the discharge are implicated in the decline of the striped bass population in the Bay. Striped bass are known to exist in Castro Cove, including areas where Zn concentrations periodically exceed chronic and acute toxicity criteria specified in the SWRCB's 1976 Ocean Plan Amendments (SWRCB, 1976). The issue of toxicity to benthic organisms is also raised by CBE. Declines in benthic grazing, resulting in increased eutrophication, could affect the entire Bay ecosystem. The petition provides data showing that Cu and Zn levels in the discharge have reached levels that are toxic to mussels (Cu at 0.01 mg/l) and polychaete worms (Ni at 0.05 mg/l). Additionally, EPA Salt Water Criteria for metals are exceeded in the discharge (Table 1). The effects of bioaccumulation and synergism, while complicated, are also considered in the evaluation of the potential hazards associated with the levels of metals in the Chevron discharge (Ramo, 1985).

Included in the CBE petition are summaries of several previous studies which address the inadequate dilution in Castro Cove. The results of these studies are used to emphasize the need for improved water

	Concentrations in mg/l (ppm)			
	Cr	Cu	Ni	Zn
CBE Proposed Limits 30 day average/daily max.	0.02/NA	0.01/0.05	0.1/0.4	0.04/0.9
State Criteria (Salt Water)	NA	0.05	1.0	0.9
EPA Criteria (Salt Water)	NA	0.004	0.0071	0.058
Max. Level in 1984 Discharge	0.02	0.04	0.18	0.012
Max. Level in 1985 Discharge	0.025	0.006	0.0047	0.262

Table 1: Metals Discharge Levels and Standards

Source: Ramo, 1985; Karras, 1985

quality standards. In proposing new effluent standards, CBE uses criteria developed by the SWRCB for the shallow subtidal water fauna of the California coast, which, the petition argues, are similar to fauna in Castro Cove and Creek. Furthermore, the proposed criteria are specifically appropriate because they are based on toxicological studies of mussels (*Mytilus edulis*, *Mya arenaria*, polychaetes (*Capitella capitata*), crustaceans (*Sphaeroma pentodon*) and fish (three-spine stickleback, staghorn sculpin, striped bass) which are found in Castro Cove (CH_2M Hill, 1981; Ramo, 1985). In addition to arguing for the imposition of proposed criteria, the petition emphasizes the need for improvements in enforcement and monitoring of the Chevron discharge.

Chevron's Analysis of Metals

The CBE petition raises many important issues concerning the Chevron discharge. Several additional topics are considered in this report. Specifically, Chevron's analytical monitoring of metals in the discharge and the problems associated with metal speciation are important issues to be investigated in the evaluation of Chevron's discharge. Following National Pollutant Discharge Elimination System (NPDES) guidelines, Chevron's water quality analysis measures only the total metals concentrations using the APHA Standard Methods (APHA, 1975; Lyon, 1985, pers. comm.; Mumley, 1985, pers. comm.). Atomic Absorption Spectroscopy (AA), used by Chevron in metals analysis, is the most common analytical method for determining both the identity and amount of metal in water samples (APHA, 1975). AA gives no indication of what forms the metals are in, since all compounds are broken down to their elemental states during the analysis. AA is quite sensitive to Cr, Cu, Ni and Zn, but accuracy is somewhat suspect due to many possibilities for error and chemical interferences (Table 2) (APHA, 1975; Burns and Higgins, 1975; Gilbert and Kakareka, 1985). Wastewaters, with their complex mixtures of chemicals, give two-to-ten times less accurate determinations and two-to-ten times higher detection limits than the clean waters used as standards in AA (Posades, 1986, pers. comm.). Although specific samples may be problematic, the instrumentation and technology of

Metal	Limits of Detection (ppm)	Interfering Elements
Cr	0.02-0.1	Fe, Ni, Ar
Cu	0.02-0.1	no serious interferences
Ni	0.02-0.2	100 ppm Fe, Co, Cr
Zn	0.01	Si

Table 2. Limits of Detection and Interferences in the Atomic Absorption Spectroscopy of Metals

Source: Kolthoff and Elving, 1981; Posades, 1986, pers. comm.

AA analysis is quite precise, allowing systematic instrumentation errors of only 1-2 percent (Labash, 1986, pers. comm.; Kolthoff and Elving, 1981).

By using an automated sample collection procedure and by minimizing the time between sample collection and analysis, Chevron's monitoring system minimizes the possibilities for human error and inconsistencies. The time period between sample collection and analysis can significantly affect results, since metals become adsorbed to sample glassware. For the past five years Chevron has participated in an NPDES audit of their metals testing. According to a Chevron Environmental Specialist, their laboratory has consistently performed well in these audits (Lyon, 1985, pers. comm.). Although Chevron has claimed some problems in their ability to analyze selenium (Karras, 1986, pers. comm.), which is generally more problematic than most metals, Chevron's analysis of Cr, Cu, Ni and Zn adequately follows the RWQCB requirements. The concentrations of metals reported by Chevron can therefore be assumed to be accurate representations of the total metal concentrations actually present in the discharge.

Metal Speciation

The concentration of total metals reported by Chevron does provide an upper limit to the amount of toxic metals present in the discharge, but it gives no information about what fraction of the total may be toxic. Although metal toxicology is a complex field with many unanswered questions, there is general agreement that the identification of the metal's biologically active species is crucial in any toxicological analysis (Wood, 1974). The most toxic forms of Cr, Cu, Ni and Zn are the free ionic or hydrated forms of the metals (Babich and Stotzky, 1983; Borgmann, 1983; Kuwabara and Leland, 1985; Sprague, 1985; Petrocelli and Rand, 1985). Several cases are known in which complexed metals, those metal ions that are bound to organic molecules or inorganic anions, are more readily assimilated by aquatic organisms. Such cases, however, are exceptions, and it is generally correct to relate metal toxicity to the concentration of free metal ions existing in specific waters (Levinson et al., 1979).

Water Characteristics Affecting Metal Toxicity

The physical characteristics of the water carrying the metal influence the metal's speciation and consequently the toxicity, mainly by affecting the susceptibility of organisms to the metal's toxic effects (Babich and Stotzky, 1983; Bradley and Sprague, 1985; Sprague, 1985; Petrocelli and Rand, 1985).

A high concentration of complexing agents, such as organic chelating molecules, in a carrying water will bind a large fraction of the metal ions even though the level of total metal remains high. The importance of complexing agents is illustrated by the case of nitrilotriacetic acid (NTA), a complexing agent which effectively can eliminate Cu and Zn toxicity to brook trout even when metals are present at levels 33 times their threshold levels for toxicity (Sprague, 1968). Furthermore, high levels of cations, such as those found in seawater, reduce the metal assimilated by organisms through competition with metal ions for binding sites on organismal membranes and extracellular surfaces (Babich and Stotzky, 1983).

Since natural waters are dynamic oxidation reduction environments (James and Leckie, 1976), the influence of reducing potential (E_h) is significant. In a reducing environment, many metals, including Ni, precipitate as sulfides, which generally are not assimilated by aquatic organisms. In the case of Cr, the oxidized form, Cr^{+6}, is more toxic than reduced Cr^{+3} (Babich and Stotzky, 1983; Burns and Higgins, 1975). Since competing mechanisms appear to exist, the influences of pH on metal speciation and toxicity are hard to generalize. As pH increases, copper carbonate tends to precipitate, removing Cu as well as Zn, through adsorption and co-precipitation, from solution (Aulenbach et al., 1976). However, as pH increases, the toxicity of free Zn ion increases, but this is countered by the tendency of non-toxic Zn precipitates to form at high pH in natural waters (Bradley and Sprague, 1985).

Complicating the scenario are the effects of pH on water hardness and metal adsorption. For each metal there appears to be a small critical pH range at which the amount of metal adsorbed onto glass, debris or colloidal particles increases dramatically (James and Leckie, 1976). Increasing hardness, although affected by pH, generally decreases metal toxicity by precipitating the metals and by decreasing the permeability of organismal tissues to metals (Sprague, 1985; Babich and Stotzky, 1983; Borgmann, 1985). The effect of hardness may be seen in tolerance experiments in which fish reared in hard-water environments are found to be more resistant to metal toxicity than fish reared in soft-water environments (Zitko and Carson, 1976).

Problems in Toxicity Studies

Another area of concern with respect to metal speciation, is the concentration of metals regarded as toxic in toxicity studies. If metal speciation is not taken into account in toxicity studies, as is usually the case, results may be misleading or meaningless when applied to non-laboratory situations and when used in the development of water quality criteria (Sprague, 1985; Borgmann, 1983). For example, fish have been observed to be healthy in natural waters where metals concentrations exceeded levels which had been designated as toxic to the fish on the basis of toxicity studies (Kuwabara and Leland, 1985). A simple solution to this problem of metal speciation is to use the natural water of the specific area being studied in the toxicity tests themselves (Horne, 1986, pers. comm.).

Conclusions and Recommendations

Although the program of water quality analysis performed by Chevron seems to follow the requirements of the RWWCB permit, there is room for improvement which should get written into future permits. The fact that toxicity is due mainly to free metal ions suggests that free metal ion concentrations should be used as a basis for analytical measurements and water quality criteria (Borgmann, 1985). Reporting the concentrations of dissolved metals, or that fraction which passes through a 0.45 µm filter, may give a better indication of the toxic metal concentration in the discharge. However, the measurement of dissolved metals may be deceptive because some complexed, and therefore non-toxic metals may pass through the filter (Sprague, 1985). Additionally, the total metal content should not be ignored, because differences in the physical states of the monitored effluent water and the receiving water may change the metal speciation by altering E_h, pH, hardness or other parameters (Sprague, 1985).

In the development of standards for refinery discharges, more study is needed on the effects of metals in Bay water and on Bay organisms. In particular, further study is needed in descriptions of sub-lethal toxicity. For example, the first effect of Cu on rainbow trout (known to exist in Castro Cove) is a cessation of feeding which may eventually lead to death. However, the levels of Cu leading to this effect may not be considered in the development of water quality criteria, which are usually based on acute toxicity studies that are easier to undertake than investigations of sub-lethal toxicity (Kuwabara and Leland, 1985). The measures that Chevron has agreed to take (construction of a deep water outflow and upgrading of treatment systems) in combination with the enforcement of restrictive limits for metals for their discharge will do much towards the improvement of water quality in Castro Cove and Creek and the entire San Francisco Bay water system.

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