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## Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)

## Mercury cycling in agricultural and managed wetlands: A synthesis of methylmercury production, hydrologic export, and bioaccumulation from an integrated field study

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### HIGHLIGHTS

- Ecosystem MeHg fluxes were studied in replicate wetlands managed for rice or wildlife.
- MeHg export from rice-growing wetlands was higher in winter compared to summer.
- MeHg production was similar among wetlands but export and soil MeHg varied.
- Contrasting effects of evaporation and transpiration were observed for water MeHg.
- Holding water on rice-growing wetlands may enhance in situ MeHg bioaccumulation.

### ARTICLE INFO

#### Article history:

Received 17 July 2012

Received in revised form 8 January 2014

Accepted 8 January 2014

Available online xxxxx

#### Keywords:

Rice

Wetlands

Microbes

Hydrology

Bioaccumulation

Mercury

### ABSTRACT

With seasonal wetting and drying, and high biological productivity, agricultural wetlands (rice paddies) may enhance the conversion of inorganic mercury (Hg(II)) to methylmercury (MeHg), the more toxic, organic form that biomagnifies through food webs. Yet, the net balance of MeHg sources and sinks in seasonal wetland environments is poorly understood because it requires an annual, integrated assessment across biota, sediment, and water components. We examined a suite of wetlands managed for rice crops or wildlife during 2007–2008 in California's Central Valley, in an area affected by Hg contamination from historic mining practices. Hydrologic management of agricultural wetlands for rice, wild rice, or fallowed – drying for field preparation and harvest, and flooding for crop growth and post-harvest rice straw decay – led to pronounced seasonality in sediment and aqueous MeHg concentrations that were up to 95-fold higher than those measured concurrently in adjacent, non-agricultural permanently-flooded and seasonally-flooded wetlands. Flooding promoted microbial MeHg production in surface sediment of all wetlands, but extended water residence time appeared to preferentially enhance MeHg degradation and storage. When incoming MeHg loads were elevated, individual fields often served as a MeHg sink, rather than a source. Slow, horizontal flow of shallow water in the agricultural wetlands led to increased importance of vertical hydrologic fluxes, including evapoconcentration of surface water MeHg and transpiration-driven advection into the root zone, promoting temporary soil storage of MeHg. Although this hydrology limited MeHg export from wetlands, it also increased MeHg exposure to resident fish via greater in situ aqueous MeHg concentrations. Our results suggest that the combined traits of agricultural wetlands – slow-moving shallow water, manipulated flooding and drying, abundant labile plant matter, and management for wildlife – may enhance microbial methylation of Hg(II) and MeHg exposure to local biota, as well as export to downstream habitats during uncontrolled winter-flow events.

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0048-9697/\$ – see front matter Published by Elsevier B.V.

<http://dx.doi.org/10.1016/j.scitotenv.2014.01.033>

Please cite this article as: Windham-Myers L, et al, Mercury cycling in agricultural and managed wetlands: A synthesis of methylmercury production, hydrologic export, and bioaccumulation..., *Sci Total Environ* (2014), <http://dx.doi.org/10.1016/j.scitotenv.2014.01.033>

## 1. Introduction

Mercury (Hg) is widely regarded as a toxic metal with no known beneficial function for living organisms. Exposure of humans and wildlife to Hg is largely mediated through dietary consumption of methylmercury (MeHg), a chemical compound that is bioconcentrated in organisms and bioaccumulated in food webs. Decades of research have shown that anoxic sediment, especially surface sediment in wetland environments, promotes the microbial methylation of divalent inorganic mercury (Hg(II)) to MeHg (Hall et al., 2008; Lacerda and Fitzgerald, 2001; Marvin-DiPasquale et al., 2003; Windham-Myers et al., 2009; Zillioux et al., 1993). The production of MeHg in sediment is enhanced when both organic matter and Hg(II) are bioavailable to anaerobic bacteria (Marvin-DiPasquale et al., 2009a, 2009b), a combination of conditions that is commonly characteristic of wetland habitats (Merritt and Amirbahman, 2009). Furthermore, the large pool of dissolved organic matter (DOM) typical of wetlands can promote aqueous MeHg export to receiving surface water (Hall et al., 2008; Wallschläger et al., 1996). Wetlands also tend to be highly productive and provide important foraging habitat for fish and wildlife (Elphick, 2000). Thus, MeHg production associated with wetland habitats may be directly associated with biotic Hg exposure (Brumbaugh et al., 2001). In this study, we sought to compare patterns and processes of MeHg cycling among neighboring wetland habitats with different management practices, specifically wetlands managed for agriculture, and those managed for wildlife.

Among wetland habitat types, rice agriculture is predominant in temperate and tropical latitudes, covering 162 million ha globally (Leff et al., 2004; Mitsch et al., 2010). In California, rice fields – including wild rice (*Zizania* spp.) and domesticated or white rice (*Oryza* spp.) – represent a 2.5-fold greater amount of area than the remaining natural (non-agricultural) United States (U.S.) Fish and Wildlife Service-delineated wetland habitats (U.S. Department of Agriculture National Agricultural Statistics Service, 2007). Rice farming creates seasonally flooded agricultural wetlands (a.k.a. rice paddies) that typically are characterized by productive, shallow-water habitats. The microbial processes and biogeochemical conditions that develop in rice-field sediment are largely a function of the pulsed-flooding management regime that provides abundant water and nutrients, and in turn, the rapid production of relatively labile carbon by rice plants. The effect of rice agriculture on MeHg exposure to biota has not been rigorously addressed. Yet, recent data from China's Guizhou province have documented high MeHg bioaccumulation in white rice grains grown in mining impacted regions (Zhang et al., 2010), and highlighted the potential for MeHg exposure to humans and wildlife through rice agriculture (Feng et al., 2008). Recent research has demonstrated that atmospherically deposited Hg is especially susceptible to methylation in rice fields (Liu et al., 2012), and is thus a prime MeHg source for uptake into rice grains (Meng et al., 2011). Beyond MeHg in edible rice grains, the on-site production of MeHg within rice fields and the hydrologic export of MeHg from these systems may be an important source of MeHg contamination to local in situ aquatic food webs, as well as waterfowl, invertebrates, mammals, and other organisms downstream.

Agricultural wetlands provide important habitat for many fish and wildlife species (e.g., Elphick, 2000). A high density of wildlife, such as migratory waterbirds, may thus be exposed to elevated MeHg concentrations produced within these habitats. Even without contamination from local mining sources, the increasing global dependence on fossil fuels (particularly coal) in both industrial and developing countries may be increasing the rate of atmospheric Hg transport and deposition to rice-growing regions, such as southeastern Asia, the western United States, the Gulf of Mexico, Brazil, and India (Selin, 2009). The result may be that agricultural wetlands, especially rice fields, could become an increasingly important source of MeHg to wildlife and humans.

Given the regional and global significance of agricultural wetlands, and the potential for episodic and site-specific pulses in MeHg production, export, and bioaccumulation, we examined Hg pools and fluxes,

and associated biogeochemical factors, in a suite of wetland habitats managed for either agriculture or wildlife purposes. Our primary goals were to: 1) quantify MeHg sources and sinks at the field scale; 2) relate sources and sinks to key biogeochemical processes; and 3) assess the relative importance of different wetland conditions that could be managed to mitigate MeHg production, export, and bioaccumulation. Herein, we synthesize the findings of seven independent research papers in this special section, focused on describing how Hg and MeHg pools and fluxes are linked in wetlands managed for agriculture (rice growing) and wildlife in California's Central Valley, U.S. In this synthesis, the value of multi-disciplinary, integrated datasets is examined for the elucidation of the relationships and factors driving Hg biogeochemistry in agricultural and managed, non-agricultural wetland settings.

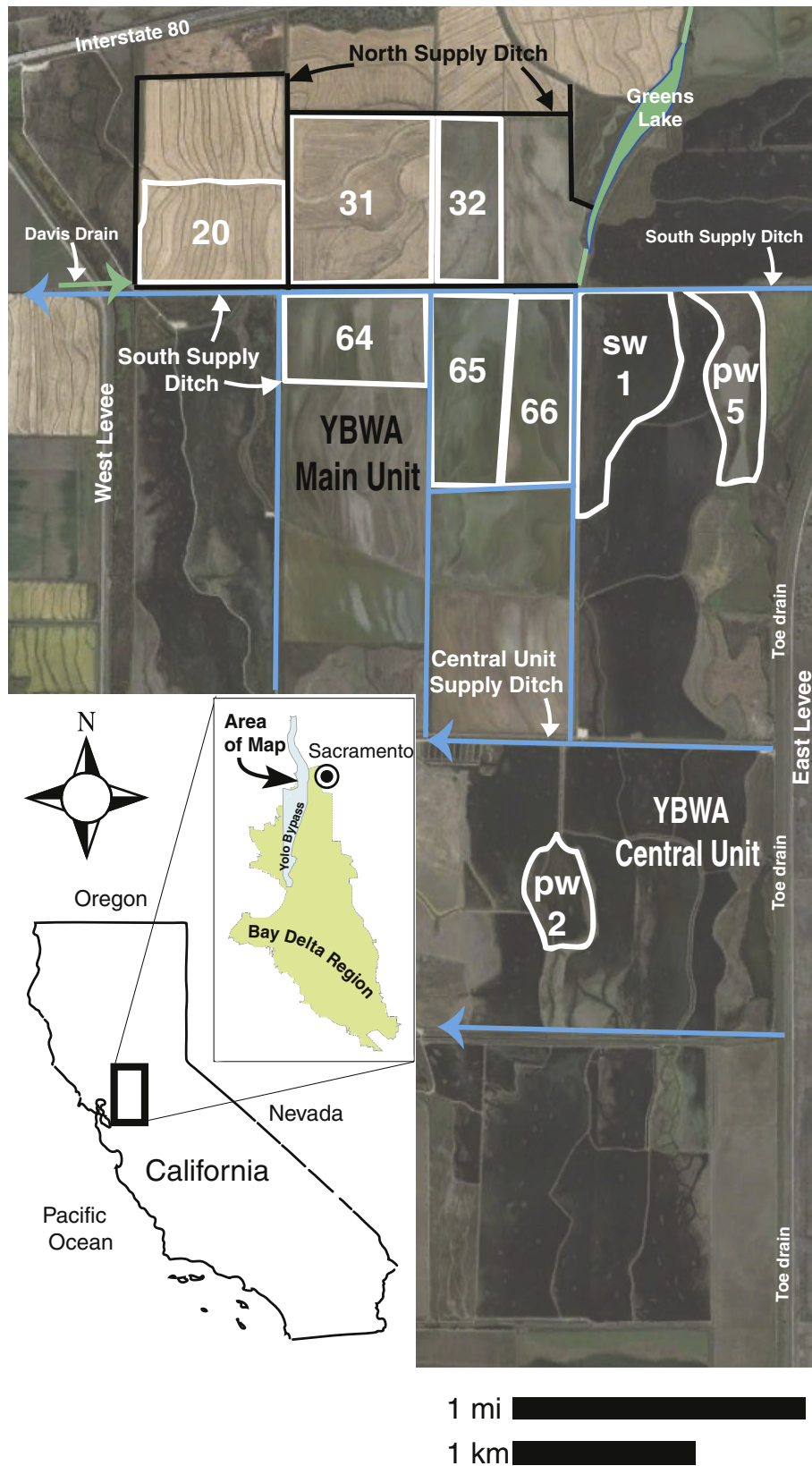
## 2. Methods

### 2.1. Field setting

The Yolo Bypass (YB) is a low-elevation depression that has been engineered as a component of the Sacramento River Flood Control Project, routing high flows in the Sacramento River around the city of Sacramento, California (Fig. 1). The Yolo Bypass Wildlife Area (YBWA) is a 6800 ha preserve representing about one-quarter of the total acreage. The YBWA is owned by the State of California, and managed by the California Department of Fish and Game (CDFG) with the primary goal of flood control, and secondary goals of promoting wildlife habitat (especially for wintering waterfowl) and recreational opportunities, in a landscape mosaic comprised of diverse upland and wetland settings. Because the primary management goal is flood control, there are restrictions on the type and density of vegetation allowed to accumulate so that flows are not impeded. One wetland habitat type that serves all land management goals, as well as providing economic return, is rice cultivation. Approximately 34% of the YBWA is managed as agricultural wetlands for production of both white rice (*Oryza sativa*) and wild rice (*Zizania palustris*). Rice cultivation along with other agricultural operations within the YBWA (e.g. livestock grazing) contributes to the economic sustainability of the preserve by providing lease income to the State. Non-agricultural wetlands within YBWA consist of duckling brood ponds, open-water ponds, and winter-flooded seasonal wetlands that are mowed often to promote higher flow velocities when the YB is inundated by high river flows from snowmelt and reservoir releases (CDFG, 2008).

The YB resides in a Mediterranean (xeric) climatological zone which experiences hot, dry summers and cool, wet winters. Average daily air temperature ranges from 5 °C to 15 °C in January to 20 °C to 35 °C during July and August. The area has average annual precipitation of approximately 50 cm, which typically occurs between October and April. Despite high evaporation rates through the summer months, due to intense solar radiation and low-humidity winds, wetlands naturally persist within the low-lying YB naturally due to surrounding flows of the large delta watershed that integrates surface flows from the Sierra Nevada, the Cascades and the Coast Range Mountains.

Water management within the YBWA is complex. During summer low-flow conditions, the dominant sources of water are agricultural drains from the north and west (Toe and Davis Drains). This water is made available by pumping based on Pacific Ocean tides, from the Sacramento–San Joaquin Delta (Delta) to the south (Fig. 1). This area is considered the northernmost extent of the statutory San Francisco Bay–Delta since it is affected by ocean tides. Water management during summer dry conditions is primarily for agriculture and includes extensive within-basin water recycling. The primary conduit of source water in summer is the Toe Drain on the eastern edge of the YB along the Sacramento River levee (Fig. 1). Toe Drain water is pumped into the YBWA via several lateral ditches running east–west (South Supply, and Central Unit Supply Ditch). The lateral ditches transport and distribute the Toe Drain water west to the agricultural fields that were part of



**Fig. 1.** Map illustrating the location of the study area within the Yolo Bypass Wildlife Area, Yolo County, CA. The location and boundaries of specific agricultural and managed (seasonal and permanently flooded) wetlands are identified to coordinate with all publications of this special section. North Block fields (20, 31, and 32) receive irrigation from the North Supply Ditch (Davis Drain and Greens Lake) whereas the South Block fields (64, 65, and 66) receive irrigation from the South Supply Ditch (Toe Drain). In the 2007–8 crop year, each block contained one replicate agricultural wetland for each of the 3 categories: rice (R31 and R64), wild rice (W32 and W65) and fallowed (F20 and F66). Additional locational information (GPS coordinates, field descriptions, and specific sampling locations) is listed in Supplementary Table 1.

the study area, and to other agricultural fields further west within the YB. Water returns to YBWA from the agricultural areas to the west within and to the west of the YB via the Davis Ditch, and mixes with Toe Drain water pumped into Greens Lake, which in turn supplies fields in the northern part of the YBWA. In the winter season of years with sufficient runoff (approximately one of every three years), the YB carries high flow from the Sacramento River, Colusa Basin Drain (Knights Landing Ridge Cut), and the Coast Range tributaries (Cache Creek, Putah Creek, and Willow Slough) and floods most of the agricultural fields (see Fig. 1 in Springborn et al., 2011).

The YB sub-basin has been identified as a significant source of MeHg to the Sacramento–San Joaquin Delta (Wood et al., 2010). One factor that likely contributes to elevated MeHg transport in the YB is elevated total Hg (THg) concentrations in YBWA surface sediment, which exceeds 600 ppb ( $\mu\text{g kg}^{-1}$ ) in some sections (W.A. Heim et al., Moss Landing Marine Laboratories, unpublished data). Sources of Hg to the YB include wastes from legacy gold and mercury mining operations throughout multiple upstream watersheds (Alpers et al., 2005; Rytuba, 2003; Springborn et al., 2011). The development of a Total Maximum Daily Load (TMDL) for MeHg in the Delta (Wood et al., 2010) has raised the need for a greater understanding of Hg cycling (particularly MeHg) in the region, so that management decisions can be made to minimize ecological and health effects caused by Hg contamination.

The selection of study wetlands within the YBWA was based on farmer cooperation, contiguity, planned crop rotations, and hydrologic infrastructure that allowed extensive hydrologic control. Two replicate fields were chosen for each crop type (white rice = R, wild rice = W, and fallowed rice fields = F), with one crop replicate in each of two blocks (North = fields 20, 31, and 32; South = 64, 65, 66), and with each block representing a different hydrologic source (Fig. 1; Alpers et al., in this issue). One seasonally-flooded wetland (SW 1 dominated by *Crypsis schoenoides*, swamp timothy), and two permanent wetlands (PW 2 and 5) dominated by open water and surrounded by *Schoenoplectus acutus* and *Typha* spp. (native bulrush and cattail, respectively) were used as non-agricultural reference sites. Wetland surface areas varied in size (16 to 78 ha). Initial sediment qualities were also variable, such as surface sediment organic matter which was elevated in non-tilled wetland environments, and surface sediment THg concentrations which generally increased with longitude (Marvin-DiPasquale et al., in this issue). Therefore, differences in initial soil conditions, due to differences in source sediment deposition (Springborn et al., 2011), and possibly due to historic land use practices (e.g. tilling), complicate direct interpretations of management practice influences on Hg cycling among wetland types. Despite these limitations, results presented in the 7 manuscripts synthesized here allowed for development of a process-based conceptual model for MeHg production, degradation and export.

## 2.2. Study design and brief description of methods

The desired outcome of this study was to provide guidance on the development of management practices that minimize MeHg production within managed wetlands of the YBWA and MeHg export to the Sacramento–San Joaquin Delta. Based on previous work we hypothesized that wetlands managed for agricultural production would have elevated MeHg production, export, and bioaccumulation due to pulsed flooding and productivity. The data synthesized here represent a coordinated, intensive one-year multidisciplinary study investigating a wide range of processes affecting MeHg cycling within 9 wetlands (hydrologic units or fields) exposed to different management practices. We examined biogeochemical and hydrologic processes during an 11-month period (June 2007 through early May 2008) representing a full crop year in 5 wetland habitat types: 3 types of shallowly-flooded agricultural wetlands (white rice, wild rice, and fallowed fields) and 2 types of naturally vegetated wetlands managed hydrologically for wildlife objectives (permanently and seasonally flooded; hereafter, managed

wetlands). Sampling schedules were designed to address representativeness and variability at critical temporal and spatial scales. Specific attention was paid to initial conditions and daily-to-annual dynamics of interacting ecosystem components, such as solar radiation, surface water chemistry, sediment and pore water chemistry, vegetation, and biota. Whereas most of the summer data reported are from June–September 2007, measurements of photolytic effects and diel cycling were conducted during the summers of both 2007 and 2008 within a subset of the wetlands (Fleck et al., in this issue). Despite having only a single year of measurements, seasonal differences between summer and winter flooding periods are predicted to be consistent from year to year, given the operational water management protocols that are used to achieve agricultural and wildlife goals within the YBWA.

Mercury speciation, fluxes, and transformation rates were assessed for water column and sediment components within each wetland type to determine the biogeochemical and hydrological processes influencing MeHg source/sink load dynamics (Fig. 2). Analyses of Hg species and associated analytes are described within individual manuscripts of this special section and were performed according to USGS-approved quality assurance procedures, including the documentation of results associated with field duplicates, laboratory duplicates, certified reference material recoveries and matrix spike recoveries, where appropriate. Specifically, surface (0–2cm) sediment MeHg production rates (Marvin-DiPasquale et al., in this issue) were calculated for 5 sediment sampling periods (June, July, August, and December 2007 and February 2008) as a function of inorganic Hg(II) availability (measured via the ‘reactive mercury’ (Hg(II)<sub>R</sub>) assay), and the activity of the native microbial Hg(II)-methylating community (measured via <sup>203</sup>Hg(II) incubation) (Marvin-DiPasquale et al., in this issue). Sulfate reduction rates were also assessed for comparison with rates of MeHg production, using <sup>35</sup>S radioisotope tracer incubations (Jørgensen, 1978). Total Hg and MeHg accumulation by plants (Windham-Myers et al., in this issue-b) were calculated at the same time points as sediment sampling. Water-column processes included more time points (>92), and diel -to-seasonal periods to assess flux rates. MeHg photodegradation rates (Fleck et al., in this issue) were estimated with in situ bottle incubations and extrapolated to daily rates based on variations in solar radiation and canopy shading. Mercury hydrologic transport and partitioning

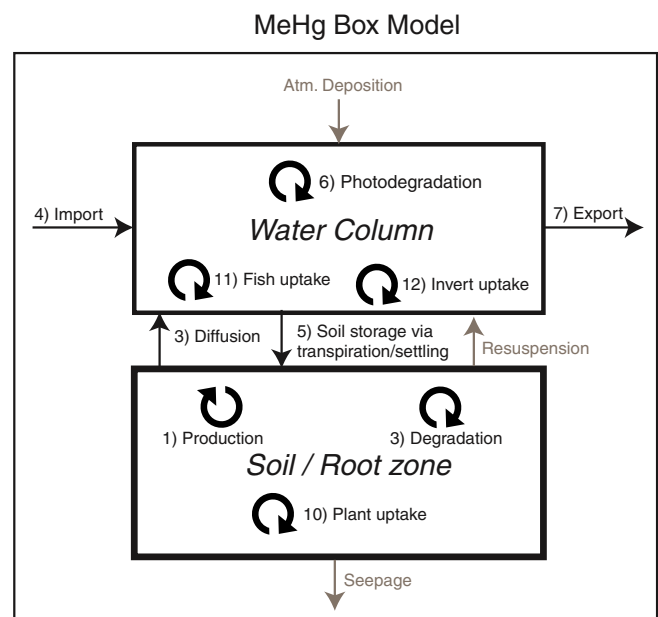


Fig. 2. Simple box model for measured, calculated, and estimated wetland processes associated with MeHg production, export, and bioaccumulation in the water column and surface sediment. Black arrows and numbers refer to line items in Table 1. Unmeasured processes are indicated by gray font and arrows.

(Bachand et al., in this issue-b; Alpers et al., in this issue) were calculated based on daily hydrologic variables, and weekly-to-monthly water quality samples for Hg and MeHg concentrations. Mercury bioaccumulation was measured in caged and wild mosquitofish (*Gambusia affinis*, Ackerman and Eagles-Smith, 2010), and Hg and MeHg concentrations were measured in aquatic invertebrates (Ackerman et al., 2010). Thus, seasonal and spatial trends in MeHg production were examined in the context of microbial processes and plant life-cycle dynamics. Similarly, MeHg sources, sinks, and transport were examined in the context of hydrologic pathways, source water composition, photo-demethylation, particle settling, and benthic exchange. MeHg bioaccumulation in fish and invertebrates was examined in the context of hydrology (inlet versus outlet locations) and habitat type during the summer months only.

Here the data are synthesized by comparing the MeHg dynamics quantitatively for all wetland types (agricultural, and permanently and seasonally flooded), and seasons (summer versus winter). Rates of MeHg production ( $\text{ng m}^{-2} \text{d}^{-1}$ ) were measured, calculated and estimated based on the 7 papers in this special section and prior work (Table 1). Rates were calculated as means and standard errors ( $N = 12\text{--}72$ ) among the two wetland categories, combining data associated with each field replicate and season. Summer data focused on the July–August period, and winter data focused on the December–February period. All MeHg flux rates are reported on an areal basis except for fish and invertebrate bioaccumulation, which is calculated on a dry weight basis (Table 1).

### 2.3. Wetland management

Management practices differed strongly among wetland types and slightly among field replicates (Fig. 3). To characterize field conditions and water flow accurately for each replicate field, management practices were assessed for each individual field with detailed attention given to hydrologic loads and internal flow paths using models fitted with field measurements of water quality and hydrology (Bachand

et al., in this issue-a). Field management actions were not predetermined, but optimized for rice-growing by the farmer for each agricultural field at different stages of crop development. Management actions included the timing of field flooding, draining, harvesting, seeding, fertilization, and other amendment practices, as well as the control of surface water flow rates and residence time. Despite the general similarities between the management of white and wild rice in terms of sulfate loading from fertilization (e.g. 119–268  $\text{kg SO}_4^{2-} \text{ha}^{-1}$  as ammonium sulfate and zinc sulfate, pers. comm. Jack DeWit, DeWit Farms, Inc.) and crop development (~4 months), specific field management practices often differed for the 2 crop types (Fig. 3). For example, wild rice fields received no herbicide and were harvested in standing water during late August to early September. In contrast, white rice fields received multiple herbicide applications (e.g. DowAgro Granite™ and Clincher™) and were drained thoroughly prior to harvest during October.

Growing season water depth was shallow (<30 cm) in all agricultural fields, but the timing and flooding depth varied between fields to accommodate different goals: 1. fallowed fields were shallowly flooded (approximately 5 cm) for 2 months, to germinate and kill resident weeds in sediment to be cropped the following year, and to accommodate migrating shorebirds, 2. white rice fields were flooded continuously over the growing season (5 months) to a standing water depth of approximately 10–20 cm for crop production and 3. wild rice fields were flooded for 4 months to 15–30 cm, for crop production and harvesting. For both crops, flow was modulated to reduce water use and also to prevent extreme increases in temperature and alkalinity. Wildlife-managed wetlands were kept permanently flooded (approximate depths of 120–150 cm at the center and 0–20 cm in the littoral zone) or were seasonally flooded (10–20 cm) during the fall and winter months for waterfowl (typically October through April). Replicate wetlands within a given category were similar in hydrologic management (Bachand et al., in this issue-b) and initial soil conditions (Marvin-DiPasquale et al., in this issue), varying primarily in their water source (Alpers et al., in this issue). Vegetation was also similar

**Table 1**

Average daily rates of MeHg production, transport, and bioaccumulation processes during peak flooding periods – summer (July–August 2007) and winter (December 2007–February 2008). Data are categorized as agricultural wetland ( $n = 2$  each for white rice, wild rice, and fallowed fields), permanent wetland ( $n = 1$  for summer,  $n = 2$  for winter), and seasonal wetland ( $n = 1$ ). Data are reported as mean  $\pm$  standard error (between field and laboratory replicates,  $n = 12\text{--}201$ ) in  $\text{ng m}^{-2} \text{d}^{-1}$  for sediment, water, and plant fluxes. Data sources are indicated by superscript. \*Fish and invertebrate bioaccumulation reported in  $\text{ng g}^{-1} \text{dry weight d}^{-1}$ . ND = no data.

Rates	Measured/calculated/ estimated	Summer (July–August)		Winter (December–February)		
		Agricultural wetland	Permanent wetland	Agricultural wetland	Permanent wetland	Seasonal wetland
<i>Sediment MeHg production (<math>\text{ng m}^{-2} \text{d}^{-1}</math>)</i>						
1) Gross potential microbial sediment MeHg production	M	<sup>a</sup> 1671 $\pm$ 540	<sup>a</sup> 844 $\pm$ 147	<sup>a</sup> 2023 $\pm$ 1014	<sup>a</sup> 306 $\pm$ 98	<sup>a</sup> 146
2) Net sediment MeHg production (by seasonal difference)	C	<sup>a</sup> 174 $\pm$ 157	<sup>a</sup> –70 $\pm$ 99	<sup>a</sup> 341 $\pm$ 125	<sup>a</sup> –35 $\pm$ 68	<sup>a</sup> 92
3) MeHg loss from soil (degradation and/or diffusion)	E	<sup>b</sup> 1497 $\pm$ 563	<sup>b</sup> 914 $\pm$ 177	<sup>b</sup> 1682 $\pm$ 1022	<sup>b</sup> 341 $\pm$ 119	<sup>b</sup> 54
<i>Ecosystem MeHg production (<math>\text{ng m}^{-2} \text{d}^{-1}</math>)</i>						
4) Import (hydrologic)	M	<sup>c</sup> 4 $\pm$ 7	<sup>d</sup> 2.3 $\pm$ 0.2	<sup>c</sup> 3 $\pm$ 2	<sup>d</sup> 1.3 $\pm$ 0.2	<sup>d</sup> 2.7
5) Temporary sediment storage (root-zone)	C	<sup>c</sup> 7 $\pm$ 9	ND	<sup>c</sup> –6 $\pm$ 28	ND	ND
6) Photodegradation	C	<sup>e</sup> 3 $\pm$ 1	<sup>e</sup> 0.7	ND	ND	ND
7) Export (hydrologic)	M	<sup>c</sup> 5 $\pm$ 3	<sup>d</sup> 0.3 $\pm$ 0.1	<sup>c</sup> 11 $\pm$ 10	<sup>d</sup> 0.3 $\pm$ 0.1	<sup>d</sup> 5.0
8) Calculated net ecosystem MeHg accumulation	C	50	5	2	1	2
9) Imbalance (Line 8–Line 2)	E	–124	+75	–339	+35	–90
<i>MeHg bioaccumulation</i>						
10) Plant uptake ( $\text{ng m}^{-2} \text{d}^{-1}$ )	M	<sup>f</sup> 39 $\pm$ 3	<sup>f</sup> 6 $\pm$ 1	<sup>f</sup> 0	<sup>f</sup> 0	<sup>f</sup> 0
11) *Fish uptake ( $\text{ng g}_{\text{dw}}^{-1} \text{d}^{-1}$ )	M	<sup>g</sup> 21	<sup>g</sup> 5	ND	ND	ND
12) *Invertebrate uptake ( $\text{ng g}_{\text{dw}}^{-1} \text{d}^{-1}$ )	M	<sup>h</sup> 3	<sup>h</sup> 5	ND	ND	ND

<sup>a</sup> Calculated from dataset used in Marvin-DiPasquale et al. (in this issue) (Supplementary Table S.1a and S.1.b).

<sup>b</sup> Calculated as Line 1–Line 2.

<sup>c</sup> Bachand et al. (in this issue-b).

<sup>d</sup> Windham-Myers et al., (2010, Tables 5.7 and 5.8).

<sup>e</sup> Windham-Myers et al., (2010, Table 5.10).

<sup>f</sup> Windham-Myers et al. (in this issue-b).

<sup>g</sup> Calculated from data used in Ackerman and Eagles-Smith (2010), white rice and wild rice fields averaged.

<sup>h</sup> Calculated from data used in Ackerman et al. (2010), white rice and wild rice fields averaged.

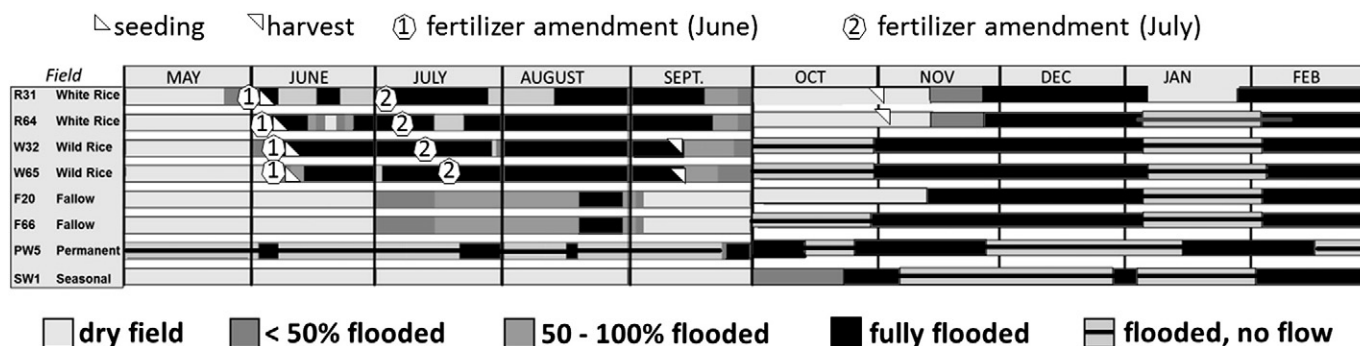


Fig. 3. Schedule of wetland management for all hydrologic units studied from May 2007 to February 2008. Flood status data collected from weekly site visits and verified where possible with pressure transducers. Fertilizer applications (normalized by sulfate concentration and provided by Jack DeWit, DeWit Farms, Inc.) were estimated at 18 to 141 kg sulfate per hectare (June) and 101 to 162 kg sulfate per hectare (July). Further amendment details are available in Supplementary Table S5.11 in Alpers et al. (in this issue).

between replicate fields, except for the fallow fields, for which one (F20) was largely non-vegetated throughout the study (Windham-Myers et al., in this issue-b).

Given the one-year, multi-field sampling design, these data provide insight to variability along time and space gradients. However, the study design lacks a true replication of seasonal treatments (e.g. multiple years). Given the fairly consistent management for the different wetlands from year-to-year we hypothesize that this one year study is indicative of what would occur during other similar water years. Further, source/sink dynamics were best constrained when and where hydrologic flows met modeling criteria. Because of this load dynamics are best estimated for the agricultural fields (with > 14 data pairs, inlet vs. outlet), whereas acceptable flow data for hydrologic modeling was limited in the permanent wetland (Bachand et al., in this issue-a).

### 3. Results and discussion

#### 3.1. Overall pattern for agricultural versus wildlife-managed wetlands

Agricultural wetlands were subject to pronounced, pulsed wetting and drying phases, including two separate flooding events per year (Fig. 3), during the summer growing season and again in fall/winter for rice straw decomposition and to provide habitat for wintering waterfowl. In contrast, the non-agricultural seasonal wetland had a single flooding event during fall/winter to provide habitat for wintering waterfowl, whereas permanent wetlands were continuously flooded throughout the year (Fig. 3).

The processes and patterns related to Hg cycling in the agricultural wetlands were markedly different from those in the permanent and seasonal wetlands managed for wildlife (see Ackerman and Eagles-Smith, 2010; Alpers et al., in this issue; Marvin-DiPasquale et al., in this issue; Windham-Myers et al. in this issue-a,b). Hydro-period characteristics – specifically the depth, duration, frequency, and timing of flooding – appeared to be the primary drivers of geochemical and biological differences among the wetlands studied, as observed in the strong seasonality between wetland types (Bachand et al., in this issue-b). In addition to direct alterations to physical flow (i.e. irrigation pathways, flow rates, residence times, and water depths) that regulated MeHg transport and benthic flux, hydrology also indirectly affected biological processes, including microbial Hg(II)-methylation rates (Marvin-DiPasquale et al., in this issue), primary productivity (Windham-Myers et al., in this issue-b), labile carbon supply (Windham-Myers et al. in this issue-a,b), Hg-bioaccumulation in resident fish (Ackerman and Eagles-Smith, 2010) and invertebrates (Ackerman et al., 2010), as well as the relative importance of benthic diffusion (Bachand et al., in this issue-a).

Using Fig. 2 as a template, the data from  $n = 10$  papers are synthesized into estimated daily rates of key MeHg fluxes for two wetland types (agricultural vs. permanently flooded) during the summer and winter hydro-periods (Table 1). In contrast to the individual papers

that provide detailed information, this discussion focuses on the primary differences among wetland types with respect to the magnitude of MeHg production, loss, and bioaccumulation fluxes (Sections 3.2 through 3.4). Further, this quantitative comparison allows for the examination of relationships between the various Hg-cycling pathways, and aids in comparing MeHg management options within managed wetlands (Section 3.5).

#### 3.2. Sediment methylmercury production

Net sediment MeHg production potential (MPP) rates were similar for each wetland type during the peak flooded periods during summer and winter (post-harvest). During both seasons, flooding led to a reduction in inorganic Hg(II) availability and an increase in the activity of the native microbial Hg(II)-methylating community (Marvin-DiPasquale et al., in this issue). Inorganic Hg availability and microbial activity associated with methylation varied 100-fold and 10,000-fold, respectively, across all study sites and sampling periods, yielding a wide range of MPP rates ( $0.34\text{--}490 \text{ pg MeHg g}_{\text{dw}}^{-1} \text{ d}^{-1}$ ). Despite similarities in daily average MPP rates between agricultural and managed wetlands (median =  $29.7$  vs.  $29.6 \text{ pg MeHg g}_{\text{dw}}^{-1} \text{ d}^{-1}$ , respectively), median sediment MeHg concentrations were nearly 50% greater in agricultural wetlands compared to managed wetlands, and up to 350% greater during winter. As described further by Marvin-DiPasquale et al. (in this issue), manipulated flooding and drying resulted in dynamic temporal changes in sediment redox conditions, microbial activity associated with Hg(II)-methylation, Hg(II)<sub>R</sub> concentration, and the concentrations of microbial electron acceptors (sulfate and ferric iron) and electron donors (e.g. acetate). The indirect effects of flooding and drying were evident in the cycles of all redox-sensitive elements studied (i.e. carbon [C], iron [Fe], and sulfur [S]). For example, the carbon cycle was altered via hydrology-dependent influences on plant productivity and decomposition rates (Windham-Myers et al., in this issue-a).

Methylmercury production was observed in sediment dominated by either microbial iron or sulfate reduction, with the former generally more dominant in the agricultural fields based on carbon flow calculations (Marvin-DiPasquale et al., in this issue). Temporal (month to season) changes in sediment pools of Fe(II), Fe(III) and total reduced S (TRS) were correlated with the activity of the Hg(II)-methylating microbial community ( $k_{\text{meth}}$ ) and patterns suggest an overall dominant role of sulfate-reducing bacteria (SRB) in the Hg(II)-methylation process across the range of sites studied (Marvin-DiPasquale et al., in this issue). However, the activity of SRB apparently was not stimulated by additions of  $\text{SO}_4^{2-}$ -based fertilizer to agricultural wetlands, suggesting that sulfate concentrations were not limiting SRB activity (Marvin-DiPasquale et al., in this issue). Rather, strong responses in microbial Hg(II)-methylation rates to seasonal and experimentally induced changes in pore water acetate suggested that, over the full annual cycle, the availability of labile organic matter (as opposed to specific

electron acceptors) was the primary factor mediating MeHg production among sites (Windham-Myers et al., in this issue-a).

The importance of sediment biogeochemistry in mediating the spatial and temporal availability of Hg(II) for methylation was also evident. Median concentrations of Hg(II)<sub>R</sub> were >20-fold higher in agricultural wetlands compared to permanently flooded wetlands, and were negatively correlated with sediment TRS concentration (Marvin-DiPasquale et al., in this issue). In contrast, the microbial activity associated with Hg(II)-methylation (measured as  $k_{\text{meth}}$ ) was approximately 15-fold lower in agricultural wetlands compared to permanently flooded wetlands. The net result of these opposing trends is that calculated MPP rates were not significantly different between wetland types during the full study period (Marvin-DiPasquale et al., in this issue). However, the similarity in MPP rates, coupled with the large differences in sediment MeHg concentration among wetland types, suggests significant variability between wetlands in benthic demethylation, and/or transport processes between soil and water phases (Bachand et al., in this issue-b). Active transpiration during the growing season in agricultural wetlands likely influenced both constituent transport and biogeochemistry, but without continuous profiles of redox within these fields we are unable to conclusively show the oxidative effect of transpiration. However, results of the revegetation experiment by Windham-Myers et al. (in this issue-a) support the role of plants in reoxidizing Fe and possibly S species during the growing season. Further, whereas potential rates may differ from in situ rates, we also note that another unmeasured storage term for MeHg may be biofilm (Dominique et al., 2007).

Water-quality data also were suggestive that  $\text{SO}_4^{2-}$  availability was not the primary driver of Hg(II)-methylation. Sulfate reducing bacteria did not appear to be  $\text{SO}_4^{2-}$ -limited because concentrations were sufficiently high (relative to known levels that limit the activity of this microbial group) in all source waters used for irrigation (11–103 mg  $\text{SO}_4^{2-} \text{L}^{-1}$  at inlets; Alpers et al., in this issue). This was likely due to regional loading of  $\text{SO}_4^{2-}$  from agricultural and natural sources. Across all wetlands, aqueous MeHg concentrations correlated more strongly with dissolved Fe and Mn concentrations than with the aqueous  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio or with  $\delta^{34}\text{S}_{\text{SO}_4}$  (indicators of sulfate reduction), which suggests that microbial Fe(III)-reduction (and possibly Mn(IV)-reduction) was associated with Hg(II)-methylation in agricultural wetlands (Alpers et al., in this issue).

### 3.3. Aqueous methylmercury transport processes

Methylmercury flux through wetlands, and into and out of the water column, was strongly influenced by water management and the resulting biogeochemical conditions. Corroborating the sediment MeHg production assays (Marvin-DiPasquale et al., in this issue), MeHg production was observed in both summer irrigation and winter flooding periods at the field scale, through hydrologic accounting of Net Ecosystem Production (NEP; Bachand et al., in this issue-b). The transport of aqueous MeHg was dependent upon the interrelationship among horizontal and vertical hydrologic fluxes (surface flow, evaporation, and transpiration), source water concentrations, photodemethylation rates, particulate settling and re-suspension, and benthic diffusion (Bachand et al., in this issue-b; Fleck et al., in this issue).

Methylmercury concentrations in surface waters within both agricultural and managed wetlands varied over a wide range (0.1 to 37 ng  $\text{L}^{-1}$  unfiltered; 0.04 to 7.3 ng  $\text{L}^{-1}$  filtered; Alpers et al., in this issue). Retention and/or degradation of MeHg loads within fields was influenced by unfiltered aqueous MeHg concentrations in source water, which played a key role in whether a given wetland served as a net source or a net sink over a specific time period (Bachand et al., in this issue-b). In all wetland types, aqueous MeHg concentrations during summer were strongly affected by evapotranspiration across fields with loss of up to 90% of incoming waters. Using chloride as a conservative tracer, Bachand et al. (in this issue-a) estimated that plant transpiration actively moved surface-water constituents into the root zone during

summer months, accounting for removal of 35% of incoming chloride loads, and 20–25% of initial MeHg and DOC loads. With the onset of winter flooding, these constituents were released from soils back to the water column. Thus, winter exports were at least in part a legacy export of MeHg produced the previous summer, representing nearly all of the MeHg source in early winter (Bachand et al., in this issue-b).

When evaporation and transpiration processes were factored into the MeHg export rates, the various wetlands exhibited a wide range of MeHg load dynamics, apparently driven more by rates of internal MeHg degradation and storage than by MeHg production. Despite relatively high areal estimates of sediment MeHg production in surface sediment (median = 391 ng  $\text{m}^{-2} \text{d}^{-1}$ ; Marvin-DiPasquale et al., in this issue), aqueous MeHg export was low if not negative (−6 to +8 ng  $\text{m}^{-2} \text{d}^{-1}$ ) across agricultural wetlands during the summer growing season (Bachand et al., in this issue-b). The largest daily exported loads of MeHg (up to 120 ng  $\text{m}^{-2} \text{d}^{-1}$ ) were observed from wild rice fields during the wet harvest period, when MeHg concentrations were elevated due to harvest disturbances of bottom sediment (Alpers et al., in this issue) and when water export was still occurring (Bachand et al., in this issue-b).

Rather than being a direct function of crop management or sediment MeHg production, MeHg export loads were more generally related to season (winter vs. summer) and source water quality (initial unfiltered MeHg concentrations 0.3–2.4 ng  $\text{L}^{-1}$ ). Although variable, daily estimated winter MeHg export loads from all wetlands (seasonal average −4.2 to +13.3 ng  $\text{m}^{-2} \text{d}^{-1}$ ) were typically greater than daily summer export loads (seasonal average −19.5 to +3.1 ng  $\text{m}^{-2} \text{d}^{-1}$ ) (Bachand et al., in this issue-b). Further, the difference among agricultural wetlands associated with incoming source water quality was the primary driver of whether a field acted as a net source or a net sink of MeHg. Up to 5-fold higher summer MeHg concentrations were observed in the northern block source water (Davis Drain), compared to the southern block (Toe Drain; see Fig. 1), which contributed to net MeHg import in the northern fields and net export in the southern fields (Bachand et al., in this issue-b). Because sediment MPP rates did not follow a similar pattern (Marvin DiPasquale et al., in this issue) this difference between fields was more likely to have been caused by 1) greater rates of photodemethylation (Fleck et al., in this issue), 2) settling of MeHg-laden particles where incoming MeHg concentrations were greater (Alpers et al., in this issue), and/or 3) a reduced diffusive gradient from sediment to water column (Bachand et al., in this issue-a).

By comparing apparent benthic flux over seasonal (summer versus winter) and diel (night versus day) periods, the expected concentration-driven diffusion of pore water MeHg into overlying surface water was not observed (J.A. Fleck et al., USGS, unpublished data). Rather, MeHg flux appeared to be moderated by plant transpiration in densely vegetated rice fields during summer months, based on chloride balances (Bachand et al., in this issue-b), and a revegetation experiment (Windham-Myers et al., in this issue-a). Hydrologic modeling and analyses of geochemical data demonstrated that a primary control on exchange between surface water and pore water was downward advective transport of surface water to the root zone, as necessary to meet the transpiration demand, which accounted for >50% of total water losses (Bachand et al., in this issue-a). By forcing the surface-pore water interface deeper into the sediment, the net effect was an inhibition of MeHg diffusion from porewater into overlying surface water, thus providing a previously unrecognized temporary sink for MeHg in surface sediment during periods of active transpiration. Although pore water MeHg flux was not directly measured, inhibited diffusion may be one reason that sediment MeHg concentrations rose in agricultural wetlands through the summer, but did not rise in permanently flooded wetlands despite similar MPP rates (Marvin-DiPasquale et al., in this issue).

Photodegradation also played an important role in reducing MeHg loads during the summer months. Rates of photodegradation for filter-passing (<0.45  $\mu\text{m}$ ) MeHg and fluorescent dissolved organic matter (FDOM) were closely related in controlled bottle incubations, yielding

maximum correlations of MeHg percent loss with shorter wavelengths (280–350 nm;  $R > 0.87$ ,  $p < 0.001$ , Fleck et al., in this issue). Methylmercury mass loss caused by photodegradation was a function of initial filter-passing MeHg concentration and the amount of photoexposure, with ~50% loss occurring over a 2-day-equivalent exposure period for water collected from all fields (Fleck et al., in this issue). Further, biophysical effects of vegetation appeared to be a primary factor in regulating photodegradation (and thus MeHg export) during the growing season. The rapid growth and abundant leaf area of crops reduced photodegradation by limiting incoming radiation (Fleck et al., in this issue) and enhanced within-field storage by limiting upward diffusion of MeHg from sediment pore water into surface water (Bachand et al., in this issue-a). Thus, biophysical processes were significant in redistributing MeHg pools within agricultural wetlands and influencing temporal dynamics of MeHg loads.

### 3.4. Methylmercury bioaccumulation

Using wild-caught and caged western mosquitofish (*G. affinis*), Ackerman and Eagles-Smith (2010) demonstrated rapid bioaccumulation of Hg (>90% as MeHg) within the agricultural wetlands of the current study, with the majority of small fish (82% of caged fish and 59% of wild fish) exceeding established toxicity levels for piscivorous fish and birds (tissue THg >0.2  $\mu\text{g g}^{-1}$  wet weight (wt.)), as well as reproductive effect thresholds (tissue THg >0.30  $\mu\text{g g}^{-1}$  wet wt.; Albers et al., 2007; Burgess and Meyer, 2008). Total Hg biomagnification in fish was much greater in rice fields than in permanent wetlands, and the THg body burden of fish increased spatially from water inlets to outlets within white rice fields. Ackerman et al. (2010) also found significant uptake of Hg (as MeHg) into invertebrates (*Corixidae* [water boatmen] and *Notonectidae* [back swimmers]), with 75% of invertebrates sampled exceeding 0.5  $\mu\text{g g}^{-1}$  dry wt., the established dietary effect levels for mallard ducks (*Anas platyrhynchos*). Invertebrate THg concentrations were higher in permanent wetlands than in white rice, wild rice, or shallowly-flooded fallowed fields, which appeared to be related to a different food web structure (C.A. Eagles-Smith et al., USGS, unpublished data). Similar to fish, invertebrate THg concentrations were higher at wetland outlets than at inlets, and increased from the time of flood-up to the time of draw-down in cultivated rice fields. The results from these companion studies illustrate the biotic implications of water management on in situ wetland exposure, whereby enhanced residence times may be a means to reduce MeHg export to downstream environments but may also enhance bioaccumulation in wetland food webs.

Vegetative stimulation of MeHg production and transport into edible rice grains also played a potentially important role in Hg bioaccumulation (Windham-Myers et al., in this issue-a,b). As seen in other studies of methylmercury concentrations in rice (e.g. Meng et al., 2010), the presence of MeHg in rice tissues and the preferential partitioning of MeHg into the grain (seed) in both white and wild rice species implies that heavy consumption of grain in these fields may be a significant pathway of Hg bioaccumulation for waterfowl and other rice consumers. Median MeHg concentrations in unhusked seed were  $4 \pm 0.8 \text{ ng g}^{-1}$  dry wt. for white rice and  $6 \pm 1.5 \text{ ng g}^{-1}$  dry wt. for wild rice. Thus, a waterfowl diet based entirely on white rice or wild rice seeds would have resulted in nearly a 3-fold or 4-fold increase, respectively, in MeHg exposure compared to a diet based upon native macrophyte seeds (bulrush or cattail). We conclude that an avian diet consisting largely of rice grain from this study area may be a significant Hg exposure pathway, and that over-wintering waterfowl migration from this area may represent a previously unrecognized Hg export pathway (Windham-Myers et al., in this issue-b).

### 3.5. Summary of MeHg fluxes during summer and winter flooding periods

With the wide range of responses for MeHg fluxes among wetland types and seasons, an important outcome of this synthesis is that MPP

rates in surface sediment (Table 1; Line 1, calculated from direct measurements of  $k_{\text{meth}}$  and  $\text{Hg(II)}_{\text{R}}$ ) were 10-fold greater than net sediment MeHg production (Table 1, Line 2, calculated by monthly difference in surface sediment MeHg pools), and were 100-fold greater than net ecosystem MeHg accumulation (Line 8, calculated from storage and load estimates). These comparisons suggest that, despite high MPP rates, MeHg degradation pathways and MeHg retention in the root zone may be important in regulating the actual rate and pattern of wetland MeHg export.

Significant differences in Hg pools and fluxes between wetland types and between seasons are discussed in more detail in specific publications of this special section. However, there are two particularly striking aspects of this synthesis that are not obvious from individual papers. First, there is evidence of a large, undocumented MeHg loss term within the wetlands (see Table 1 – item 9 imbalance). Although not directly measured, microbial degradation may be the single most important sink to explain the limited MeHg accumulation in agricultural sediment and the net loss of MeHg from permanently flooded sediment. It is also possible that the measured loss terms were systematically underestimated. Winter import and export terms for aqueous MeHg were calculated during controlled flooding conditions, whereas the larger, uncontrolled, regional flooding event during February 2008 may have exported a greater amount of MeHg than was documented.

Second, all seasonally flooded wetlands accumulated MeHg in sediment during the period studied, whereas MeHg concentration decreased in permanently flooded sediment and this loss is not accounted for. It is possible that both diffusion to surface water and demethylation losses – whether microbial or photolytic – are greater in permanently flooded wetlands. The continuous flooding, open water, and longer residence time of the permanently flooded habitat prevented the lagged responses observed in seasonally flooded wetlands, and may help explain why the conditions in permanent wetlands often generate a net sink for MeHg.

## 4. Synthesis of study information

### 4.1. Seasonal variation within agricultural wetlands

This study documented that wetlands associated with rice-production, a type of seasonally flooded wetland, had different spatial and temporal patterns of MeHg production, transport, and bioaccumulation compared to naturally vegetated, managed wetlands. Physical controls on hydrology – both natural and managed – strongly altered the dynamics of MeHg sources and sinks. In particular, periodic flooding and active plant transpiration decoupled periods of MeHg production from periods of MeHg export. We found that similar processes of MeHg production, degradation, transport, and biotic uptake occurred in all wetlands studied but their relative importance to the MeHg budget varied profoundly.

This study showed how the fluxes of MeHg varied seasonally between multiple compartments of agricultural and wildlife-managed wetlands over one year. Although potential MeHg production was high in both summer and winter seasons, within-wetland processes of MeHg retention and/or degradation greatly reduced export (Table 1). Other long-term whole-ecosystem Hg cycling studies, using either isotopic Hg additions (e.g. Harris et al., 2007) or experimental flooding (e.g. St. Louis et al., 2004), have shown similar patterns of temporal variability and lagged effects between Hg availability, MeHg production, MeHg export, and biotic uptake. Constructed wetlands with pulsed flooding also show similar relationships (Gustin et al., 2006; Stamenkovic et al., 2005). Of the few biogeochemical assessments of MeHg production within rice fields, a recent study by Rothenberg and Feng (2012) points toward high MeHg production rates in rice-planted sediment during the growing season, and relates the pattern to an indirect influence of Fe cycling on MeHg production. These data, in connection with our findings, suggest that seasonal wetlands have



strong temporal sensitivity, and thus require data on annual time scales to assess MeHg budgets and biotic exposure, due to lagged responses in MeHg production, export, and bioaccumulation.

Because of the consistent management of the YBWA, one year of data was valuable for determining key processes for future monitoring and management. Concomitant sampling of MeHg fluxes in neighboring (but hydrologically distinct) wetlands illustrated the critical time points associated with MeHg flux and exposure. Despite a single year of measurements, hydrologic modeling results (Bachand et al., in this issue-a) suggest that the annual data are at a density sufficient to bridge the hydrologic discontinuities of seasonal wetlands and provide a blueprint for further development of management practices that may limit MeHg export and bioaccumulation. By using a process-based approach to understanding why, when, and where MeHg is produced or removed from surface water, this study provides a framework for designing future monitoring and modeling studies in seasonal wetlands. Our integrated data also call into question the categorization of seasonal wetlands as a MeHg “hot spot” (sensu McClain et al., 2003), as this requires both a clarification of the process in question, as well as an appreciation for lagged responses due to hydrologic and seasonal variability.

When considered as an integrated study, our synthesized data set yielded at least 3 emergent findings and new questions. First, hydrologic flow rates and source water quality altered the magnitude of within-field MeHg fluxes, including relative rates of net MeHg production, storage and degradation, as well as in situ MeHg bioaccumulation in fish, invertebrates and plant tissues. Second, vegetation had physical, chemical and microbial influences on MeHg cycling in sediment and water across a range of temporal and spatial scales, both during the growing season and during senescence. Third, rates of MeHg production, bioaccumulation and export were incongruous in seasonal wetlands due to temporal lags and active biophysical control of MeHg fluxes. In agricultural wetlands in summer, for example, rates of fish bioaccumulation were remarkably high, potential MeHg production rates in sediment were only moderate and rates of MeHg export were low.

While these field-scale observations are compelling for the design of future monitoring plans, and also point to important management options available for controlling MeHg exposure, we note that we were unable to statistically identify specific changes and thresholds in management practices that may optimize control of MeHg export and exposure. Still, given the natural variation observed and the importance of hydrology and vegetation as a control on MeHg production, export, and bioaccumulation across wetland types and seasons, we propose that MeHg dynamics can be manipulated by moderate changes in field management of agricultural and managed wetland habitats. While cultivar management may reduce MeHg concentrations in rice grain (e.g. Rothenberg et al., 2012), we suggest that the most fruitful management options for control of ecosystem MeHg production, export, and bioaccumulation in agricultural and/or seasonally flooded wetlands appear to be related to 1) control of hydrologic flows, and 2) control of microbial production through carbon quality and quantity (crop residue) management, or grazing, as described below.

#### 4.2. Hydrologic controls on MeHg production, export, and bioaccumulation

The primary driver behind the different temporal patterns of MeHg production and export among the various wetlands was water management. By tracking surface–water flows and conservative tracers of water movement (e.g. chloride), we found a number of distinct time points and conditions that could be targeted and modified to reduce MeHg export or bioaccumulation.

Relatively high aqueous MeHg concentrations within the first month after re-wetting previously dried wetland sediment suggest MeHg remobilization from sediment to surface water for both agricultural wetlands and fall/winter-flooded seasonal wetlands (Alpers et al., in this issue). An initial “first flush” event with relatively high MeHg

concentrations has been observed in neighboring YBWA seasonally-flooded (non-agricultural) wetlands soon after the onset of flooding (Marvin-DiPasquale et al., 2009a; W. Heim et al., Moss Landing Marine Laboratories, unpublished data), as well as in experimental wetland mesocosms in Nevada (Gustin et al., 2006). Low rates of sediment MeHg production at the onset of flooding, and limited evaporative concentration suggest that the high MeHg concentrations may be largely attributed to the diffusion of previously-formed MeHg stored in dry sediment (Marvin-DiPasquale et al., in this issue). Prevention or targeted treatment of this preserved MeHg pool may limit early season MeHg e-flux to surface water export during flood-up, whether in early summer or early winter. One management option that should be further studied is incremental flooding, to facilitate an initial pulse and allow that water cohort to be exposed to either maximal photodegradation, coagulation (Henneberry et al., 2011), or post-field treatment by routing outlet waters to a permanently flooded wetland or “polishing pond” (e.g. tail-water processing, W. Heim et al., Moss Landing Marine Laboratories, unpublished data).

The practice of harvesting wild rice during flooded conditions led to a large, harvest-related export of MeHg (Alpers et al., in this issue; Bachand et al., in this issue-b). The pulse of elevated MeHg that occurred during the wild rice harvest was not accompanied by an elevated concentration of suspended particles, so the MeHg appears to have been mostly dissolved or in filter-passing colloids (Alpers et al., in this issue). Restricting drainage during wet harvest operations and allowing post-harvest settling of particulate MeHg prior to field drainage may offer a mechanism to reduce export.

Treating agricultural water either by routing tail-waters into permanent wetlands, irrigating rice fields in series, or recycling effluent back into rice fields to promote within-field MeHg removal processes is a potential way of limiting MeHg export. Despite an increase in aqueous MeHg concentration along the flow path from inlet to outlet in the agricultural wetlands, MeHg loads were often in balance across fields, with zero or negative net flux of MeHg from agricultural wetlands. Within-field loss of MeHg may have been enhanced by particle settling, as well as seasonally-driven rates of photodemethylation, and/or transpiration causing downward advection.

Conditions associated with permanently flooded wetlands resulted in less annual MeHg production, export, and bioaccumulation in fish than was observed in agricultural wetlands. Although the activity of SRB in permanent wetlands was among the highest observed, the pool of  $Hg(II)_R$  available for  $Hg(II)$ -methylation was limited, because of relatively high concentrations of solid-phase reduced S and organic matter (Marvin-DiPasquale et al., in this issue). Rather than exporting MeHg hydrologically, permanently flooded wetlands served primarily as a sink for incoming MeHg, likely due to a combination of particle settling and photodemethylation. Thus, moving water from agricultural wetlands to deeper permanently flooded wetlands, coupled with limited water release from those areas, may be another mechanism to lower net MeHg export to downstream water bodies (e.g. the Sacramento–San Joaquin Delta).

The relatively long hydraulic residence times during the growing season, in both agricultural wetlands ( $6–10 d^{-1}$ ) and permanent wetlands ( $32–45 d^{-1}$ ), were important in promoting MeHg degradation and retention. Despite these positive aspects of holding water to limit MeHg export, in situ bioaccumulation was a major concern in rice fields, where MeHg concentrations increased significantly as water flowed across wetlands during the growing season. In white rice wetlands, caged mosquitofish exhibited a 12-fold increase in THg concentrations, to levels well over toxicity thresholds for piscivorous birds, and within 60 days of exposure (Ackerman and Eagles-Smith, 2010). Further, variations in aqueous MeHg concentrations across wetland types showed a positive relationship with MeHg uptake in some resident organisms (e.g. rice plants, L. Windham-Myers et al., USGS, unpublished data; mosquitofish, C.A. Eagles-Smith, USGS, unpublished data). These data point toward optimizing residence times to promote internal removal

processes, such as particle settling and photodemethylation, while minimizing exposure of resident fish and wildlife to elevated MeHg concentrations. With a deeper (>1 m) water column and longer residence time, permanent wetlands may provide a useful independent means for limiting MeHg export to downstream environments, without affecting on-field management decisions. We do note, however, that elevated Hg bioaccumulation in invertebrates was observed in permanent wetlands (Ackerman et al., 2010), suggesting that invertebrates have a different pathway of exposure that may be exacerbated by the low-flow conditions (C. Eagles-Smith, USGS, unpublished data).

#### 4.3. Carbon and biogeochemical controls on microbial MeHg production

In view of the limited ability that resource managers may have to achieve management goals and optimize water flow simultaneously, we also considered constraints on MeHg production through crop management, especially fertilizer application and post-harvest rice residue management.

We found that the areal application of  $\text{SO}_4^{2-}$ -bearing fertilizers (119–268 kg  $\text{SO}_4^{2-}$  ha<sup>-1</sup>, primarily as  $(\text{NH}_4)_2\text{SO}_4$ ) had no observed impact on sulfate reduction rates or on MeHg production, likely because  $\text{SO}_4^{2-}$  concentrations were not limiting to the resident community of sulfate-reducing bacteria (SRB) in this region (Marvin-DiPasquale et al., 2009a, 2009b; Alpers et al., 2014; Marvin-DiPasquale et al., in this issue). However, this finding may be regionally specific due to the YB location at the downstream end of the Sacramento Valley, a large agricultural watershed (Domagalski et al., 2001); in other agricultural regions, especially where source irrigation waters are low in  $\text{SO}_4^{2-}$ , the application of  $\text{SO}_4^{2-}$ -containing fertilizers may indeed enhance the activity of SRB and increase MeHg production, as observed in the Florida Everglades (Orem et al., 2011). Manipulated flooding and drying regimes associated with agricultural wetland management (drawdown during harvest and re-flooding during the post-harvest period to promote the decay of rice straw) strongly controlled microbial biomass and activity (J. Holloway, U.S. Geological Survey, unpublished data). In lieu of  $\text{SO}_4^{2-}$  amendments stimulating the activity of SRB, and with microbial Fe(III) reduction being potentially an important metabolic pathway for organic carbon degradation and Hg(II)-methylation in agricultural fields (Marvin-DiPasquale et al., in this issue), labile carbon availability appears to be the primary factor regulating microbial Hg(II)-methylation rates in YBWA seasonal wetlands, whereas Hg(II) availability is the primary limiting factor in the permanently flooded wetlands.

Optimal rice crop productivity during the growing season results in high rates of C fixation caused by abundant water, nutrients, light, and relatively oxic-to-suboxic conditions. Because the large pool of decaying post-harvest rice straw was found to promote MeHg production, we suggest that techniques be considered to limit labile C availability. This study demonstrated that flooding a rice field to decompose straw residue resulted in high concentrations of sediment labile organic matter (reflected in elevated porewater acetate concentrations, Windham-Myers et al., in this issue-b), which were correlated with enhanced sediment MeHg concentrations and production rates, as well as with elevated MeHg concentrations in surface water during late winter (Marvin-DiPasquale et al., in this issue). As hydrologic exports from YBWA wetlands to the Sacramento–San Joaquin Delta are greatest during winter, agricultural wetland MeHg export was greatest during this period as well (Table 1; Bachand et al., in this issue-b). In the absence of post-harvest burning to remove rice straw from surface sediment (a practice that is now discouraged to benefit air quality), alternative crop residue management options to limit MeHg production may include disking the straw into the sediment or physical consolidation (e.g. baling) and removal of the straw from the site, a practice currently being pursued for reduction of methane emissions in rice fields (e.g. Wong, 2003).

## 5. Conclusions

Based on integrated experimental and comparative field studies, we conclude that seasonally flooded wetlands, especially agricultural (e.g. rice-growing) wetlands, can be a major site of net MeHg production and represent areas of elevated MeHg bioaccumulation during and after the growing season. However, abiotic and biotic degradation or retention of this MeHg can alter the magnitude, direction and seasonal pattern of MeHg flux to the water column. Therefore, seasonally flooded wetlands can be a net MeHg source or sink to downstream environments depending on active management practices as well as seasonal variations in biophysical controls. Temporal spikes in MeHg production, export, and bioaccumulation varied by season, and all processes could be linked to specific seasonal hydrologic practices. Methylmercury concentrations in sediment and water of agricultural wetlands exceeded observed concentrations in neighboring permanently flooded wetlands for the entire annual cycle, and were similar in range to a neighboring seasonal, non-agricultural wildlife managed wetland during its fall/winter flooded period.

Methylmercury biotic exposure was significant in YBWA wetlands studied with resident fish and invertebrates, and during a caged fish experiment, typically exceeding toxicity thresholds for fish and wildlife and birds within only 30 days of exposure (Ackerman and Eagles-Smith, 2010). In regions where THg availability in sediment is relatively high, the expansion of agricultural wetlands may stimulate MeHg production within watersheds. This will also be exacerbated by periodic flooding and drying and the influence on redox-sensitive elements (C, S, Fe and Mn) as well as the production of relatively labile organic matter. This implies enhanced bioaccumulation and potentially toxic effects to resident or migratory organisms and rice consumers. Slower water movement may promote in situ MeHg removal and storage; therefore, recycling field water or using tail-water treatment ponds may be a reasonable method to limit MeHg export during and after the growing season. In addition, rice straw management options aimed at limiting labile C supplies to surface sediment and overlying waters during the post-harvest fall/winter period may be a useful tool in limiting post-harvest MeHg production, bioaccumulation, and export.

Future efforts could include attention to 1) the potential supplemental role of microbial Fe(III) and Mn(IV) reduction in Hg(II)-methylation, 2) quantification of interactions between surface water and pore water constituents, and 3) emphasis on detrital and biofilm components in MeHg cycling. Finally, these data strongly suggest that water quality monitoring programs should consider internal hydrologic processes and both seasonal and diel variability in their sampling plan to ensure accurate characterization of MeHg loads.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.01.033>.

## Acknowledgments

We gratefully acknowledge the State Water Resources Control Board for financial support, the USGS Toxics Program for ongoing support, the USGS Cooperative Water Program, and the land managers of the Yolo Bypass for broad access and field support. Detailed comments from Peter van Metre (USGS), Stephen McCord (MEI), 3 anonymous reviewers and the associate editor Mae S. Gustin greatly improved the clarity of the manuscript. Especially helpful were the logistical assistance of David Feliz, Mary Schiedt and Chris Rocco (California Department of Fish and Game) and Jack DeWit (DeWit Farms). We thank Ann Brice and Robin Kulakow (Yolo Basin Foundation) for supporting outreach and bi-directional information exchange between land managers and the scientific team. We thank many USGS staff members for exemplary field and laboratory support: Elizabeth (Beaulieu) Stumpner, Frank Anderson, Will Kerlin, Jennifer Agee, Le Kieu, Evangelos Kakouras, Pilar Heredia-Middleton, Sherrie Wren, Steven Quistad, Justin Kanerva, Cayce Gulbransen, and Kathy Akstin. The use of trade or product

names is for identification purposes only and does not constitute endorsement by the U.S. Government.

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