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Methylmercury Dynamics in Upper Sacramento Valley Rice Fields with Low Background Soil Mercury Levels

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Abstract

Few studies have considered how methylmercury (MeHg, a toxic form of Hg produced in anaerobic soils) production in rice (*Oryza sativa* L.) fields can affect water quality, and little is known about MeHg dynamics in rice fields. Surface water MeHg and total Hg (THg) imports, exports, and storage were studied in two commercial rice fields in the Sacramento Valley, California, where soil THg was low (25 and 57 ng g^{-1}). The median concentration of MeHg in drainage water exiting the fields was 0.17 ng g^{-1} (range: <0.007–2.1 ng g^{-1}). Compared with irrigation water, drainage water had similar MeHg concentrations, and lower THg concentrations during the growing season. Significantly elevated drainage water MeHg and THg concentrations were observed in the fallow season compared with the growing season. An analysis of surface water loads indicates that fields were net importers of both MeHg (76–110 ng m^{-2}) and THg (1947–7224 ng m^{-2}) during the growing season, and net exporters of MeHg (35–200 ng m^{-2}) and THg (248–6496 ng m^{-2}) during the fallow season. At harvest, 190 to 700 ng MeHg m^{-2} and 1400 to 1700 ng THg m^{-2} were removed from fields in rice grain. Rice straw, which contained 120 to 180 ng MeHg m^{-2} and 7000–10,500 ng m^{-2} THg was incorporated into the soil. These results indicate that efforts to reduce MeHg and THg exports in rice drainage water should focus on the fallow season. Substantial amounts of MeHg and THg were stored in plants, and these pools should be considered in future studies.

Core Ideas

- MeHg dynamics were studied in two rice fields with soil THg near background levels.
- Surface water MeHg and THg imports and exports and soil and plant storage were quantified.
- Net surface water MeHg and THg import occurred in the growing season.
- Net surface water MeHg and THg export occurred in the fallow season.
- Annual MeHg and THg pools in straw and grain were similar to surface water loads.

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THE production of methylmercury (MeHg), a particularly toxic and bioaccumulative form of Hg produced by some anaerobic microbes, is a concern in flooded rice (*Oryza sativa* L.) fields (Compeau and Bartha, 1985; Gilmour et al., 1992, 2013; Chan et al., 2003; Fleming et al., 2006; Kerin et al., 2006; Parks et al., 2013; Windham-Myers et al., 2014a). Methylmercury can accumulate in rice grain, threatening human health (Horvat et al., 2003). Additionally, wildlife in rice fields can be affected by MeHg produced there, and wildlife in downstream ecosystems can be affected by MeHg exported in rice drainage water (Crump and Trudeau, 2009; Ackerman and Eagles-Smith, 2010; Alpers et al., 2014).

Research on rice field MeHg dynamics has been conducted primarily in areas of known Hg pollution, such as Guizhou Province, China (Zhang et al., 2010b; Li et al., 2014; Meng et al., 2014; Zhao et al., 2016) and Hg-affected areas of the California Central Valley (Eagles-Smith et al., 2014; Windham-Myers et al., 2014a). In Hg mining areas of Guizhou Province in inland China, human MeHg exposure through rice consumption exceeds that from fish consumption (Feng et al., 2008; Qiu et al., 2008; Hong et al., 2016; Zhang et al., 2010a). Many studies have compared total Hg (THg) and MeHg concentrations in rice grain and soil at sites with soil THg content ranging over four orders of magnitude from 40 ng g^{-1} in Thailand (Zarcinas et al., 2004) to 34,600 ng g^{-1} near Hg mines in the Wanshan mining district, Guizhou, China (Zhang et al., 2010b).

In places where rice is the dominant land use, export of MeHg in rice drainage waters can potentially have large impacts on water quality. Methylmercury in surface water can bioaccumulate in wildlife, reaching levels in sport fish that are a concern for human health, and negatively affecting wildlife fitness (Chan et al., 2003; Crump and Trudeau, 2009; Ackerman et al., 2014). Little is known about Hg biogeochemical cycling in rice fields or soil and water fluxes (Rothenberg et al., 2014). Understanding of MeHg export is further complicated by MeHg degradation processes such as photodemethylation (Seller et al., 1996; Fleck et al., 2014), microbial demethylation (Spangler et al., 1973; Marvin-DiPasquale et al., 2003), and

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Abbreviations: MDL, method detection limit; MeHg, methylmercury; RL, reporting limit; THg, total mercury; TSS, total suspended solids.

MeHg storage within fields (Bachand et al., 2014; Windham-Myers et al., 2014a).

Export of MeHg from rice fields is a concern in the Sacramento Valley, California, where rice is grown on 240,000 ha of the valley (USDA-NASS, 2016), and Hg and gold mining resulted in Hg contamination in the surrounding mountains (Churchill, 2000; Rytuba, 2003; Alpers et al., 2016). Downstream in the Sacramento-San Joaquin Delta (hereafter referred to as the "Delta"), MeHg concentrations are elevated and negative impacts of Hg on wildlife have been documented (Ackerman et al., 2014). Both field-scale and watershed-scale studies report rice field drainage waters have elevated MeHg concentrations and/or loads during the fallow season (Alpers et al., 2014; Bachand et al., 2014; Eagles-Smith et al., 2014; Tanner et al., 2017), when fields are flooded to decompose rice straw. However, the field-scale studies (Alpers et al., 2014; Eagles-Smith et al., 2014) report concentrations that are considerably higher than observed at the watershed scale (Tanner et al., 2017). This may be because field-scale studies were conducted in areas known to receive Hg-laden sediment from mining regions during flood events (Singer et al., 2013), whereas sediment transport from mining areas into the main Sacramento Valley rice-growing region is limited by dams (Slotton et al., 1995; Supplemental Fig. S1). Thus, there is a need to better understand MeHg export from rice fields in the Sacramento Valley rice-growing region.

We studied rice fields in the Sacramento Valley, where soil THg was lower than in previously studied fields in California. Research focused on surface water imports and exports of THg and MeHg throughout a full annual cycle, and storage of MeHg and THg in soil and plant pools. The hypothesis that MeHg and THg exports in surface water will be elevated in the fallow season compared with the growing season was tested by addressing the following objectives: (i) characterize Hg dynamics in rice fields that were typical of California rice production, (ii) measure the field-scale impact of rice production on Hg-related surface water quality. Findings here will help identify periods of high MeHg export from the fields that could be reduced by modifying management practices.

Materials and Methods

Site Description

Two commercial rice fields were studied, one in Butte county ("Butte," area: 22.1 ha) in the northeast Sacramento Valley and the other in Yolo county ("Yolo," area: 48.6 ha) in the southwest Sacramento Valley (Supplemental Fig. S1). The study period started before planting in May and continued through the end of the following fallow season in February of 2014–2015 and 2015–2016 for Butte and Yolo, respectively. Both fields had heavy clay soils preferred for rice production (Supplemental Table S1). The fields represent the two primary surface irrigation water sources for rice in the region: the Sacramento River (Yolo) and the Feather River (Butte). Yolo also received some recycled irrigation water from surrounding rice fields. Butte irrigation water was diverted from the Feather River downstream of Lake Oroville and stored in the Thermalito Afterbay before entering irrigation canals (Supplemental Fig. S1).

Field Management

Both fields were managed by commercial rice growers using common management practices and rice cultivars for California's Central Valley (University of California Davis Cooperative Extension, 2015). Dates of management events were determined by the growers (Supplemental Table S1). The fields were laser leveled to ensure uniform water height. Irrigation water was supplied to each field through a single inlet. Drainage water exited fields at the outlets through a rectangular weir. Butte had two outlets and Yolo had seven, but drainage occurred through a single outlet per field throughout most of the study (exceptions discussed below).

Soil tillage, field leveling, and seed-bed preparation occurred in April. In early May, fields were flooded prior to planting and pre-germinated rice seed was broadcast by airplane. No outflow occurred from Butte until 10 July, and water level was managed by adjusting inflow rates. Yolo was drained using all outlets 3 d after planting and reflooded 3 d later—a common practice to promote even stand establishment. Often the water level must be lowered to expose weeds for herbicide applications, either by turning off irrigation water and allowing the water to subside through evapotranspiration and percolation (Butte) or a combination of surface outflow drainage and subsidence (Yolo). When water was lowered, areas of shallow standing water were visible, and these conditions lasted no more than 3 d. In July, water inflow was adjusted to maintain a constant level of water in the field with a small amount of surface water drainage (referred to as maintenance flow). Three weeks prior to harvest in September the fields were drained (Supplemental Table S1).

After harvest, soils were tilled to incorporate rice straw and flooded to promote decomposition during the winter fallow (Linquist et al., 2006). Winter flood-up at Butte occurred on 28 October but was delayed at Yolo until 18 December due to water availability (Supplemental Table S1). Fields were drained again in January (Butte) and February (Yolo).

Sample Collection

Samples of irrigation water entering the field (inlet), and drainage water exiting the field through the outlet weir (outlet) were collected every 1 to 2 wk at the inlet and outlet of each field when flow was occurring. Inlets and outlets did not always have flows at the same time, so sampling was targeted to capture each flow period. Samples included initial inflow and outflows during both the growing and fallow seasons, as well as drainage events. There was no inflow or outflow between the preharvest drain and winter flood up, so no samples were collected. Butte received precipitation in November and December, whereas Yolo precipitation occurred from November through February (Supplemental Fig. S2). Precipitation occurring when fields were not flooded resulted in soil saturation and runoff in only one instance. This occurred at Butte in February, and a sample was collected to capture the event (Supplemental Fig. S2e and S2g). Precipitation in November and early December at Butte did not result in flooded conditions before the field was flooded in mid-December. To ensure that the study sites were not anomalous, outlets of four other commercial rice fields near each study site were sampled during the growing season and again in the fallow season (if flooded).

Four soil and plant sampling plots were established in each field, at least 30 m from field edges. Soil samples were collected four times in each field: (i) after spring tillage prior to flooding and planting (May), (ii) prior to drainage for harvest (August), (iii) after fall tillage but before winter flooding (October), and (iv) prior to draining the fields in late winter (February). Rice straw (stems and leaves) and grain samples were collected at harvest.

Sampling Methods and Mercury Analysis

All samples for MeHg and THg analysis were collected using trace-clean sampling techniques (USEPA, 1996). Soil samples were collected differently depending on whether the soil was flooded or dry and tilled. Flooded samples (August and February) were collected as 5-cm-diam., 15-cm-deep soil cores. At each sampling point, two cores were collected and composited. At Butte, these samples were subsampled into four depth intervals (0–2, 4–6, 8–10, and 12–14 cm). No significant effect of depth was found for MeHg or THg at Butte, so only the 0- to 5-cm subsample of Yolo samples was used for laboratory analysis. When dry soil was sampled following tillage (May and October, mixed to a depth of ~15 cm, subsampling by depth was not possible) five scoops (each ~150 cm^3) were collected from a 1-m^2 area and composited in a Ziploc bag. All soil samples were field frozen with dry ice for transport and subsequently stored at −80°C prior to subsampling and analysis. Soil samples were analyzed for MeHg, THg, bulk density, and loss on ignition (Marvin-DiPasquale et al., 2011). Briefly, samples (0.5 g) were digested with aqua regia overnight and analyzed for THg after heated oxidation with BrCl according to USEPA Method 1631 (USEPA, 2002), and quantified on an automated Tekran 2600 total Hg analyzer with a method detection limit (MDL) of 7 pg across matrices. Methylmercury samples were extracted with 25% KOH in methanol for 4 h at 60°C and were then distilled, ethylated (De Wild et al., 2002), and quantified on an automated MeHg analyzer (Brooks Rand, MERX unit) with a MDL of 0.2 pg across matrices. Quality assurance measures included analysis of certified reference materials, laboratory duplicates, and matrix spikes for all MeHg and THg analyses (Supplemental Tables S2, S3, and S4, respectively). Reporting limits (RLs) were 0.11 and 0.065 ng g^{-1} for THg and MeHg, respectively, and all sediment samples had concentrations greater than the RL. New polyethylene terephthalate (PETG) bottles were double bagged in the laboratory prior to water sample collection. Immediately before sample collection, plastic seals on bottles were removed, and bottles were rinsed three times with sample water. Samples were stored on ice until acidified in the field by adding 5 mL of 50% trace-metal-clean HCl. Field blanks and field duplicates were collected for quality assurance of sampling methods (Supplemental Tables S5 and S6). Duplicates were averaged for data analysis. Unfiltered water samples were analyzed for THg and MeHg as described by Marvin-DiPasquale et al. (2011). For surface water, the MDL was 0.007 ng L^{-1} for MeHg and 0.1 ng L^{-1} for THg. Reporting limits were 0.02 and 0.3 ng L^{-1} for MeHg and THg, respectively. For samples less than the MDL, estimated values based on instrument readings were used in statistical analysis. Water samples were also analyzed for total suspended solids (TSS) by USEPA Method 160.2 (USEPA, 1983). Briefly, a known volume of sample is filtered through a preweighed, 1.2-μm glass fiber filter, which is then dried at 105°C to a constant weight.

Rice yield was determined at physiological maturity by harvesting the total aboveground biomass from a 1-m^2 quadrant at each sampling point ($n = 4$), from which 10 to 15 tillers were collected and separated into straw and panicle portions for MeHg and THg analysis. Samples were stored in plastic bags, transported on dry ice, and stored at −80°C. We chose to analyze rough rice (unmilled rice with the husk intact) to better represent all material (and associated MeHg and THg) that was removed from the field at harvest. Rough rice and straw were lyophilized, ground to a fine powder using a coffee grinder cleaned with ethanol between samples (Drennan-Harris et al., 2013), and then analyzed for MeHg using the same approach as for soil (Marvin-DiPasquale et al., 2011). For THg analysis, plant samples were digested with concentrated HNO_3 in an autoclave at 138 kPa and 126°C for 3 h (Kleckner et al., 2017), before addition of BrCl and quantification (Marvin-DiPasquale et al., 2011). All plant tissues had THg concentrations above both the MDL (0.1 ng g^{-1}) and RL (0.23 ng g^{-1}). Three straw samples were less than the RL for MeHg in plant tissues (0.11 ng g^{-1}), but greater than the MDL (0.06 ng g^{-1}).

Irrigation and Drainage Water Volume

Irrigation water applications were measured by the irrigation districts by measuring water flow through a fully submerged inlet pipe with the Remote Tracker System (H2OTech, http://www.h2otechonline.com). This system has a measurement error of <5% (Davids et al., 2013).

To measure outlet flow through a rectangular weir, pressure transducers (Global Water Instrumentation, Model WL16) were installed on the outlet weir, as well as on the soil surface in the field, at a distance of more than four times the maximum head away from the weir. This arrangement allowed for the calculation of head over the weir, and thus flow rates (Aydin et al., 2011), while allowing the farmer to adjust weir height. Staff gauges were installed at inlets and outlets. Gauges were read manually during field visits and photographed daily to verify the logger data. In cases where there was a need to quickly drain the fields from multiple outlets, the volume of water exported during these events was determined by measuring the water height in the field and multiplying by the field area.

Methylmercury and Total Mercury Load Calculations

Loads of MeHg and THg in irrigation and drainage water were calculated by integration. The volume of water entering or leaving the field (measured daily to weekly at inlets and every 2 h at outlets) was multiplied by the temporally closest concentration measurement (at the inlet or outlet, respectively). Loads are reported on a per area basis to account for differences in field size. Net loads were calculated as the difference between surface water inflows (irrigation) and outflows (drainage). Export via percolation, seepage, and evapotranspiration is outside the scope of this study.

Methylmercury and THg pools in grain, straw, and soil were calculated as the product of the concentration and the mass in a 1-m^2 area. We did not want changes in soil pools to be an artifact of shrinking and swelling in response to wet–dry cycles; thus,

pool sizes were calculated based on the (constant) mass of soil in the plow layer. We used the average annual soil bulk density at each plot and a volume of 0.15 m^3 (1-m^2 × 15-cm-deep plow layer) to calculate the mass of soil in the plow layer. Pools were calculated independently for each plot (n = 4 per field), then averages and SDs were calculated.

Statistical Analysis

Because data were collected as a longitudinal survey, autocorrelation potentially exists due to repeated measures and sampling at multiple (soil) depths. The data were analyzed using linear mixed effects regression modeling, the generally accepted method of dealing with potential autocorrelation (Pinheiro and Bates, 2000; Krupa et al., 2012; Bates et al., 2015). Soil and plant samples were collected at plots (n = 4 per field), and water samples were collected at weirs (an inlet and outlet for each field). Repeated measures and autocorrelation were accounted for by including random intercepts for plots or weirs (nested within field) in all models.

Statistical analysis was conducted using R (version 3.3.3; R Core Team, 2016). Tests with $p < 0.05$ were considered significant. Models were initially fitted with the parameterization described below. Parameters (first random effects, then fixed effects) were removed stepwise if not significant. Model assumptions of normalcy and homogeneity of variance were checked using standard diagnostic plots. Environmental data are often skewed, so natural log transformations of response variables were used when necessary to ensure that model assumptions were met. Packages lme4 (Bates et al., 2015), lmerTest (Kuznetsova et al., 2016) and lsmeans (Lenth, 2016) were used to fit and test linear mixed effects regressions, and to calculate least-squares means of model parameters for plotting. All values reported in the text are mean ± SD, unless otherwise noted.

To assess changes in soil THg, MeHg, and %MeHg (MeHg/THg × 100) content by depth, data from Butte in August and February were modeled as Model A: $Y = D + E + (D \times E) + (1|P)$, where Y is the response variable (THg, MeHg, or %MeHg in soil), D is the depth interval (0–2, 4–6, 8–10, or 12–14 cm), E is the sampling event (August or February), $(D \times E)$ is the interaction between D and E, and $(1|P)$ is a random intercept for plot. April and October soil samples could not be divided into meaningful depth intervals because they were collected after tillage events and were excluded from this analysis.

Differences in soil Hg content between fields and sampling events were tested using data from both fields and all four sampling events, but where measurements were made at multiple depths (at Butte in August and February), the 0- to 2- and 4- to 6-cm depths were averaged at each plot. These data were modeled as Model B: $Y = F + E + (F \times E) + (1|P)$, where F is the field (Butte or Yolo), and $F \times E$ is an interaction term. Other terms are defined above.

Water data was analyzed to identify differences in surface water %MeHg, MeHg, THg, and TSS concentration between fields, seasons, and sites. Because only one or two samples were collected at the inlet during the fallow season at each field, inlet samples were not separated by season. These data were modeled as $Y = S + F + (S \times F) + (1|W)$ (Model C), where S is the sampling weir and season (inlet, outlet-growing, or outlet-fallow), $(S \times F)$ is an interaction term, and $(1|W)$ is a random intercept for weir. Other terms are defined above.

Methylmercury, %MeHg, and THg concentration in plant tissues were modeled as Model D: $Y = F + T + (1|P)$, where T is plant tissue type (grain or straw). Other terms are defined above.

Results and Discussion

Soil Mercury and Methylmercury

Butte and Yolo soil THg content (25 ± 7 and 57 ± 4 ng g^{-1}, respectively) were similar to background soil THg reported for the United States and China (Shacklette and Boerngen, 1984; Mingcai and Qinghua, 1997; Obrist et al., 2016), and five to ten times lower than reported for fields in the Delta (Marvin-DiPasquale et al., 2014). Prior studies suggest that MeHg production can be limited when soil THg is <1000 ng g^{-1} (Rudd et al., 1983; Krabbenhoft et al., 1999), as is the case in Butte and Yolo. Total Hg content did not change significantly between sampling events (Supplemental Table S7).

Soil MeHg content was 0.7 ± 0.3 and 0.18 ± 0.04 ng g^{-1} at Yolo and Butte, respectively, and both MeHg and THg were significantly higher at Yolo than at Butte (Model B, Supplemental Table S7). Butte %MeHg in soil (0.8 ± 0.2%) was significantly lower than at Yolo (1.3 ± 0.5%). Methylmercury content increased significantly during the growing season from 0.17 ± 0.05 and 0.49 ± 0.09 ng g^{-1} prior to planting to 0.19 ± 0.06 and 1.0 ± 0.22 ng g^{-1} prior to harvest at Butte and Yolo, respectively (Supplemental Table S7). This increase indicates net MeHg production during the growing season, because the increase in soil MeHg storage was orders of magnitude larger than the amount of MeHg imported in surface water (Table 1, Supplemental Table S7).

Soil MeHg and THg content did not differ significantly by depth in either August or February sampling events in the Butte field (Model A, Supplemental Fig. S3). The lack of differences between depths is likely due to regular mixing of the plow layer from twice-annual tillage.

Surface Water Mercury Concentrations

Surface water MeHg and THg concentrations ranged over three orders of magnitude, from <0.007 to 2 and <0.1 to 70 ng L^{-1}, respectively (Fig. 1). Spikes in MeHg, THg, and TSS concentration were observed at the beginning of the fallow season at Butte, and the end of the fallow season at Yolo (Fig. 2). The cause of these spikes is unknown, and their implications are discussed further below. Both MeHg and THg concentrations were five and six times higher, respectively, in Yolo than Butte (Fig. 2, $p < 0.05$). Between-season trends were similar in both fields (no significant interaction, Model C). Outlet MeHg and THg concentrations were significantly higher than inlet during the winter fallow season but were not significantly different from (MeHg) and lower than (THg) the inlet during the growing season (Fig. 2). Percentage MeHg did not differ significantly between the fields. Growing season outlet %MeHg was significantly higher than both inlet and fallow season outlet (Fig. 2). The TSS concentrations showed similar patterns to THg in drainage water, particularly in the winter (Fig. 1), and differences in TSS between fields and among sites and seasons closely mirrored THg (Fig. 2).

Methylmercury and THg concentrations in outlets of neighboring fields were consistent with Butte and Yolo (Fig. 1). Butte and Yolo are located within the area studied by Tanner et al.

Table 1. Surface water methylmercury (MeHg) and total Hg (THg) budgets for studied fields.

Parameter	Butte				Yolo			
	Water	MeHg	THg	%MeHg†	Water	MeHg	THg	%MeHg
	$m^3\ m^{-2}$	——— ng m^{-2} ———			$m^3\ m^{-2}$	——— ng m^{-2} ———		
Growing season								
Irrigation imports	2.61	82	2027	4.0	1.94	148	7809	1.9
Total export	0.42	5.7	80	7.1	0.32	38	585	6.5
Maintenance drainage‡	0.34	5.4	72	7.5	0.16	27	224	12
Early season drain	–	–	–	–	0.036	6.2	304	1.1
Harvest drain	0.08	0.33	7.7	4.3	0.12	5.2	57	9.1
Export – import	−2.19	−76	−1947	–	−1.62	−110	−7224	–
Fallow season								
Irrigation imports	0.41	4.7	479	0.98	0.36	14	960	1.5
Drainage exports	0.20	40	727	5.5	0.17	214	7456	2.9
Export – import	−0.21	35	248		−0.19	200	6496	
Annual								
Irrigation imports	3.02	87	2506	3.4	2.3	162	8769	1.8
Drainage exports	0.62	46	807	5.7	0.49	252	8041	3.1
Export – import	−2.35	−41	−1700		−1.81	90	−728	

† %MeHg = (MeHg/THg) × 100.

‡ Total export = mainenance drainage + early season drain + harvest drain.

(2017) who reported similar irrigation and drainage water MeHg concentrations and seasonal patterns.

Hydrologic Methylmercury and Total Mercury Budget

Consistent with our hypothesis, both fields were MeHg and THg sinks (net importers) during growing and sources (net exporters) during the fallow season (Table 1). During the growing season (May–September), only 16% of irrigation water applied was exported as drainage water. Because concentrations in irrigation and drainage water were not significantly different during the growing season, and there was net water loss due to evapotranspiration, the fields acted as MeHg and THg sinks. During the fallow season, 50% of irrigation water applied was exported as surface drainage water (remaining water was retained in saturated field soil and lost via percolation, seepage, and evaporation), but concentrations of MeHg and THg were 6 to 18 times higher in drainage compared with inflow water (Fig. 2). Thus, the fields were MeHg and THg sources during the

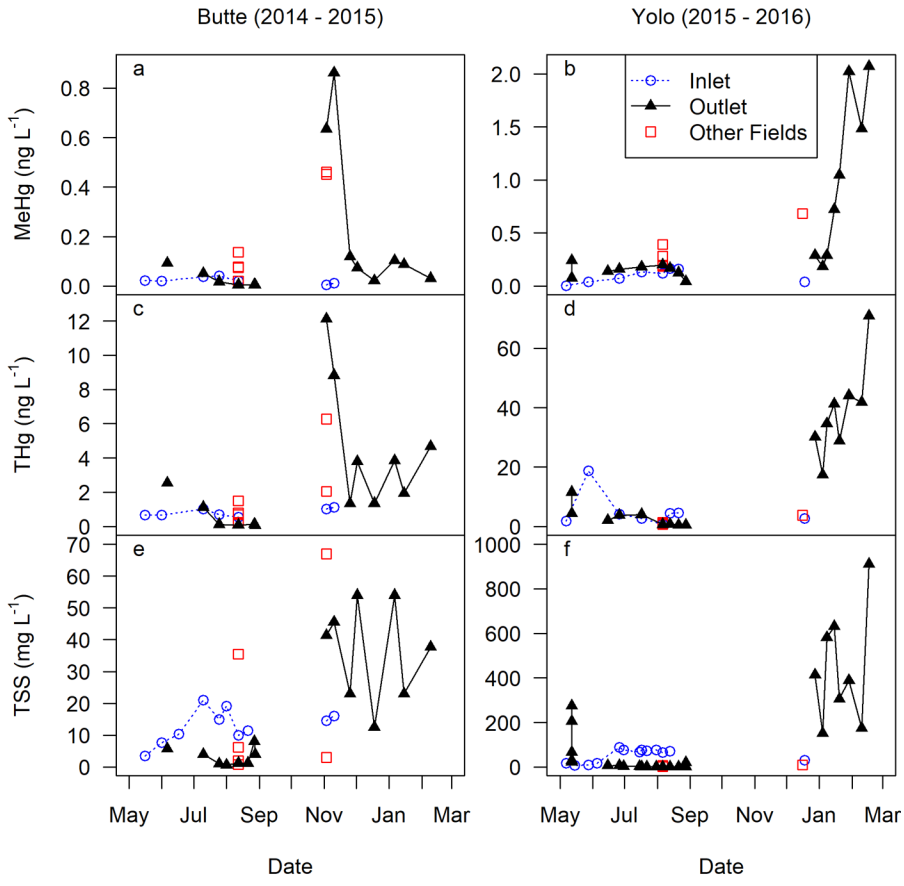

Fig. 1. Time series of surface water methylmercury (MeHg; a, b), total Hg (THg; c, d), and total suspended solids (TSS; e, f) data for Butte (left) and Yolo (right). Red squares show outlet water sampled from neighboring fields. Note the different *y*-axis scales between Butte and Yolo plots. Growing season (May–September) is on the left, and fallow season (November–March) on the right of each panel.

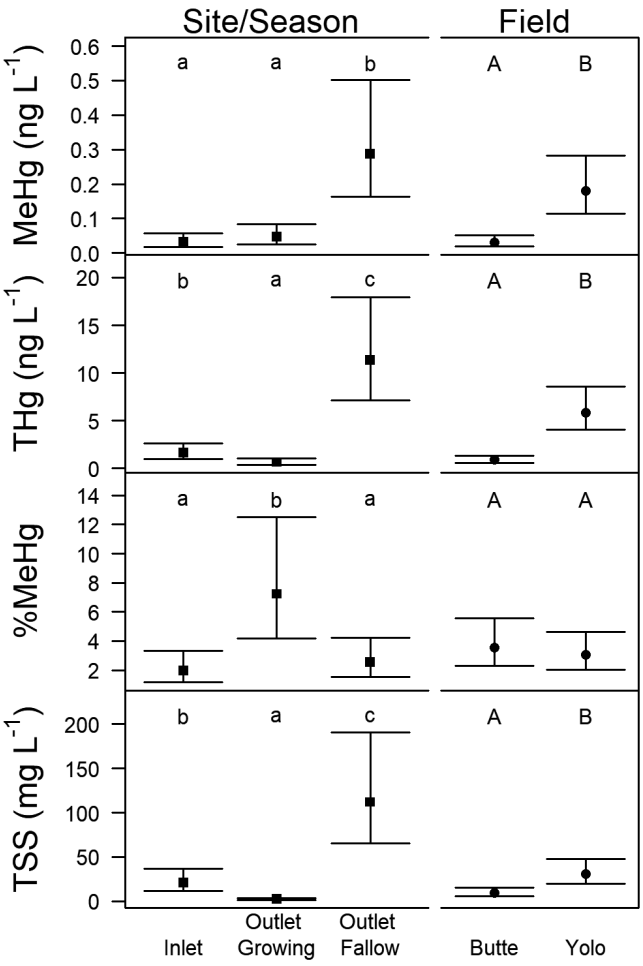

Fig. 2. Surface water least-squares means and SE of (from top to bottom) methylmercury (MeHg), total Hg (THg), percentage MeHg (%MeHg), and total suspended solids (TSS) from Model C. The effect of each factor (site and season [left] and field [right]) are shown, corrected for differences due to other factors. There were no statistically significant (site × season)] interactions. Inlet data were not divided by season because only one or two samples were collected at inlets during the fallow season.

fallow season. Annually, 85 to 86% of exported MeHg and 90 to 93% of exported THg occurred during the fallow season. Loads were consistently higher at Yolo than at Butte, with total annual imports being 1.7 and 3.5 times higher and total annual exports being 5.5 and 10 times higher for MeHg and THg, respectively.

Annually, both fields were net sinks for THg based on surface water budgets, with annual net import of 1700 and 730 ng m^{-2} for Butte and Yolo, respectively. Butte was a net MeHg sink, with an annual import of 41 ng m^{-2}, whereas Yolo was a net source of MeHg, with 90 ng m^{-2} exported annually. Considering the many factors that make rice fields ideal sites for Hg(II)-methylation, it is notable that one of the fields (Butte) was a net MeHg sink on an annual basis. Similarly, some fields in the Delta are MeHg sinks on an annual basis (Eagles-Smith et al., 2014), and others are sources (Bachand et al., 2014). This may indicate that MeHg degradation processes (i.e., microbial demethylation or photodemethylation) can reduce MeHg pools in rice fields, or that MeHg export in harvested rice grain is significant (discussed below).

Total Hg can enter ecosystems through wet deposition and plant uptake and be lost through evasion from the soil and plants (Eckley et al., 2016). It was not feasible to measure atmospheric exchange in this study. However, surface–air mercury fluxes are unlikely to drive differences between Butte and Yolo because controlling variables related to management (plant cover and soil moisture) and atmospheric conditions (wet deposition and air concentration; National Atmospheric Deposition Program, 2014) were similar between fields.

Rice Plant Mercury

Methylmercury content in rough rice from Yolo (0.7 ± 0.2 ng g^{-1}) was four times higher than in rice from Butte (0.16 ± 0.04 ng g^{-1}) (Model D, $p < 0.05$, Table 2). Total Hg in rough rice did not differ significantly between fields (Table 2, overall mean = 1.4 ± 0.4 ng g^{-1}). In previous studies, brown rice grain and husks were separated prior to Hg analysis, whereas rough rice (unprocessed grain with husk) was analyzed in this study. The rice husk is ∼20% of the mass of rough rice (Gariboldi, 1974), and it has lower MeHg and higher THg concentrations than brown rice alone (Meng et al., 2010). If no MeHg was present in the husk, the concentration of MeHg in brown rice in this study would be at most 0.88 and 0.2 ng g^{-1} at Yolo and Butte, respectively (see the supplemental material for calculations). Mean brown rice THg concentrations could not have been >1.75 ng g^{-1} and were most likely lower than the reported rough rice concentration. In a comprehensive review, Rothenberg et al. (2014) found published values of rice MeHg content ranged from 0.86 to 63 ng g^{-1}, whereas THg content ranged from 1 to 510 ng g^{-1}, although lower concentrations have been reported more recently (Rothenberg et al., 2015). Keeping in mind the biases caused by analyzing rough rice rather than brown rice, the rice MeHg and THg concentrations reported here are still among the lowest published values.

Methylmercury in rice plants has been shown to originate in the soil (Strickman and Mitchell, 2017). Thus, low concentrations in rice grain and between-field differences reflect soil MeHg content at Butte and Yolo. However, concentrations of MeHg and THg in grain are weakly correlated ($R^2 \sim 0.2$), and concentrations of those species in soil (Horvat et al., 2003; Zhang et al., 2010b) as well as other factors such as rice cultivar (Li et al., 2013) or sources of Hg to the system (e.g., soil, source water, atmospheric deposition) (Zhang et al., 2010b; Meng et al., 2011) can also influence Hg uptake by rice plants.

Straw had 62% lower MeHg content than grain ($p < 0.05$), but five to eight times higher THg ($p < 0.05$). Grain and straw differed significantly in %MeHg, with grain ranging from 16 ± 9 (Butte) to 40 ± 13% (Yolo) and straw ranging from 1.2 ± 1.1 (Butte) to 2.7 ± 0.8% (Yolo) MeHg (Table 2). Higher %MeHg in grain compared to straw is consistent with previous studies (Meng et al., 2010, 2014). Total Hg content did not differ significantly between fields for straw (overall mean = 9 ± 3 ng g^{-1}).

Removal of rice grain from the field at harvest resulted in the export of 190 ± 50 to 700 ± 200 ng MeHg m^{-2} and 1400 ± 500 to 1700 ± 400 ng THg m^{-2} in Butte and Yolo, respectively (Table 2). Rice straw, which was tilled into the soil after harvest, contained 120 ± 80 to 180 ± 80 ng MeHg m^{-2} and 10,500 ± 3000 to 7000 ± 3000 ng THg m^{-2} in Butte and Yolo, respectively. Methylmercury and THg storage in rice plants is comparable in magnitude with annual surface water imports and exports (Table 1). Plant tissues differ in their primary source of Hg: grain Hg originates in the soil, whereas straw Hg is from the

Table 2. Methylmercury (MeHg) and total mercury (THg) in rice straw and grain. All values are means ± SD (n = 4).

Parameter	Butte		Yolo	
	MeHg	THg	MeHg	THg
Grain				
Concentration (ng g^{-1})	0.16 ± 0.04	1.2 ± 0.4	0.7 ± 0.2	1.7 ± 0.3
Pool (ng m^{-2})	190 ± 50	1400 ± 500	700 ± 200	1700 ± 400
%MeHg†	16 ± 9		40 ± 13	
Straw				
Concentration (ng g^{-1})	0.12 ± 0.09	10 ± 3	0.20 ± 0.06	8 ± 1.8
Pool (ng m^{-2})	120 ± 80	10,500 ± 3000	180 ± 80	7000 ± 3000
%MeHg	1.2 ± 1.1		2.7 ± 0.8	
Soil				
Concentration (ng g^{-1})	0.19 ± 0.06	28 ± 5.2	1.0 ± 0.2	57 ± 2.0
Pool (ng m^{-2})	24,000 ± 4600	3,600,000 ± 950,000	120,000 ± 23,000	6,500,000 ± 190,000
%MeHg	0.73 ± 0.26		1.8 ± 0.36	

† %MeHg = (MeHg/THg) ×100.

atmosphere (Yin et al., 2013). Thus, plant pools of Hg and their sources should be accounted for in mass balance studies of Hg species in rice fields.

Periods of Elevated Methylmercury and Total Mercury Export

Our results showed that MeHg and THg export from rice fields in the Sacramento Valley are primarily of concern during the winter fallow period. This is supported by significantly higher MeHg and THg concentrations in fallow season drainage water (Fig. 1), higher total export loads, and higher net export compared with the growing season (Table 1). Efforts to reduce export would be most effective in the fallow season.

Other studies of MeHg export from rice also found that net MeHg exports and concentrations were higher in the fallow season than the growing season (Alpers et al., 2014; Eagles-Smith et al., 2014; Tanner et al., 2017). There are several possible reasons for this. First, Bachand et al. (2014) found that crop transpiration during the growing season results in a net downward movement of surface water into the soil profile, and this may serve to trap MeHg, limiting its export during the growing season. As there are no transpiring plants during the fallow season, MeHg stored in the soil profile may be released into surface water via diffusion, where it may then be exported. Second, we found the pools of MeHg and THg accumulated in plants were 3 to 4 times and 1 to 12 times larger, respectively, than gross annual export in surface water. It is possible that plant uptake during the growing season limits MeHg and THg export. Grain is removed from the field at harvest; however, straw decomposes in the field during the fallow season and may be an important source of MeHg (120–180 ng m^{-2}) and THg (7000–10,500 g m^{-2}) for surface water export from the field (Windham-Myers et al., 2014a). Finally, decomposing rice straw may promote Hg(II)-methylation by providing labile organic carbon, if the Hg(II)-methylating microbes are limited by carbon (Marvin-DiPasquale et al., 2014; Windham-Myers et al., 2014b). However, the relationship between increased MeHg production and bioaccumulation or export is complex (Eagles-Smith et al., 2014; Zhu et al., 2015; Tanner et al., 2017).

One objective of this study was to identify periods of MeHg export that could be targeted for mitigation. Though we observed spikes in MeHg export, they accounted for a small fraction of annual exports or did not occur at the same time in both fields. Early growing season outlet MeHg and THg concentrations were somewhat elevated (Fig. 1), and the early-season draining event at Yolo accounted for 16 and 52% of growing season MeHg and THg exports, respectively. However, this export was only 2.4 and 3.8% of annual MeHg and THg exports annually. Field draining prior to harvest did result in a small pulse of export (5.8 and 14% of MeHg exports and 9.6 and 9.7% of THg exports during the growing season from Butte and Yolo, respectively), but this was a negligible percentage of annual export.

During the fallow season, concentrations and export were elevated, but within-season trends differed between fields. In Butte, both MeHg and THg concentrations were high at the start of the fallow season and decreased, whereas Yolo fallow season outlet concentrations started low and increased as the season progressed (Fig. 1). These data, combined with time series of MeHg concentrations in rice drainage water from previous studies, suggest that temporal patterns of MeHg concentration with in the fallow season are highly variable among fields (Alpers et al., 2014; Eagles-Smith et al., 2014).

More research is needed to understand fluctuations of MeHg concentrations in rice drainage water during the fallow season before management recommendations are identified. Furthermore, previous studies of MeHg export from rice systems included a flooded fallow season for straw decomposition (Eagles-Smith et al., 2014; Windham-Myers et al., 2014b; Tanner et al., 2017). Cropping systems with different annual cycles of dry and wet periods (such as the absence of a flooded fallow season, or production of multiple crops per year), likely have different seasonal patterns of MeHg export. Hydroperiod and management practices are important controlling variables of MeHg production (Marvin-DiPasquale et al., 2014) and export, and more studies will be needed to understand MeHg dynamics in these systems.

Conclusion

Surface water MeHg and THg budgets revealed clear differences between the growing and fallow seasons. During the growing season, drainage water and irrigation water had similar MeHg and THg concentrations. Due to irrigation water volumes being larger than drainage volumes, the fields were net sinks for

MeHg and THg in the growing season. In the fallow season, the fields were MeHg and THg sources because drainage water concentrations were elevated compared with irrigation water, whereas the volume of irrigation and drainage water were more similar. These results indicate that efforts to reduce MeHg and THg exports in rice drainage water should focus on the fallow season. Further, rice plants accumulated substantial amounts of MeHg and THg into their tissues annually, at a scale similar in magnitude to annual surface water loads. Plant tissue pools, and differences in MeHg and THg accumulation in straw and grain tissues, should be considered in future studies.

Supplemental Material

The supplemental information includes calculations of the impact of husk on rice grain MeHg and THg concentrations, a map of the study area (Supplemental Fig. S1), a time series of hydrological data (Supplemental Fig. S2), soil MeHg and THg by depth (Supplemental Fig. S3), comparison of studied fields (Supplemental Table S1), quality control and quality assurance data (Supplemental Tables S2–S6), and soil MeHg and THg concentrations and pools by sampling event (Supplemental Table S7).

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