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Decision Support for Control of Salt and Methylmercury Export from Managed Seasonal Wetlands

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Abstract: Monomethylmercury (MeHg) is a toxic mercuric compound that, even at very low concentrations, can lead to MeHg bioaccumulation within the aquatic food web and cause high levels of MeHg contamination in fish and humans. The behavior of inorganic mercury (Hg) and MeHg in the environment depends on numerous chemical, physical, and biological factors that vary in time and space driven by biogeochemical and hydrodynamic processes. Managed seasonal wetlands are a major source of both MeHg and salinity to the Sacramento – San Joaquin Delta which discharges into San Francisco Bay and is the source of drinking water for 2/3 of California's citizens. Whereas the source of the wetland salinity is well established – present in parent soils and in supply water - the primary sources of Hg and MeHg contamination have yet to be established. Management options to control Hg and MeHg export require a scientifically valid conceptual model as a basis for action. The Watershed Risk Management Framework (WARMF) water quality simulation model has been used extensively to provide TMDL-related decision support for salinity and nutrient TMDL's impacting the water quality-impaired San Joaquin River. Successful calibration of the WARMF salinity and mercury modules in the WARMF model that simulate non-point discharges from seasonal managed wetlands requires improvements to the existing method for simulating wetland hydrology. This paper describes how this was accomplished. The calibrated WARMF salinity and mercury model will be used to guide future wetland monitoring and assess likely success of innovative wetland management practices to limit salt and MeHg export.

Keywords: Mercury; salinity; decision support; conceptual models; WARMF hydrology.

1 INTRODUCTION

Salinity levels in the San Joaquin River Basin (SJR), located in California's Central Valley, have been ever increasing as the basin's agricultural production and resident population have increased. The wetland acreage has diminished by more than 90% from pre-1900 extent. The Grassland Water District (GWD), together with the adjacent State and Federal refuges, constitute the largest contiguous wetland complex remaining in the State of California (~160,000 acres) (GWD, 2011; Shuford et al., 1998). As more and more of California's wetlands are lost to development, this area's value to wildlife increases proportionately - as the area's wildlife value increases, so must the intensity of wetland management. Management strategies have traditionally focused on the successful growth of plants to supply migrating birds and over-wintering waterfowl with food/forage, however, more recently, attention is being given to the water quality of released water since the enactment of a salinity TMDL in 2014 and a Phase 1 mercury TMDL process that began in 2012 for the Grasslands Ecological Area (GEA), which contains the impacted wetland areas. Desirable wetland moist soil plants like swamp timothy require flooding in fall and drawdown in spring, i.e., the ponds are flooded over the winter. This water management strategy creates optimal conditions for germination and plant growth (Fredrickson and Laubhan, 1995).

Germination of an optimal moist soil plant habitat requires carefully timing the moisture status of the soil and soil temperature.

Management strategies addressing methylmercury present several challenges, because they can create conflicts with other management objectives (McCord and Heim, 2015). Siegel, Bachand, & Gillenwater (2011) conducted a study of 19 best management practices in a similar brackish marsh to identify strategies for resolving low dissolved oxygen and methylmercury events - several practices appeared conflicted. Combinations of management practices may have to be adapted to individual wetland impoundments. A wetland hydrology and water quality model for salt and mercury is needed to test underlying hypotheses of management strategies and to test management practices prior to conducting field experimentation.

2 WETLAND HYDROGEOCHEMISTRY

Inorganic mercury (Hg) is a toxic metal that is found both naturally and as an introduced contaminant in aquatic environments. Methylation of Hg produces the toxic monomethylmercury (MeHg) species which increases mercury toxicity and increases the risk of accumulation in aquatic biota particularly fish and other predators high in the food chain. Hg enters the aquatic ecosystem through one of two paths: point and non-point source discharges and atmospheric deposition. Emissions from coal-fired power plants are the largest source of Hg to the atmosphere causing Hg to be deposited from the atmosphere. Hg has the ability to change state rapidly which in turn affects its reactivity and mobility. Numerous chemical, physical, and biological processes affect the fate and transport of Hg causing variation in Hg concentration in both time and space. In the conterminous US about 80% of inorganic Hg found in the terrestrial environment is derived from atmospheric deposition. However- in both northern and central California, atmospheric deposition is a relatively minor contributor of Hg and MeHg to aquatic environments compared to Hg from historical mining sources (Sparks, 2015). Considerable Hg was released into the Delta watershed due to historic mercury mining and the historic use of mercury for gold mining. Even today, the amount of Hg in the environment is still increasing due to emissions from global industrial sources, and mercury and gold mines (Windham-Myers et al., 2014). In 2003, 2140 fish and wildlife consumption advisories have resulted from mercury; this amounts to 76% of all advisories in the State California (Alpers et al., 2005). MeHg is produced in anaerobic sediments of both seasonal and permanent wetlands where Hg can be transformed to this form. The upper San Joaquin Basin, which includes the Los Banos Wildlife Management Area, contributes nearly half of all MeHg loading to the Delta even though it supplies less than 20% of the water flow (Foe et al., 2008). More research is needed to evaluate the mercury cycle in wetlands.

Water supply for the wetland complex is elevated in salinity, with electrical conductivity (EC, a surrogate for dissolved solids) usually in the range of 500 to 1,000 microsiemens per centimeter [$\mu\text{S}/\text{cm}$] (375 to 750 mg/L). As the flooded season progresses, the wetland surface water increases in salinity from climatic processes (evaporation and evapotranspiration) as well as through contact with the environment (soil residues, ground water inputs, bird usage, etc.). When the flooded season ends, spring releases are discharged into tributaries of the Lower San Joaquin River. These releases, along with agricultural and municipal return flows, contain varying loads of total dissolved solids (TDS) and boron. These constituents have been identified as stressors that lead to frequent exceedance of water quality objectives established for the San Joaquin River by State and Federal agencies (Quinn et al., 1997, 2011). This spring drawdown in the seasonal wetlands is timed for optimal germination conditions for the desirable moist-soil vegetation. However, at times these spring releases coincide with higher salt concentrations in the SJR during lower flows and with downstream agricultural withdrawals from the SJR. The response of moist-soil plants and of migratory waterfowl and shorebirds to an altered drawdown regime has been assessed relative to potential impacts on seed germination rates, water bird foraging rates, habitat availability, and species diversity and abundance. While early drawdown can make food sources available to wildlife without negatively effecting wetland vegetation community and plant species diversity and benefiting both wildlife and the health of the San Joaquin River, late drawdown has been shown to increase soil salinity and habitat productivity if practiced on individual impoundments for more than two seasons (Quinn et al., 2011).

3 WETLAND HYDROGEOCHEMICAL MODELING

3.1 Conceptual wetland flow and water quality models

Modelling salt and mercury loading to waterbodies requires a conceptual understanding of the hydrologic, and biogeochemical processes involved in releasing the contaminant from its natural reservoir. In the case of salt loading the contaminant is typically treated as a conservative substance where the mass flowing into a wetland either ends up in a return flow or in the groundwater system. Hg loading is highly regionally variable, and understanding its complex depositional, storage, and transport pathways for a given system is important. Hg and MeHg mobilization is also closely tied to redox potential and the presence of certain chemical ions and various forms of organic matter and can be highly variable over time. A mercury conceptual model of Alpers et al. (2008) was developed for the CALFED Bay-Delta Delta Regional Ecosystem Restoration Implementation Plan (DRERIP) to describe fate and transport of Hg and MeHg in the Sacramento-San Joaquin Delta. A variant of this conceptual model (Maven's Notebook, 2017) together with a conceptual model of wetland salinity mass balance are shown in Figure 1. In Figure 1 the mercury pathway includes both the formation of reactive (inorganic) Hg and microbial transformation of reactive (inorganic) Hg to (organic) MeHg, and the process of MeHg bioaccumulation in biota. The Alpers et al. (2008) conceptual model distinguishes between intermediate outcomes (MeHg in water, sediment, and biota) that affect MeHg bioavailability and exposure and final outcomes that include health effects on humans and wildlife, and transport of Hg and MeHg to downstream water bodies, such as the Sacramento San Joaquin Delta.

The role of the conceptual model tends to be overlooked in simulation model development especially as computer-based simulation models have become more accessible and user-friendly. Analysts are enticed to leap right into steady-state model development as a first step toward transient model calibration and validation neglecting the conceptual modeling step and occasionally proceeding without a complete understanding of the physical processes and chemistry being simulated. In the current situation salt, Hg and MeHg management application - the complexity of the modelling task and high cost of the associated data collection task in remote and sometimes inaccessible areas will drag out the model development process. The conceptual model for the fate and transport of Hg and MeHg can help to guide data collection activities. Sensitivity analysis performed with the simulation model can also help to prioritize deployment of resources associated with data collection.

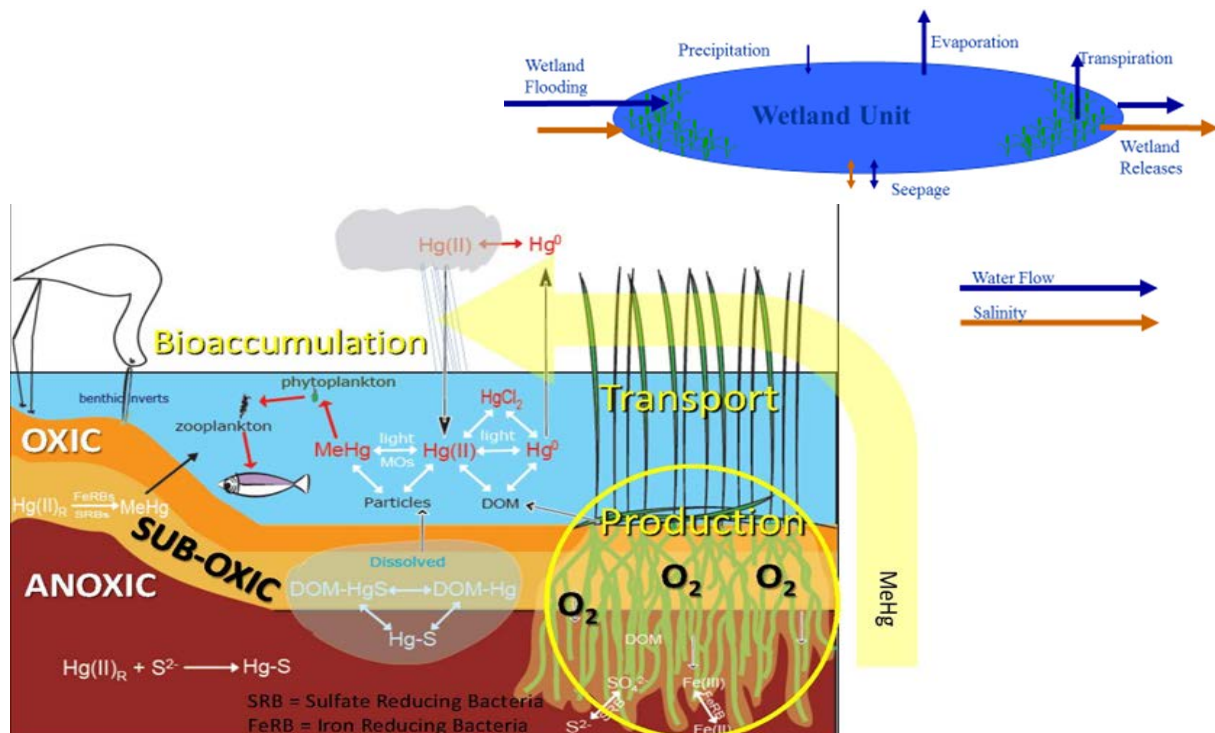


Figure 1. Conceptual hydrogeochemistry models for (a) salinity and (b) mercury and methylmercury in seasonally managed wetlands in the San Joaquin River Basin. (Source mercury conceptual model: <https://mavensnotebook.com/2017/04/06/mercury-and-rice-in-the-delta-lessons-linking-wetlands-to-water-and-wildlife/>).

The WARMF (Watershed Analysis Risk Management Framework) is a comprehensive and robust water quality simulation model that has been extensively used for salinity, nutrient and phytoplankton applications in the San Joaquin River Basin for well over a decade. The GIS-based model and its user interface is capable of representing catchments, river segments, reservoirs, and wetlands as a network of continuously stirred tank reactors. Physical, chemical, and biological processes can be simulated, that relate to the environmental processes such as deposition, transpiration, mineral weathering, organic matter decay, adsorption, and accumulation of contaminants in the food web. The model relies on a number of hydrologic, atmospheric, and aqueous chemical data to parameterize watershed processes, and then uses a calibrated version of the model to simulate future control and watershed management scenarios. Mass-heat balance equations are solved for every time step and compartment to simulate contaminant concentrations and changes in temperature (Chen, 2006). The WARMF salinity model is unusual in that it sums the anions and cations to directly estimate total dissolved solids (TDS) in solution rather than the more typical approach of using EC as a surrogate for TDS using a known conversion factor of 0.61. This allows the model to estimate depositional processes such as those essential for Hg modeling.

The WARMF model code was enhanced in 2006 to simulate the processes of atmospheric deposition, evasion, methylation and demethylation, transport, and bioaccumulation of Hg. The model partitions total mercury concentrations into elemental Hg (Hg(0)), inorganic Hg(Hg(2)), and MeHg. WARMF simulates processes which occur in uplands, wetlands, surface water, and river/lake beds. The relative importance of these processes depends on the characteristics of the ecosystem as illustrated in (Chen, 2006). To simulate bioaccumulation a bioenergetics approach was adapted by expanding the food web and by using the simulated MeHg concentration as input instead of a constant MeHg concentration. The food web includes benthos, phytoplankton, settled phytoplankton, zooplankton, forage fish, and piscivores. The WARMF model differentiates between different Hg sources (atmospheric deposition versus legacy Hg), it accounts for sediment properties, simulates water properties, and simulates three different Hg species. MeHg in water and fish, and Hg in water over time are simulation outputs from the WARMF model. Additionally the WARMF model can display output for all the associated model parameters simulated over time. Another advantage of the WARMF model is that it, unlike all other water quality models that have been applied to the San Joaquin Basin, considers chemical deposition and makes computations of Hg loading by summing the individual ions in solution. This makes the model a powerful tool in helping to improve the understanding of not only watersheds but also managed wetland Hg hydrochemistry and the dynamics of wetland Hg loading to the San Joaquin River and the Sacramento San Joaquin Delta.

3.2 WARMF model hydrology

To better represent managed wetland operations in WARMF, the model code and graphical user interface were reformulated to a new "bathtub" conceptual model of seasonal wetland impoundments which replaced the original conceptual model which treated these wetlands as a slow-moving river passing over the landscape. Although the original conceptual model was successful in simulating natural wetland and water quality in a number of applications – the intensely managed wetlands in the San Joaquin Basin exhibit a sharper pulse flow during the wetland drawdown period when boards are pulled on the impoundments and ponded water released to the San Joaquin River from approximately 160 private duck clubs and wetland impoundments in the State and federal refuges. Hence the first step was to create an option to read inputs of prescribed wetland pond depths and adjust surface water outflow based on those values. The 140,000 acre GEA incorporates all the private, state and federal wetland ponded areas within the Basin. Eleven wetland units were recognized within the study area and the hydrology and water quality characteristics of each of the areas was treated as an individual catchment in the new WARMF wetland module (Figure 2).

A representative time series of prescribed pond depth (Figure 3) was created to test the updates based on available depth data from a previous 3-year wetland study which measured flow and EC continuously at wetland inlets and outlets during the winter flooded season (Van Werkhoven, 2015). Pond outlet depth gave reasonable guidance for the timing of flooding and drawdown periods, but did not reflect the actual magnitude of depth throughout the pond area which typically varied between 0.5 - 1 ft. Seven of the eleven study sites had complete data sets for the entire flooded season and were used to determine the average temporal pattern of the rise and fall of pond depth, with the maximum depth defined as 1 ft.

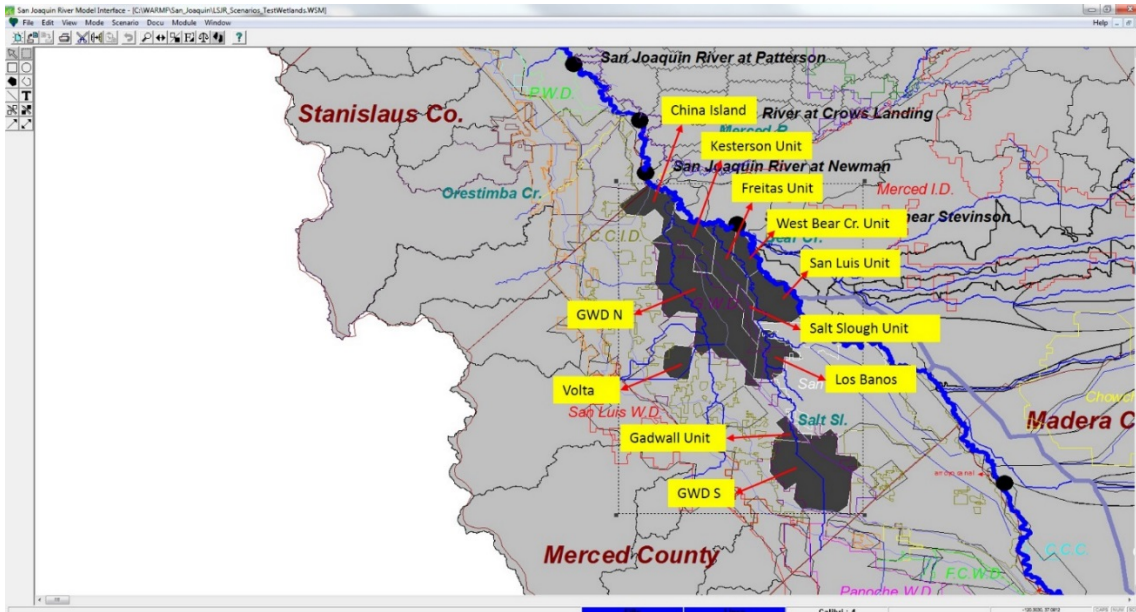


Figure 2. Study area is represented by eleven seasonally managed wetland watersheds in the WARMF model.

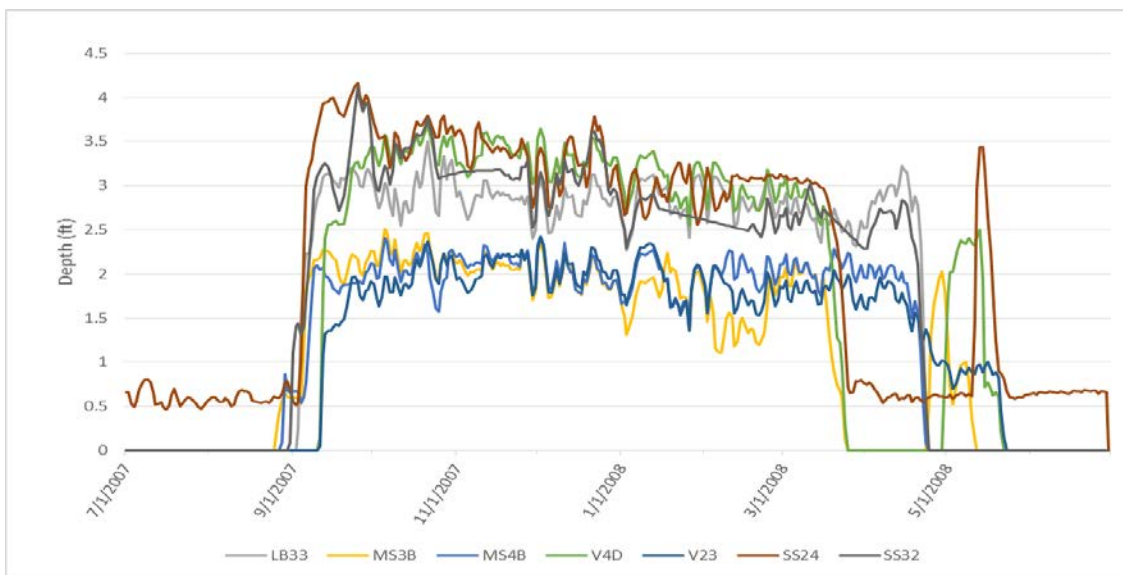


Figure 3. Outlet depth at the seven drains used to generate the average temporal pattern for model input of pond depth.

For each of the 7 drains, the measured outlet depth was normalized by the maximum outlet depth to obtain a temporal pattern of the fraction of maximum outlet depth for each pond. It was assumed that although the magnitude of depth would be greater at the pond outlet than in the pond center, the rise and fall of the pond center depth would follow the same temporal pattern as the rise and fall of the outlet depth. The average pattern was smoothed by a 30-day running average to remove high frequency fluctuations that would cause repeated excessive flushing of ponded water out of the system in the wetland model simulation and then create artificial demand for additional water supply. The smoothed values were transformed from fraction of maximum depth to average areal pond depth by multiplying the expected maximum pond depth. Due to differences in pond bed shape between the model and reality, one final adjustment to the pond depth values was necessary in order to use the data for simulations. In WARMF, ponds are assumed to have vertical sides with a constant depth across the pond area (for a given volume) and constant water surface area for all depths. In reality, the pond sides are not vertical, with depth varying across the pond area and the water surface area varying for different

depths. Thus for a given volume, the WARMF representation of a pond spreads the water out across the maximum pond area resulting in a lower depth than the real pond depth. The effect is most pronounced at low depths when the difference between simulated and observed water surface area is greatest. The magnitude of the depth adjustment was determined based on an area-volume-elevation relationship where the actual average pond depth for a given volume was calculated as: actual average pond depth = volume/wetted surface area. The final smoothed, adjusted pattern was applied for all years to result in a model input time series of wetland pond depth from 2000-2015. A WARMF observed hydrology (ORH) input file was created using these data and applied to all seasonal wetland areas and refined as appropriate for specific wetlands' management plans (e.g. flood-up and drawdown timing) and pond bed shape (volume-depth relationship).

The WARMF Graphical User Interface (GUI) was updated to allow the managed seasonal wetland module for a given wetland catchment to be activated and to provide the filename for the prescribed pond depth input file. The option to add a wetland input file was added to the irrigation tab within the catchment input dialog. A file selection box was added to the lower portion of the window, as shown in Figure 4. Using the "Select" button next to the box, the user can navigate to and select the appropriate input file which can be used for multiple wetland catchments. To separate the pre-existing WARMF wetland land use category into managed seasonal wetland areas receiving irrigation water as opposed to natural wetlands, an additional land use classification was created in the GUI for "irrigated wetland". The total irrigated wetland area was estimated based on acreage tables included for each refuge in US Bureau of Reclamation Water Management Plans (GWD, 2011).

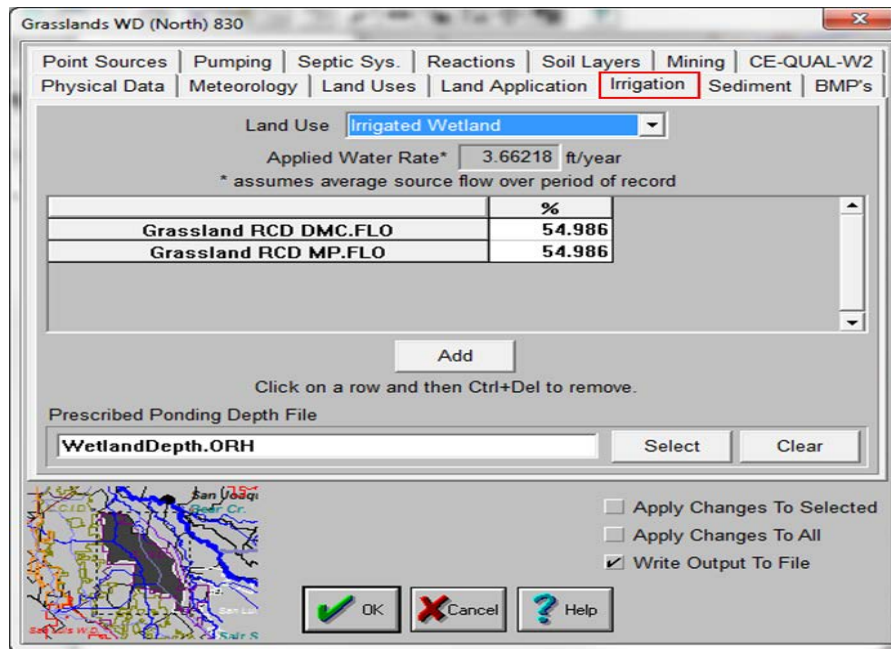


Figure 4. Upgraded irrigation input dialog of the WARMF GUI, showing the new option to define a prescribed pond depth file within the new wetland module.

3.3 Wetland module hydrology simulation

Initial results confirmed that the WARMF model adjusted the surface water depth for all eleven seasonally flooded wetland catchments however outflow peaks were unreasonably high during rainfall events and other periods of wetland inflow. Adjustments were made to catchment parameters to increase outflow attenuation and account for factors such as seepage and wind-enhanced evapotranspiration that resulted in a better fit between simulated and observed flow. The quantity of water available in excess of the prescribed depth is subject to overland routing by Manning's method, whereby a portion of the outflow reaches the outlet in the current time step - simulating the process of attenuation over the distance between the middle of the wetland catchment and outlet. This process is important for reducing unrealistically high peaks of outflow that would otherwise occur on days with a sudden reduction in prescribed depth or days of precipitation on a full pond.

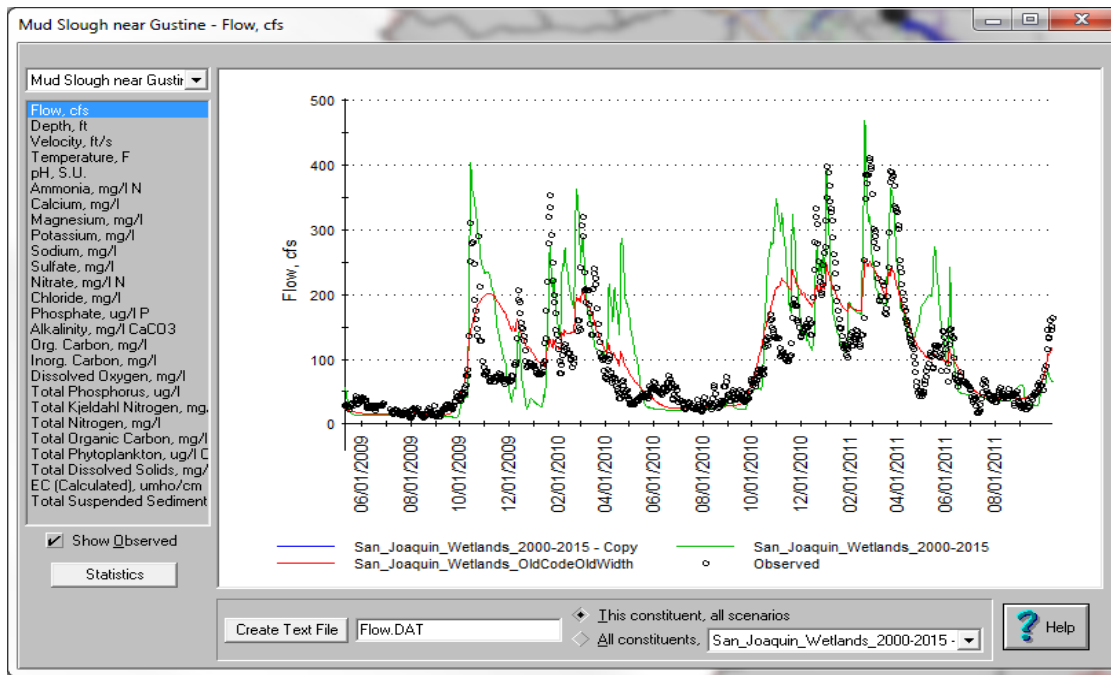


Figure 5. Comparison of original model wetland simulation (red) with flow output from the new wetland module after flow routing (green) and observed flow at the Mud Slough monitoring station.

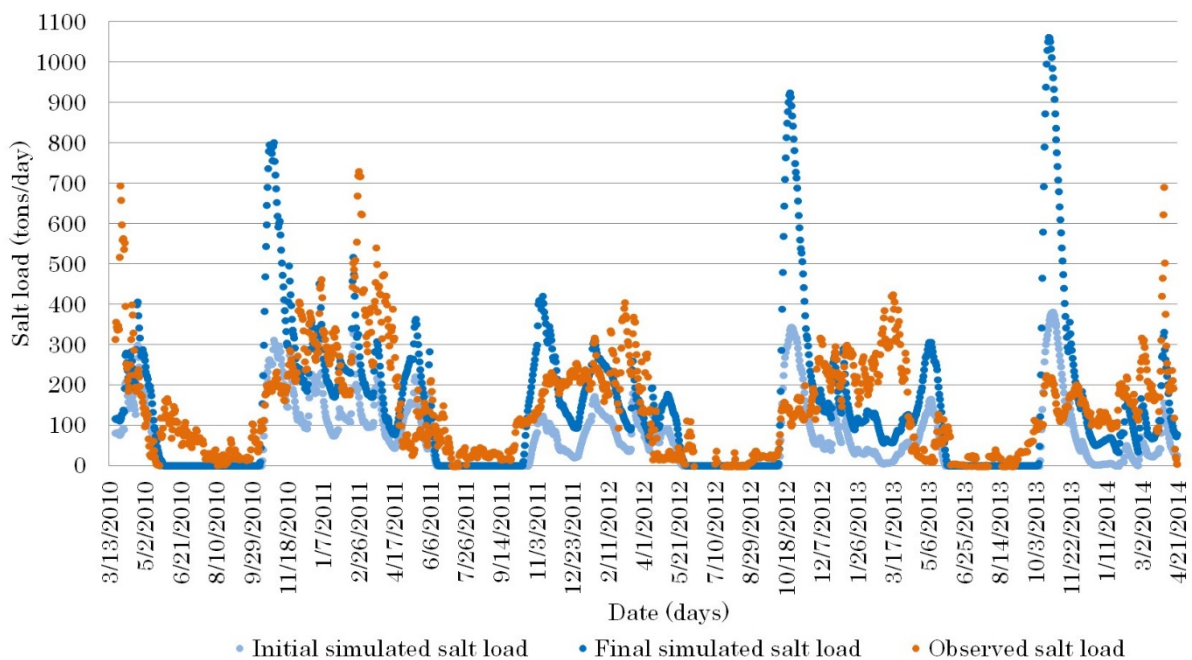


Figure 6. Salt load output from the WARMF model with the updated wetland module (final simulated salt load) compared to the legacy model (initial simulated salt load) and observed salt loads from GWD (comparable to the outflow measured at Mud Slough).

The Mud Slough monitoring near Gustine records flow and salt loads from more than 80% of the private wetlands within GWD and was one of the sites used for wetland module validation. The two years of simulations shown in Figure 5 were average years in terms of rainfall and applied water deliveries. The updated wetland module shows a better fit to observed data in Mud Slough near Gustine, particularly for peak flows, than the prior wetland module. Residual errors in the new module may be attributed to WARMF input files time series for water delivered to refuges in those months during periods of shortage or excess when water deliveries to GWD can vary and irrigated wetland area can rise or fall in response. The irrigated seasonal wetland catchment area is a static value in the WARMF model.

3.4 WARMF model salinity simulation

Salinity is assumed to be a conservative constituent in WARMF wetland simulations as depicted in the conceptual model in Figure 1 whereby salt imported into the wetlands that comprise the GEA is stored in wetland impoundments during the late fall and winter. The portion that does not seep into groundwater is available for discharge during the wetland drawdown period. The WARMF model simulation with the new wetland module does not demonstrate the same good agreement with observed salt loads as the hydrology at the Mud Slough monitoring site and when compared to the total outflow from GWD which is within 10-15% of the Mud Slough flow and salt load (see figure 6). Experiments conducted to improve inflow accounting in the new module and include the effect of daily wind velocity on increase in average wetland ET did not significantly enhance the model calibration and agreement with observations. Clearly the inability to adequately simulate the fate of a conservative constituent like salt is an impediment to progress on the WARMF wetland mercury modelling where there is a dearth of time series and speciation data for mercury model calibration and validation.

3.5 WARMF model mercury simulation

The WARMF model requires substantial input data from national databases and the published literature to enable mercury simulation and independent data sets to help validate the model by comparing model output to observations. Data to verify the simulation output are more difficult to gather because of the large number of parameters and the fact that the ambient environmental conditions at the time of data collection is relevant to the interpretation of the data. Water quality data that are of most importance to simulate the fate of Hg in managed seasonal wetlands are temperature, redox conditions, sulfate, organic carbon, and suspended sediments.

Major sources of uncertainty in the model performance are tied back to the assumptions and simplifications made in the original conceptual model as well as sampling errors in the field data and those associated with literature values of certain input parameters. Uncertainties from analytical methods propagate throughout the WARMF mercury model. Proxy relationships can be used to estimate values when measurements for the desired parameter are not available. In general, proxy relationships involving inorganic Hg are stronger than those involving MeHg. It is well known that MeHg concentrations vary temporally and spatially within watersheds, and the important factors controlling MeHg variability may not be well known in all environments.

Strong proxy relationships have been established between:

- Suspended sediment concentration (SS) and volumetric particulate total mercury concentration
- Flow and SS and volumetric particulate total mercury concentration
- Dissolved organic carbon (DOC) and filtered total Hg (THg)

Slightly weaker proxy relationships have been established between:

- SS and particulate MeHg
- DOC and filtered MeHg
- Distribution coefficients between particulate and filtered Hg and MeHg and DOC and SS

The organic content and character of suspended particles likely have an influence on the ability of the particles to adsorb and transport THg and MeHg. In general first-order processes affecting THg and MeHg transport can serve as a basis for preliminary modeling efforts, whereas some second-order processes can be used to fine-tune the model after its initial development.

4 SUMMARY

This paper has described a work in progress in California to develop a modeling tool to simulate salt and mercury fate and transport in managed seasonal wetlands. The primary motivation for the project was the lack of a decision support tool to guide actions that might be taken by the private, state and federal wetland entities in reducing mercury loading to the San Joaquin River. Conceptual models of Hg and MeHg fate and transport can play a helpful role in explaining the science underpinning Hg and MeHg modeling leading to the eventual development of a robust decision support tool for assessment of salinity and mercury management practices. Although the new WARMF hydrology module appears to be an improvement on the legacy simulation model the simulation of salt load still requires

improvement to develop greater confidence in the model. Mercury simulations with the new wetland module will get underway when the model demonstrates better agreement with salt load observations.

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