

Part G— Chromium (Cr) and Mercury (Hg) TMDLs

This support document provides the technical details of the accompanying TMDL document and has been provided for readers interested in the approach, the assumptions, and the data used to develop the mercury and chromium TMDLs. The organization of this document is as follows:

Section I, Pollutant Properties, outlines the chemical and physical properties of mercury and chromium for which TMDLs have been developed. Because of the persistent nature of these pollutants and their known impact on the environment, there is a substantial body of literature available that describes their properties. This section also provides a summary of the possible sources of mercury and chromium to the Rhine Channel.

Section II, Calculation of Loading Capacities and Existing Loads, outlines the process and scientific rationale used to calculate the loading capacities and existing loads and presents the calculations for mercury and chromium. For each compound, all equations, input parameters, and assumptions have been included, along with text that describes how the information was used in the analysis.

Section III, References, includes complete citations for each of the references included in the document.

Appendix 1, Data Analysis and Source Assessment, includes the data used to support the mercury and chromium TMDL analysis.

I. Pollutant Properties

The mercury and chromium TMDLs have been presented in a single document because they are similar in physical and chemical properties and are identified as needing TMDLs in Rhine Channel only. Although these properties differ for the two compounds, they both exhibit an ability to associate with sediments or other solids, and to accumulate in the tissue of invertebrates, fish, and mammals.

The summaries have been developed by reviewing published reports and are focused on the properties that influence their behavior in the environment. This information provides a better understanding of these compounds and supports the TMDL analysis through the selection of values to represent environmental processes.

Mercury (Hg)

Mercury is naturally occurring metal that has several chemical forms: Hg(0), Hg(I) and Hg(II). It may enter the water or soil from natural mineral deposits and volcanic activity. Mercury combines with other elements, such as chlorine, sulfur or oxygen to form inorganic mercury salts, which are usually white powders or crystals. Metallic mercury is used to produce chlorine gas and caustic soda, and is sometimes used in thermometer, dental fillings, and batteries. Inorganic mercury enters the air from mining ore deposits, coal-fired power plants, chlor-alkali plants, cement manufacturing. Cinnabar (HgS) is the most common ore of mercury. Mercury is also used in seed dressings, fungicides, paints, and slimicides. Mercury laden soils or sediments may be a source of mercury in various chemical species.

Mercury also combines with carbon to make organic mercury compounds. Methylmercury (CH_3Hg^+) is produced primarily by microscopic organisms in the water or soil. The formation of methylmercury is the most significant transformation because methylmercury is far more toxic than any other form of mercury. Most scientists observe that anaerobic conditions are required for conversion of inorganic mercury to methylmercury. Organic forms of mercury build up in animal tissues; methylmercury is the prominent chemical species. Since mercury bioaccumulates in tissues, animals at higher trophic levels, such as larger and older fish or birds, tend to have the highest levels of mercury.

The human nervous system is very sensitive to all forms of mercury. Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the kidneys and brain. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems. Short-term exposure to high levels of metallic mercury vapors may cause effects including lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes and eye irritation. Mercury's harmful effects may be passed from mother to nursing infant via breast milk. Developmental problems may result such as brain damage, mental retardation, incoordination, blindness, seizures, and inability to speak (ATSDR 2001).

Possible Mercury Sources

Most sources of mercury to the Rhine Channel are anthropogenic. Monitoring results suggest that existing sediments in Rhine Channel are the largest source of mercury. The Regional Board technical report (1998) defines the Rhine Channel as a toxic hot spot and states that historical uses of ship anti-fouling paints containing mercury and other metals may be responsible for elevated sediment levels. However, no investigation has been completed to explain the elevated (total) mercury sediment concentrations within Rhine Channel.

Orange County Coastkeeper (1999) measured mercury concentrations in one sediment core and the results provide a historical perspective. The highest concentrations of total mercury (11 mg/kg dry) were found at the bottom of the core and the lowest concentrations (3.4 mg/kg dry) were found at the top of the core. Other researchers have found similar sediment concentrations in Rhine Channel; the most recent data reported by SCCWRP (2001) reports 5.8 mg/kg dry and SARWQCB (1998) reports (8.7 mg/kg dry). However, these levels are still high enough to contribute to the degradation of benthic organisms. Mercury exceeds the Effects Range-Median (ERM) guidelines in the Rhine Channel (SARWQCB 1998). Table G-1 summarizes observations of mercury and chromium levels in the Rhine Channel sediments.

Table G-1. Chromium and Mercury Sediment Monitoring Results for Rhine Channel

| Organization (cite) | Collection dates | Location | Cr conc. (mg/ kg dry) | Hg conc. (mg/ kg dry) | |
|----------------------------------|------------------|-------------------|-----------------------|-----------------------|----------------------------|
| SCCWRP (2001) | 5/01 | Boatyard launch | 44.0 | 5.80 | |
| | 9/00 | See above | 26.0 | 5.30 | |
| OCPFRD (2000) | 4/96 -- 6/00 | Rhine -- bend | 13.3 – 60 | N/a* | Mean = 24.4 Median = 17 |
| BPTCP (1997) | 1996 | N/A | 69.6 | 8.74 | |
| | 1994 | N/A | 51.5 | 7.62 | |
| Coastkeeper (1999) | 1999 | Rhine -- middle | 13 | 4.4 | |
| Coastkeeper Sediment core (1999) | 1999 | Rhine -- bend Top | 16 | 3.4 | |
| | 1999 | Top-middle | 15 | 7.6 | |
| | 1999 | Mid-bottom | 13 | 9.8 | |
| | 1999 | Bottom | 12 | 18 | |

*currently, OCPFRD does not monitor for mercury; mean and median values are for chromium.

N/A= not available

Mercury-containing sediments may also have been transported from the San Diego Creek watershed into the Rhine Channel. Historic records show mercury mining occurred at Red Hill mine between 1880 and 1939 (CA Division of Mines 1976). According to this report, 130 seventy-six pound flasks of mercury were produced between 1927 and 1929. Minor mercury production is also reported for 1932-33 and 1939. Insufficient information is available to accurately interpret sediment transport from this historic mining site.

Atmospheric deposition is believed to be an active source of mercury; however, compared to inputs from existing sediments and contributions from freshwater sediment deposition, atmospheric deposition of mercury is considered negligible. In addition, ambient seawater concentrations of mercury are extremely low, typically less than 1 ng/L, indicating that seawater is an insignificant source of mercury in the Rhine Channel.

Chromium (Cr)

Chromium is a naturally occurring element found in plants, rocks, soils, and volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium (0), chromium (III), chromium (VI). Metallic chromium (0) is used for making steel. Chromium (III) and (VI) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving.

Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. Fish do not accumulate much chromium in their tissues from water. Chromium (III) is an essential nutrient that helps humans metabolize sugar, protein and fat. Chromium (VI) is classified as human carcinogen by the World Health Organization. Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (III) or chromium (VI). Allergic reactions consisting of severe redness and swelling of the skin have been noted (ATSDR 2001).

Possible Chromium Sources

A wide range of information was accessed to identify potential sources of chromium and mercury and to characterize contributions, including monitoring data, data from national, state and local databases, and scientific literature. The source analysis section focused on possible point, nonpoint, and tributary sources. Sources of chromium in the Rhine Channel include existing sediments in Newport Bay, historic deposits in the San Diego Creek watershed, and possibly atmospheric deposition. Sources of chromium may include paint chips, dust, and grit from shipyard operations, leaching of anti-fouling paints from boat hulls, and storm water runoff from industrial areas. Chromium may also be leaching from treated wood pylons in marine areas (Warner and Solomon 1990). Recently reported levels of chromium in Rhine Channel sediments are shown in Table G-1.

According to Regional Board records, a potential source of chromium inputs to the Rhine Channel is the former Newport Plating facility located at 2810 Villa Way in Newport Beach (see Figure A-7, TSD Part A). Chromium has been found at excessive levels both in soil samples (maximum concentrations of 8,160 mg/kg total chromium and 34.7 mg/kg Cr⁶) and in groundwater (0.03 – 1.98 mg/L as total Cr) beneath the facility (Petroleum Industry Consultants, Inc., 1987; Remedial Action Corporation, 1988). (Other contaminants identified in borings and groundwater monitoring wells at the facility include cadmium, copper, nickel, and zinc.) On March 19, 1987, Orange County cited (Notice to Correct) the operator of the plating facility for leaking of finishing wastewater (OCHCA, 1987). The facility was the site of several spills during its period of operation (approximately 20 years) and many of the solutions used in the plating process were disposed to a floor drain that discharged directly to the soils beneath the facility (SARWQCB facility investigation reports, March 25 and April 7, 1987). A Cleanup and Abatement Order (CAO No. 87-83) was issued to the property owner and the operator of Newport Plating on May 18, 1997. On December 11, 1987, the operator discharged wastewater to City of Newport Beach surface drains in violation of the CAO (SARWQCB staff report, February 11, 1988). A storm drain that connects directly to the Rhine Channel is located at the southern end of the plating facility property (Figure A-7, TSD Part A).

The plating facility closed in March 1988 after the owner evicted the operator of the facility. In 1990 the case was referred to the Attorney General for collection of ACL assessments (Resolution No. 90-100). It appears that the site has not yet been remediated based on a visit to the facility on February 7, 2002, by Regional Board staff (the facility and property did not appear to have been disturbed). OCHCA staff indicated that the plating waste inside the facility was cleaned and disposed of on March 3, 1988, but they have no records indicating that the soils and groundwater beneath the facility were cleaned up or remediated (pers. comm., B. Pepki). Therefore, soils and groundwater beneath the facility are likely continuing to contribute to the pollutant loading in the Rhine Channel.

Currently, there is not sufficient information to estimate chromium atmospheric deposition rates in the Newport Bay watershed.

Review of Sediment Targets

As discussed in the TMDL document, two targets have been identified for each chemical, one for sediment and one for tissue levels. The primary target value (sediment) is for TMDL development, whereas the alternate target (tissue) is designed to provide another means of assessing desired water quality conditions of Rhine Channel.

There are several available screening values for mercury concentrations in sediment and fish tissue. For mercury in Rhine Channel, EPA applied the sediment numeric target, 0.13 mg/dry kg, as the most appropriate indicator of desired water quality. This threshold effect level (TEL) is associated with no observed effect on benthic organisms as part of a study by MacDonald et al. 1996 and cited in NOAA SQuiRTs (Buchman 1999). For comparison, the TEL value is much lower than the probable effects level (PEL = 0.696 mg/kg dry). The NOAA Effects Range-Low (ERL) value for mercury (ERL = 0.15 mg/kg dry) is close to the TEL target value.

EPA has also evaluated the available water quality criteria and levels for sediments and fish tissue to determine the appropriate numeric target for chromium TMDL in Rhine Channel. EPA selected the sediment target (52 mg/kg dry, Buchman 1999) as the best available target to protect both wildlife predators and benthic organisms.

Table G-2. Sediment Targets Used in the TMDL Analyses

| | Mercury (mg/kg)* | Chromium (mg/kg)* |
|---------------|---------------------|----------------------|
| Rhine Channel | 0.13 | 52 |

* dry weight

II. Calculation of Loading Capacities and Estimate of Existing Loadings

General Conceptual Approach

The loading capacity for each pollutant represents the maximum loading that a waterbody can assimilate and still meet and maintain water quality standards. For the mercury and chromium addressed in these TMDLs, long-term loadings at or below the loading capacities should eventually result in reduction in concentrations of these compounds in bottom sediment to levels protective of the standards. A review of available data (see Appendix 1 for a summary of the data used in the TMDL analysis) indicates that bottom sediments currently exhibit elevated mercury and chromium concentrations. The higher the current concentrations in bottom sediments, the longer it will take to meet standards, even if external sources are reduced.

The approach to determining the loading capacities for mercury and chromium is similar to the approach used for the organochlorine compounds (TSD – Part F) and was based on an understanding of the sources of these compounds (past, present, and future) and the transport and ultimate fate of these compounds in various environmental media. Based on a review of literature sources, it was observed that mercury and chromium environmental persistence and affinity for adsorbing to sediment and accumulating in biota generally limits their presence in the water column, at least relative to sediment and biota. The loading capacities were determined by “back-calculating” the allowable load from the selected sediment target (Table G-2) and the associated estimates of sediment loads.

The calculation of existing mercury and chromium compound loads, which are not required components

of the TMDLs, allows for a relative comparison the estimated current loading to the calculated loading capacity. In contrast to the calculation of the loading capacities, which was accomplished through back calculation from the sediment targets, the existing loadings were based on review and analysis of available sediment data.

Calculation of Newport Bay Loading Capacity and Existing Loads

Previous modeling studies, completed by RMA for the U.S. Army Corps of Engineers (USACE) have examined the circulation patterns, and transport and deposition of sediments in Newport Bay (RMA 1998, 1997). By examining model calibration results (RMA 1997) for Newport Bay from 1985-1997, the sediment deposition in Rhine Channel was estimated. Historic pollutant loads to the bottom sediment were estimated by using observed pollutant concentrations in bottom sediments and net sedimentation rates. Sediment volume was converted to dry weight using an estimated porosity of 0.65.

Figure G-1 presents a schematic of the approach used to calculate the loading capacity and existing loads for Mercury and Chromium for Rhine Channel.

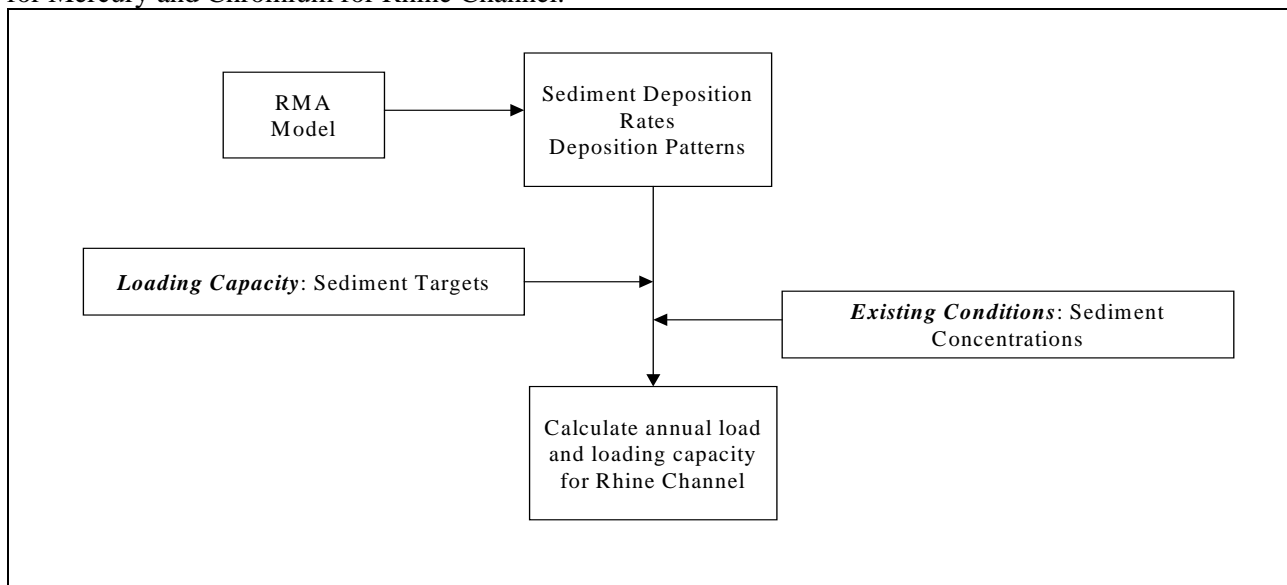


Figure G-1. Schematic of Loading Calculation Steps

The approach relies on the following key information:

Sediment deposition rates (from the RMA (1997) model)

Sediment deposition patterns (from the RMA (1997) model)

Sediment pollutant targets (used for loading capacity) (see Table G-2)

Sediment mercury and chromium concentrations from observation data (used for existing loads) (see Table G-1 and Appendix 1)

The remainder of this section presents the loading capacity calculations for mercury and chromium. For each compound, all equations, values applied, and references used in the calculations are included.

Summary of Approach for Calculating Loading Capacities and Existing Loads of Mercury and Chromium Compounds for Rhine Channel

The following equation was used with sediment target concentrations (C_s) (Table G-2) to calculate the

loading capacities. For existing loadings, the same equation was used with concentrations from existing sediment data substituted for the sediment targets.

$$\text{Load (g/yr)} = C_s \times D_s \times \rho_s \times (1 - P_s) \times CF$$

where:

| | | |
|----------|---|--|
| C_s | = | sediment concentration (mg/kg dry) |
| D_s | = | sediment deposition (m^3/yr) |
| ρ_s | = | sediment density (kg/m^3) |
| P_s | = | sediment porosity |
| CF | = | conversion factor from mg to kg |

The values for all parameters used in the analysis for Newport Bay and Rhine Channel are presented in Table G-3.

Table G-3. Parameter values used in the Rhine Channel TMDL analysis.

| | g/kg dry) | | ρ_s (kg/m^3) | P_s | CF |
|----------|----------------------|--------------------------|-------------------------------------|-------|----------|
| | Target Concentration | Observed Concentrations* | | | |
| Mercury | 0.13 | 5.8 | 2,500 | 0.65 | 0.000001 |
| Chromium | 52 | 44 | | | |

D_s (m^3/year): Rhine Channel: 859.23

*SCCWRP (2001), 2001 sampling data

Calculations

Mercury

Loading Capacity

$$\text{Rhine Channel Loading Capacity (kg/yr)} = 0.13 \times 859.23 \times 2,500 \times (1 - 0.65) \times 0.000001$$

Existing Loading

$$\text{Rhine Channel Existing Loading (kg/yr)} = 5.8 \times 859.23 \times 2,500 \times (1 - 0.65) \times 0.000001$$

Table G-4. Existing and Loading Capacity for Rhine Channel for Mercury

| Mercury | Existing Load (kg/year) | Loading Capacity (kg/year) |
|---------------|-------------------------|----------------------------|
| Rhine Channel | 4.39 | 0.10 |

Chromium

Loading Capacity

$$\text{Rhine Channel Loading Capacity (kg/yr)} = 52 \times 859.23 \times 2,500 \times (1 - 0.65) \times 0.000001$$

Existing Loading

$$\text{Rhine Channel Existing Loading (kg/yr)} = 44 \times 859.23 \times 2,500 \times (1 - 0.65) \times 0.000001$$

Table G-5. Existing Loading and Loading Capacity for Rhine Channel for Chromium

| Chromium | Existing Load (kg/year) | Loading Capacity (kg/year) |
|---------------|----------------------------|-------------------------------|
| Rhine Channel | 33.1 | 39.10 |

III. References

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Appendix 1: Data Analysis and Assessment

This appendix presents the data available to characterize the level of contamination by chromium and mercury in Rhine Channel. Monitoring data are available for three media: water, sediment, and tissue. The following data summaries are organized by the source/agency.

Bay Protection and Toxic Cleanup Program Data (BPTCP): This study reports sediment concentrations at various locations in the Newport Bay for Mercury and Chromium. Sediment sample data in mg/kg was available from two sampling events that took place in 1994 and 1996. This data was not used in the analysis but is reported in Table G-1.

Newport Bay Sediment Toxicity Studies (SCCWRD, 2001): Sediment samples collected at 10 Newport Bay stations in May 2001 were available. Sediment data in mg/kg for Cr and Hg at selected locations in Rhine Channel was used to estimate the existing loading capacity.

Resource Management Associates report (RMA, 1997): Estimates of the sediment distribution for the Upper Bay, Lower Bay and Rhine Channel were made using the results of sediment transport model developed by RMA. The model simulates wet and dry conditions as well as the largest storm event from 1985-1997. Because most sediment entering Upper Newport Bay occurs during the storm events, mean daily stream discharge records for San Diego Creek were used to develop a five-day hydrograph which were used to simulate storm event for RMA model. The peak flows for each model simulation years are shown in Table 2 below. A detailed description can be found in the RMA report (RMA, 1997). The sediment deposition rates for Newport Bay were derived from 12-year model simulation results. Although the mean values are used to estimate the sediment budget for the Newport Bay, the sediment deposition rates represents a net deposition over the years.

The following tables list data from different sources by the various sources used in the analysis. The most recent sediment data (May 2001) was used from the Newport Bay Sediment Toxicity Studies Report, October 23, 2001 (Tables 8, 9 and 10) (SCCWRD, 2001).

Table 1. Sediment Chemistry Toxicity Data used in the TMDL

| Location | Chromium | Mercury |
|---------------------|-----------|-----------|
| | mg/kg dry | mg/kg dry |
| Rhine Channel (NB3) | 44 | 5.8 |

All non-detects were taken as zero

Table 2. Sediment Deposition rates in Newport Bay – Estimated from the RMA (1997)

| Location | Sediment Deposition (m3/year) |
|--------------------------------|-------------------------------|
| Unit I basin | 31474.17 |
| Unit II basin | 30327.34 |
| South of Unit II | 11659.46 |
| Downstream to PCH Bridge | 7772.97 |
| Upper Newport Bay Total | 81233.95 |
| Lower Bay | 17444.29 |
| Turning Basin | 6782.52 |
| Newport channel | 5697.20 |
| Lower Newport Bay Total | 29924.01 |
| Rhine Channel* | 859.23 |

*Rhine Channel deposition rates used for this analysis.