Estimated Atmospheric Deposition Fluxes of Dioxins in the San Francisco Estuary

by
Rachel Allen and Don Yee

SAN FRANCISCO ESTUARY INSTITUTE
4911 Central Avenue, Richmond, CA 94804
p: 510-746-7334 (SFEI), f: 510-746-7300,
www.sfei.org

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Introduction and Background

Polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs), often collectively referred to colloquially as "dioxins", impair the human fish consumption beneficial use of the San Francisco Estuary. In 1994, the California Office of Environmental Health Hazard Assessment (OEHHA) issued a fish consumption advisory for San Francisco Bay due to the presence of pollutants in fish, including dioxins. Fish caught from the Estuary have shown dioxin (and PCBs with dioxin-like activity) concentrations above the threshold for unrestricted consumption (SFEI and CDHS 2001, Davis et al. 2011), and as a result, the Bay was listed in 1999 under section 303(d) of the Clean Water Act as a water body that fails to meet water quality standards for dioxins. Although the majority of the dioxin-like activity was from PCBs, dioxins typically accounted for about 20% of the total risk.

Due to the low ambient concentrations and high analytical costs of dioxin analyses in environmental matrices, there are relatively few sets of data on local ambient dioxin concentrations. The available data was synthesized in a conceptual model/ impairment assessment prepared for regional environmental managers and stakeholders (Connor et al. 2004), where many data gaps in our understanding of regional dioxin sources and environmental processes became apparent. As a result, the Regional Monitoring Program (RMP) for Water Quality in the San Francisco Estuary, in concert with interested stakeholders, developed a "dioxin strategy" to address the numerous gaps in understanding, ranging from the ambient distribution and inventories of dioxins in various matrices, to the sources and loadings from various pathways.

The Bay Area Air Quality Management District (BAAQMD), in collaboration with the California Air Resources Board (CARB) and United States Environmental Protection Agency (USEPA), conducted a study to measure ambient air concentrations of dioxins in various urban locations in California, including a number of stations in the San Francisco Estuary region. That study collected data from late 2001 to mid-2006, but the reporting and data interpretation did not include analyses to estimate resultant impacts on other media (e.g. deposition). As a result, this special study for the RMP was conducted to apply the indirect (modeled) methods previously used for estimating PCB and PAH deposition to estimating dioxin deposition, which will help in development of a mass budget for dioxins in the region.

Sources of Dioxins.

Various dioxin compounds are often produced as byproducts of combustion of various materials, although they are also produced as byproducts in the manufacture of other chlorinated organic compounds (e.g., 2,4,5-Trichlorophenoxyacetic acid (infamously a component of Agent Orange), and pentachlorophenol (a wood preservative)), but improvements to manufacturing methods have generally reduced the amount of the more toxic dioxin isomers present as by-products in these chemicals. The Bay Area Air Quality Management District (BAAQMD) listed PVC production, wood-burning, and diesel emissions as the major regional sources (Figure 1). EPA is in the process of refining its estimates of the importance of wood-burning and diesel emissions. Currently, these estimates are subject to a high degree of uncertainty. Dioxin congener sums are reported as Toxic Equivalency Quotients (TEQ), where each congener is weighted relative to the most toxic dioxin, 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin. Total 2002 regional emissions were estimated by BAAQMD to be about 3.1 g TEQ/yr. As national regulations of dioxins have

tightened, it is thought that most of the large, regulated point sources have been significantly reduced (Figure 2).

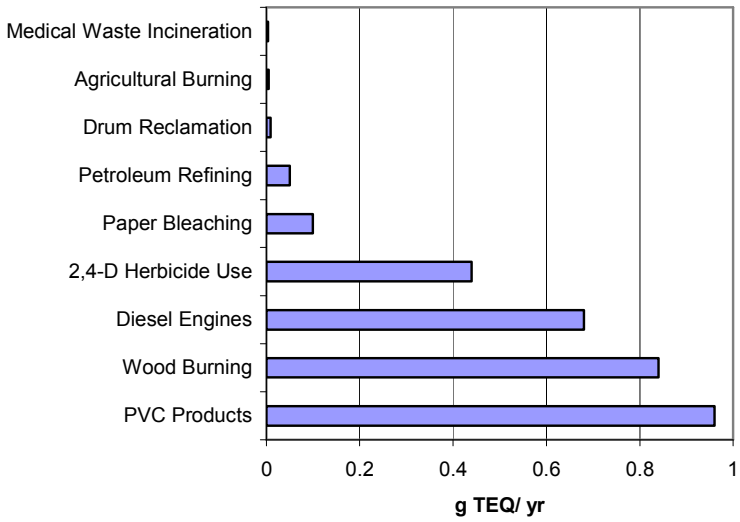

Figure 1. Sources of dioxin and furan emissions in the San Francisco Bay Area (BAAQMD 2002).

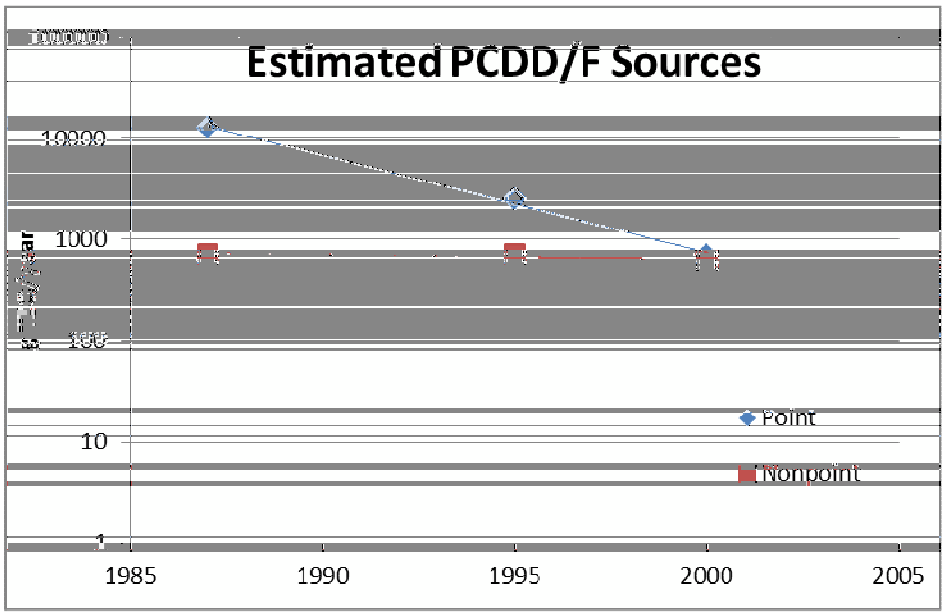

Figure 2. Past and projected PCDD/F emissions from point and non-point sources in the United States (U.S. EPA 2006).

The largest current sources of dioxins emit these compounds into the atmosphere. Once in the atmosphere, dioxins can deposit either directly onto the surface of the Bay (direct deposition) or onto the watershed, where they may be transported to the Bay in stormwater runoff. Dioxin concentrations in ambient air and precipitation can therefore provide an important indication of

sources. Prior to the BAAQMD/CARB/EPA study there were few readily available data on PCDD/Fs in ambient air in California, with only two sites operated by the National Dioxin Air Monitoring Network (NDAMN) in operation during 2000 (one during 1999). Nationally, atmospheric PCDD/F TEQs (calculated from (Cleverly et al. 2007) using World Health Organization 2005 Toxic Equivalency Factors) from 1999-2002 at 24 rural NDAMN sites averaged 10.0 fg TEQ/m^3, while the average TEQ in air measured at 7 remote sites was 1.0 fg/m^3. These data, from rural and remote sites, provide information on background ambient concentrations of dioxins in the United States.

Data on concentrations of PCDD/Fs in precipitation for the San Francisco Bay area were not available in this recent BAAQMD/CARB/EPA study nor were they available in earlier studies in California. Studies in other areas have indicated roughly equal wet deposition loads and particulate dry deposition estimates (Koester and Hites 1992, Correa et al. 2006, Wang et al. 2010). However, due to the Mediterranean climate of the region, there is effectively no wet deposition during the summer months (average <3 cm precipitation May-Sep from 1981-2010 in San Francisco (Null 2011)), and therefore a lower proportion of wet deposition to dry deposition would be expected in this region than for most other areas of the United States. These and other data gaps and uncertainties in estimating atmospheric deposition loads of dioxins are explored in the discussion of results.

Methods

The methodology for estimating atmospheric deposition loads overall followed that used previously by Tsai et al (2002) for estimating loads of PCBs and PAHs to San Francisco Bay surface waters. However, although air samples were collected using similar methods for trapping particulate and vapor phase pollutants, the collected fractions were not analyzed separately. As a result, distributions between particulate and vapor phase fractions for use in estimating deposition had to be calculated using average concentrations of atmospheric particulates and partitioning constants derived from the literature adjusted to San Francisco conditions.

Data

Air and water data from three different sources were used in these deposition calculations. Ambient air concentrations of dioxins came from the BAAQMD/CARB/EPA study conducted 2001-2006, and concentrations of atmospheric particulates were obtained from routine CARB monitoring from 2006 to 2009. Meteorological data were obtained from the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center for 2006 to 2009. Ambient concentrations of dioxins in San Francisco Bay surface waters were obtained from RMP data, which so far includes only a single year (2009) of dry season (summer) data.

CARB data

The data set of concentrations of dioxin congeners in air from the BAAQMD/CARB/EPA study represents the only set of measurements for the region containing at least a year's worth of atmospheric dioxins concentrations. The data were collected roughly monthly between December 2001 and May 2006 at air stations around the state. The stations at Oakland and San Jose were selected to represent the Central and South Bay, respectively. The average monthly concentrations for each congener at Richmond and Crockett stations were averaged together to represent the North Bay. One Bay Area station monitored by CARB was not used in the calculation: the Livermore station was too far downwind and east of the Bay to be considered relevant for estimating Bay deposition; although had it been the only Bay area site, the data would have been used for lack of any better alternatives (e.g. a Concord site was used to represent regional PCB and PAH concentrations in Tsai et al. (2002)).

Data collected and reported by CARB were only reported as total concentrations. Because the rate of deposition is highly dependent on the mode of deposition, we needed to calculate the fractionation of dioxins between particulate and gaseous (vapor) phases. A previous study by NOAA for modeling dioxin emissions and transport on a nationwide scale (Cohen et al. 2002) determined partitioning based on PM10 concentrations and temperature for urban and non-urban land use categories. Particulate concentrations assumed for urban areas in that study were slightly higher than typically measured in the Bay area (mean 20 $\mu g/m^3$ vs 26 $\mu g/m^3$ for urban areas in the NOAA study), so partitioning was linearly scaled to adjust for the differences in average ambient particulate concentrations. The PM10 concentration for the Bay Area was determined based on air quality data from Bay Area stations from 2006 to 2009, available from CARB at http://www.arb.ca.gov/adam/select8/sc8start.php.
Of the 2414 dioxin congener results for analyses performed on air samples at the Crockett, Richmond, Oakland and San Jose stations, 69 of them were reported as "not detected". To account for these non-detects, the ratio between each congener and OCDD (r_{sample}) was calculated for all of the detected values, and averaged across each congener (r). The non-detected values were then replaced by this average ratio multiplied by the OCDD concentration for the sample date and location (OCDD was detected and quantified in all samples). These substituted values were used in the calculation of monthly mean concentrations at each site of interest. The impacts of this technique are discussed in the sensitivity analysis.

NOAA climate stations

Meteorological data were obtained from NOAA National Climatic Data Center to represent North, Central, and South Bay regions. San Jose was used to represent the South Bay, Alameda, Oakland, and San Francisco represented the Central Bay, and for lack of a station more centrally located in that segment, Richmond was used to represent the North Bay. Wind speed and temperature data collected hourly from 2006 to 2009 were used to determine an average wind speed and temperature for each month for each Bay segment. The more recent meteorological data were chosen in order to include meteorological stations added since 2006 which are more proximate to the dioxin monitoring locations. Wind speeds at the height of meteorological stations (typically 10m above ground) are generally higher than those at the land (or water) surface (Andreas et al. 2006), so transfer rate estimates based on these meteorological station data tend to represent upper limits. Temperature is critical for determining the air water interface (gaseous) mass transfer, and measurements of water temperature are generally taken at some depth below the water surface, so air temperatures (taken concurrently with wind speeds) are likely a better approximation of water surface layer temperature.

RMP bay surface water

Besides the RMP set of dioxin concentrations in ambient Bay surface water, there are very few other measurements of dioxin congeners in Bay water. Dioxin concentrations for three stations (one each in North, Central, and South Bay) were measured in a special study for the RMP in 2002 and 2003, but all three were RMP historical stations located in deep water areas of those Bay segments, likely biased towards lower suspended particulate and contaminant concentrations than most (generally shallower) areas of the Bay nearby. For this work, data was collected during the summer of 2009 from a mix of 13 shallow and deep water stations representative of Bay ambient conditions. The concentrations from the two or three stations in each of the five Bay segments were averaged together, and then weighted by segment area to compute each of the North, Central and South Bay average concentrations. Dioxins were measured in whole water samples at 11 sites, and in particulate and dissolved phase fractions at 2 sites. While there are no data for surface water concentrations during the winter season in the Bay, we do not expect dioxin concentrations to vary more than 0.5 to

2 times the summer levels, based on an analysis of seasonal variations in PCB and PAH concentrations from 1993 to 1999 (San Francisco Estuary Institute 2012). For PCBs, winter concentrations are 1-1.7 times the summer concentrations in the South and Central Bays, but 0.5-0.7 times summer concentrations in San Pablo and Suisun Bays. This seasonal and spatial pattern is consistent with a conceptual model of PCB sources that includes increased wet season loading from urban areas due to point sources and greater relatively clean freshwater flow from the Delta in the North Bay. PAHs vary less seasonally, with winter concentrations in the South and Central Bays 0.9-1.4 times the summer concentrations, while winter concentrations in San Pablo and Suisun Bays were 0.5-0.9 times the summer concentrations. Therefore, we expect winter dioxin concentrations to remain within conservative bounds of 0.5-2 times the summer concentrations. The implications of this bounding will be discussed in the sensitivity analysis.

Of the 267 analyses performed on surface water samples, 110 of them were reported as "not detected". We applied the same technique of substitution for non-detects with RMP surface water data as for the air data, and evaluated the effect of this approach in the sensitivity analysis below.

Calculation

An estimate of net loading for each congener for each month was determined from calculations of loading due to particulate dry deposition, loading due to wet deposition, loading due to gas absorption, and loss due to volatilization.

Particulate Dry Deposition

Particulate dry deposition occurs when dioxin molecules attached to suspended particulate matter settle from the air onto the water surface. Loading due to dry deposition of particulate phase dioxin (*L(p)*: g/year) is determined as follows,

$$L(p) = \left(A * C(a,p) * V_d\right)/1000 \qquad \textbf{Equation 1}$$

where A (km^2) is the surface area of the Bay segment, $C(a,p)$ (ng/m^3) is the particulate concentration of the congener in air, and V_d (m/year) is the particulate deposition velocity.

The particulate deposition velocity, V_d, was determined based on the geometric mean of literature values of particulate deposition velocities in urban areas, 0.00143 m/s (45200 m/year) (Table 1) (Dueri et al. 2010). The particulate deposition velocities were calculated or modeled for individual dioxin and furan compounds; however, we aggregated the values under the assumption that the estimate of gas/particle partitioning accounts for differences in particle deposition velocity. Because the partitioning of dioxins onto different particle sizes and the particle size distribution in this region are not known, any estimate of distinct deposition velocities for individual compounds would be overly precise for this calculation.

Table 1. Reported values for dry deposition velocity

Dry deposition velocity (m/s)	Reference
0.00086 – 0.006	(Koester and Hites 1992)
0.0004-0.0008	(Moon et al. 2005)
0.0015-0.0035	(Correa et al. 2006)
0.00143	**geometric mean**

The particulate concentration in air is the fraction of the total concentration, *C(a)* (ng/m^3), that is sorbed to particulate matter (Equation 2).

$$C(a,p) = C(a) * F_p \qquad \textbf{Equation 2}$$

The partitioning coefficient of each congener, F_p, is dependent on the concentration of particulate matter in the air and the air temperature. This calculation is given in Equation 3-Equation 6, and further details are well described in the supporting information of the NOAA study (Cohen et al. 2002).

$$F_p = \frac{cS_t}{P(T) + cS_t} \qquad \textbf{Equation 3}$$

The total surface area of the particles is S_t (cm^2/cm^3), $P(T)$ (atm) is the saturation vapor pressure of the dioxin congener at the temperature of interest, and c is an empirical constant, estimated to be about $1.7*10^{-4}$ atm-cm. Because the average Bay Area PM10 concentration was about 25% lower than the average value for urban areas used in the NOAA study, we reduced S_t by the same amount in the partitioning coefficient calculation, yielding an area of $2.7*10^{-6}$ (cm^2/cm^3). This decreased the partitioning onto particulate matter by at most 20% for the relevant temperature range.

The saturation vapor pressure for aerosol partitioning, $P(T)$, is best approximated by the subcooled liquid vapor pressure, P_l, which is related to the solid vapor pressure, P_s, as shown in Equation 4.

$$\ln\left(\frac{P_l}{P_s}\right) = \frac{\Delta S_f (T_m - T)}{RT} \qquad \textbf{Equation 4}$$

In this equation, ΔS_f (atm m^3/ mol K) is the entropy of fusion, which is approximated by 6.79 R (R is the gas constant); T_m (K) is the melting temperature of the solid dioxin congener; and T (K) is the ambient temperature.

The solid vapor pressure of each dioxin congener, P_s, at the temperature of interest is estimated from Equation 5,

$$\ln\left(\frac{P_1^s}{P_2^s}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \textbf{Equation 5}$$

where P_1^s and P_2^s (atm) are the solid vapor pressures at temperatures T_1 and T_2 (K), respectively, and R is the gas constant. The enthalpy of vaporization ΔH (J/mol) can be estimated from the boiling point of the congeners, T_b (K), with Trouten's Rule, Equation 6.

$$\frac{\Delta H}{T_b} = 84\frac{J}{molK} \qquad \textbf{Equation 6}$$

Wet Deposition

Rain scavenges both particulate-bound and vapor phase dioxins from the atmosphere, depositing a flux ranging 0.3-1.3 times (median 0.65) the particulate dry deposition rate for various sites in the literature (Koester and Hites 1992, Correa et al. 2006, Wang et al. 2010). As in previous efforts (U.S. EPA 2004), wet deposition $(L(w))$ was estimated by scaling to dry deposition (Equation 7). Because unlike the other locations studied in the literature, the San Francisco Bay region is almost exclusively dry during 5 months of the year, wet deposition was included in the calculation only during the rainy season months (m) of October through April.

$$L(w)_m = \begin{cases} 0.65 * L(p)_m \; if & m \in Oct - Apr \\ 0 & m \in May - Sep \end{cases} \qquad \textbf{Equation 7}$$

Gas Absorption

Loading of gas phase dioxins to surface water is subject to two resistances at the surface interface layer: resistance through the air, and resistance through the water. Because air (advective) motion must essentially stop at a phase boundary, there is a narrow layer of air immediately adjacent to the boundary that is effectively still. Therefore, turbulent diffusion is assumed to be negligible at this layer, and diffusion of gaseous molecules is resisted (Cohen et al. 2002). Similarly, advective water motion towards a phase boundary must effectively stop, and transport is resisted by the small layer of immobile water at the interface insulating the surface from the bulk water concentration.

Thus, loading due to gas absorption of dioxins (*L(g)*: g/year) is given by Equation 8,

$$L(g) = A * k_{OL} * C(a,g) * \frac{R*T}{H*1000} \qquad \textbf{Equation 8}$$

where k_{OL} (m/year) is the air-water mass transfer resistance coefficient and incorporates both resistances at the air-water interface, and $C(a,g)$ is the concentration of the gaseous congener in air, as determined by the partitioning coefficient F_p. The air temperature data (T), from the NOAA climate stations, was averaged for each region for each month. The gas constant R is 8.314 J/mol K, and Henry's Law constants (H) for each congener are given by Cohen et al (2002).

The resistance coefficient k_{OL} combines the effects at the boundary layer (Equation 9).

$$k_{OL} = \left(\frac{1}{k_{w,Dx}} + \frac{R*T}{H*k_{a,Dx}} \right)^{-1} * 365.25 \qquad \textbf{Equation 9}$$

The air-side mass transfer resistance coefficient is given by $k_{a,Dx}$ (m/day), the water-side mass transfer resistance coefficient is given by $k_{w,Dx}$ (m/day), and R, T, and H, are defined as in Equation 8. The air-side and water-side mass transfer coefficients are based on the mass transfer coefficients of water and carbon dioxide in air and water, respectively, with an adjustment for the diffusivity of each of the congeners described below, in Equation 10 and Equation 13. Turbulent motion near the surface in either phase decreases resistance and thus increases mass transfer across the interface; adjustments to the air- and water-side mass transfer coefficients for these conditions are discussed in their respective sections.

Air-Side mass transfer coefficient

The air-side mass transfer coefficient, $k_{a,Dx}$, represents the resistance to gaseous deposition due to diffusion of dioxin molecules through air at the surface boundary layer.

$$k_{a,Dx} = k_{a,H_2O} * \left(\frac{D_{a,Dx}}{D_{a,H_2O}} \right)^{0.61} \qquad \textbf{Equation 10}$$

The ratio of the diffusivity of dioxin congeners in air and the diffusivity of water in air, $\left(\frac{D_{a,Dx}}{D_{a,H_2O}} \right)$ (Equation 11), is used to scale the air side mass transfer coefficient of water ($k_{a,H2O}$: m/day)(Equation 12) to account for the differences in molecular properties of dioxins relative to water.

Although the diffusivity of molecules in air are temperature dependent (Fuller et al. 1966), the ratio of diffusivities is independent of temperature and pressure. Therefore, this calculation is simplified to Equation 11.

$$\left(\frac{D_{a,Dx}}{D_{a,H_2O}}\right)=\frac{\left(\frac{1}{MW_{air}}+\frac{1}{MW_{Dx}}\right)^{1/2}}{(V_{fuller,air}{}^{1/3}+V_{fuller,Dx}{}^{1/3})^2}*\frac{(V_{fuller,air}{}^{1/3}+V_{fuller,H_2O}{}^{1/3})^2}{\left(\frac{1}{MW_{air}}+\frac{1}{MW_{H_2O}}\right)^{1/2}}$$ **Equation 11**

This ratio depends on the molecular weights (*MW*) of air, water, and the dioxin congeners, and the Fuller volumes (V_{fuller}) of each, which correspond to diffusion volumes based on molecular structure (Fuller et al. 1966). The Fuller volumes for air and water are 20.1 and 12.7, respectively, and the Fuller volumes of the dioxins were calculated based on their molecular structures (Fuller et al. 1966).

The air-side mass transfer coefficient of water, $k_{a,H2O}$ (m/day), increases with turbulence at the surface, which is related to the average wind speed above the surface.

$$k_{a,H_2O}=\frac{0.2*u+0.3}{100*60*60*24}$$ **Equation 12**

The average wind speed data (u: m/s) came from the NOAA climate stations.

Water-Side mass transfer coefficient

The water-side mass transfer coefficient, $k_{w,Dx}$, represents the resistance to mass transport due to diffusion of dioxin molecules through water at the surface boundary layer.

$$k_{w,Dx}=k_{w,CO_2}*\left(\frac{Sc_{Dx}}{Sc_{CO_2}}\right)^{-0.5}$$ **Equation 13**

The Schmidt constants, Sc_{Dx} and Sc_{CO2}, calculated in Equation 15, relate the viscosity of water to particle diffusivity. The water-side mass transfer coefficient of carbon dioxide in water ($k_{w,CO2}$) is determined by Equation 14,

$$k_{w,CO_2}=\frac{0.45*u^{1.64}}{100*24}$$ **Equation 14**

where u is the average wind speed.

The Schmidt number (Sc) for CO_2 and dioxins is given by the diffusivity in water, Equation 15.

$$Sc=\frac{10^{-2}}{D_w}$$ **Equation 15**

The diffusivity of dioxin in water ($D_{w,Dx}$) is calculated by the Hayduk and Laudie (1974) method, Equation 16.

$$D_{w,Dx}=\frac{13.26*10^{-5}}{\mu_w^{1.4}V_{LeBas,Dx}^{0.589}}$$ **Equation 16**

The viscosity of water, μ_w, is temperature dependent (Weast and Astle 1981), and $V_{LeBas,Dx}$ represents the LeBas volume of the dioxin congeners, which is calculated based on their molecular structure. The diffusivity of carbon dioxide in water is determined by Equation 17.

$$D_{w,CO_2}=\frac{6.566*10^{-8}*T}{\mu_w}$$ **Equation 17**

The temperature, T, and viscosity of water μ_w, are defined as above.

Volatilization

Loss of dioxins due to volatilization from ambient surface water is given by *V(g)* (g/year) (Equation 18).

$$V(g) = A * k_{OL} * C(w) * 1000 \qquad \textbf{Equation 18}$$

Similar to gaseous deposition, volatilization is also subject to the boundary layer resistance, k_{OL}.

Dissolved concentrations in ambient surface water (*C(w): ng/m³)* were calculated from the whole water concentrations *(C(w, t))* based on theoretical partitioning coefficients *(k_{ow})* from the literature (van Noort 2009). The k_{ow} was converted to a distribution coefficient *(k_d)* for each congener for each segment of the bay by accounting for percent organic carbon in the ambient bay water. This distribution coefficient was then used to calculate the dissolved concentration *(C(w))* based on the total concentration *(C(w, t))* and the suspended sediment concentration *(SSC)*, as given by Equation 19.

$$C(w) = C(w,t)/(1 + SSC * k_d) \qquad \textbf{Equation 19}$$

However, because the partitioning coefficients are based on QSPRs, they do not take into account the possibility for increased dioxin solubility in dissolved organic carbon present in natural seawater. Calculations therefore likely underestimated the dissolved component of dioxins in bay surface water. This is evident in the existing dissolved component data (from two sites in the north bay), which was six to eight orders of magnitude larger than the calculated dissolved concentrations for the north bay. The concentration of dioxins available to be volatilized from the surface water was likely between these values, since the empirically measured concentrations also included a fraction that was sorbed to colloidal matter that would not be volatilized.

Net Loading

Net loading (or loss) of each dioxin congener in each segment of the Bay for every month was determined by Equation 20.

$$L(net) = L(p) + L(w) + L(g) - V(g) \qquad \textbf{Equation 20}$$

The loading components *L(p)*, *L(w)*, *L(g)*, and *V(g)* are defined in equations Equation **1**, **Equation 7**, Equation **8**, and Equation **18**, respectively.

Sensitivity Analyses

Substitution of Non-Detects

Of the 2414 results for analyses performed on air samples at the Crockett, Richmond, Oakland and San Jose stations and 267 results for analyses on surface water samples, 69 and 110 of them, respectively, were reported as "not detected". Therefore, sensitivity analyses were performed to determine the effect of varying the substitution method for non-detects on the calculated loadings. Non-detects in air and water were replaced with 0, the method detection limit (MDL), or a value computed based on the average ratio between each congener and OCCD, as described above.

The loading estimates were higher when the air concentration non-detects were substituted by the MDL than when they were assumed to be 0, indicating that adjustments to the air concentration had a larger effect on the loading estimates than adjustments to the water concentrations. On average, the dioxin and furan loading estimates changed by 3% between the estimates based on substitution by 0, the MDL, or the ratio method. The 123789 HxCDF isomer was the most sensitive to the substitution method, differing by 15-50% between the treatments. The other dioxin and furan isomers typically showed less than 2% difference between the loading estimates for the non-detect

handling cases. In general the loading estimates for individual isomers were not sensitive to the handling for this data set. Therefore, we used the ratio technique described above to produce reasonable estimates of the samples that had concentrations below detection limits, with the understanding that the specific approach to incorporating non-detects would not have a large effect on the overall loading estimate.

Particle Deposition Velocity

Particle deposition velocity was not determined from specific data for the Bay Area, but rather averaged from values from the literature from around the country. Therefore, because the local deposition velocity was not precisely known, a sensitivity analysis was performed using the minimum, 12600 m/year, and maximum, 189000 m/year, deposition velocities from the literature compared to the base case scenario, the particle deposition velocity (63000 m/year) used in a previous RMP study for PCBs (Tsai et al. 2002). Because the majority of dioxin loading from the atmosphere was estimated to result from particulate phase partitioning and deposition (dry and wet), the loading estimate was nearly directly proportional to the particle deposition velocity applied. Therefore, the Baywide loading estimate varied 10-fold (g TEQ/year) between the lowest and the highest particle deposition velocities tested (Table 2). Assuming that the literature values assembled (Koester and Hites 1992, Moon et al. 2005, Correa et al. 2006) represent a rough distribution of the possible deposition velocities in urban areas, we selected the geometric mean of the available values, 45200 m/year, for the final estimate of atmospheric deposition of dioxins.

Wet Deposition

Because wet deposition was not modeled explicitly, but rather estimated based on dry deposition, we allowed wet deposition to vary between 0.3-1.5 times the dry deposition estimates. Previous measurements and models of wet and dry deposition have estimated that wet deposition varies between 0.7-1.3, 0.62 and 0.3-0.52 times the dry deposition at locations in Indiana, USA, Texas, USA, and Taiwan, respectively (Koester and Hites 1992, Correa et al. 2006, Wang et al. 2010). The largest estimates of wet deposition caused the total loading (g TEQ/year) to increase by 0.5-0.7 times the total loading determined based on the lowest estimate of wet deposition, indicating that while variations in wet deposition do cause significant variation in the total loading estimates, the uncertainty due to wet deposition estimation is much lower than the uncertainty due to the estimation of the particle deposition velocity (Table 2).

Table 2. Analysis of the effect of variations in particle deposition velocity and wet deposition on the total loading estimate (g TEQ/ year).

Estimated Total Loading (g TEQ/ year) given varying Wet Deposition and Particle Deposition Velocities		**Estimate of Particle Deposition Velocity (m/ year)**		
		Low (12600)	**Geometric Mean (45200)**	**High (189000)**
Estimate of Wet Deposition (times Particulate Deposition)	**Low (0.3)**	5.4	14.1	52.5
	Median (0.65)	6.1	16.7	63.7
	High (1.5)	7.9	23.3	90.9

Seasonal Variations

Because surface water data exist only for the summer season, a sensitivity analysis was performed to determine the possible effect of seasonal variations in water concentrations on loading. Winter season (October to April) concentrations were estimated based on summer concentrations, using 0.5 to 2 times the measured values from the summer sampling. Because volatilization is minimal compared to deposition, seasonal variations in water concentrations have very little (<0.002%) effect

on total loading. Even much larger ranges of variation in water concentrations (0.1 to 10 times) would have very little (<0.003% change) impact on net loading.

Comparison to Other Loadings

The estimated loading due to atmospheric dry deposition to San Francisco Bay is 16.7 g TEQ/year, using the ratio method to substitute for non-detects. This value could range between 5.4 and 90.0 g TEQ/year depending on the assumed particle deposition velocity and contribution of wet deposition. This is a fourteen-fold increase from the previous estimate of atmospheric deposition loading to the Bay of 1.2 g TEQ/year, Table 3 (Gervason and Tang 1998).

For comparison, Table 3 includes loading estimates for other pathways from a previous conceptual model/ impairment assessment synthesizing data for the region (Connor et al. 2004). These estimates for atmospheric deposition, provided by the local Regional Water Quality Control Board (Gervason and Tang 1998) were determined using data from 1996 and an undocumented approach, so it is difficult to diagnose the primary causes of the different estimates. The 2004 impairment assessment review used a simple order of magnitude (10x) factor higher or lower as an estimate of uncertainty in the reported loads for pathways for which only a single value was known. Since that time, additional data have been collected for two pathways: an updated estimate of loading from the Sacramento- San Joaquin River of 3.4 g TEQ/year came from 16 samples collected at the Mallard Island station during 2010 (David et al. In press); and loadings from small tributaries were updated with new data from monitoring locations in San Jose and Hayward.

Given current estimates, atmospheric deposition could account for approximately half of all dioxin loading to San Francisco Bay (Figure 3). Although this number is highly uncertain and very dependent on assumptions about particulate deposition velocity and the relationship between wet and dry deposition, the range, entirely above the previous Regional Board estimate (Gervason and Tang 1998), suggests a much higher loading rate than previously believed. Surrounding local watersheds cover an area about 6 times that of the open waters of San Francisco Bay, so assuming that they experience a similar rate of dry and wet deposition, current atmospheric dioxin loading to watersheds (~100 g TEQ/year) would easily account for all of the loads from local tributaries (~9 g TEQ/year). In addition, ambient dioxin air concentrations in the Bay Area (13.3, 21.3, and 20.5 fg TEQ/m^3 in the North, Central and South Bays, respectively) are higher than the Nationwide average concentration in rural areas (10 fg TEQ/m^3, (Cleverly et al. 2007)). Concentrations above the nationwide rural average suggest contributions of local sources, and reductions in local dioxin emissions and ambient concentrations could reduce loading of dioxins to the Bay via direct and indirect (i.e., tributary loading) pathways. As management actions are developed and implemented to reduce loading and exposure, additional studies to better quantify concentrations and loads in specific loading pathways should be conducted to evaluate potential benefit and measure progress.

Table 3. Estimated loads of PCDD/Fs to San Francisco Bay (g TEQ/year), updated from (Connor et al. 2004).

	Past Estimate (Gervason and Tang 1998)	Past Estimate (Connor et al. 2004)	Current Best Estimate
Small Tributaries	5.1	5.1	8.9
Air Deposition	1.2	1.2	16.7 (5.4-90.0)
Municipal Effluent	0.13	0.67	0.67 (0.035-13)
Refinery Effluent	0.004	0.019	0.019 (0.0033-0.11)
Other Effluent	-	0.019	0.019 (0.0073-0.051)
Sacramento River	-	0.88	3.4
Total	6.4	7.9	30 (17.7-115)

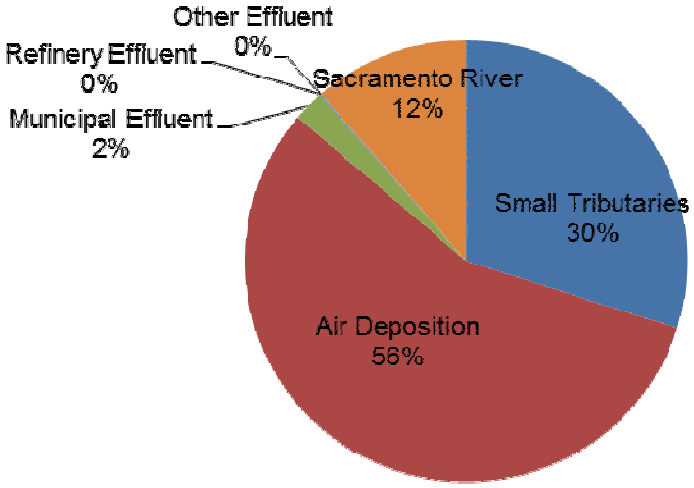

Figure 3. Relative estimated contributions to total dioxin loading, based on best current estimates.

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