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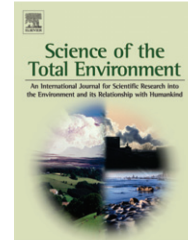

Apparent rates of production and loss of dissolved gaseous mercury (DGM) in a southern reservoir lake (Tennessee, USA)

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ABSTRACT

Apparent rates of dissolved gaseous mercury (DGM) concentration changes in a southern reservoir lake (Cane Creek Lake, Cookeville, Tennessee) were investigated using the DGM data collected in a 12-month study from June 2003 to May 2004. The monthly mean apparent DGM production rates rose from January (3.2 pg L^{-1}/h), peaked in the summer months (June–August: 8.9, 8.0, 8.6 pg L^{-1}/h), and fell to the lowest in December (1.6 pg L^{-1}/h); this trend followed the monthly insolation march for both global solar radiation and UVA radiation. The monthly apparent DGM loss rates failed to show the similar trend with no consistent pattern recognizable. The spring and summer had higher seasonal mean apparent DGM production rates than the fall and winter (6.8, 9.0, 3.9, 5.0 pg L^{-1}/h, respectively), and the seasonal trend also appeared to closely follow the solar radiation variation. The seasonal apparent DGM loss featured similar rate values for the four seasons (5.5, 4.3, 3.3, and 3.9 pg L^{-1}/h for spring, summer, fall, and winter, respectively). Correlation was found of the seasonal mean apparent DGM production rate with the seasonal mean morning solar radiation ($r=0.9084$, $p<0.01$) and with the seasonal mean morning UVA radiation ($r=0.9582$, $p<0.01$). No significant correlation was found between the seasonal apparent DGM loss rate and the corresponding afternoon solar radiation ($r=0.5686$ for global radiation and 0.6098 for UVA radiation). These results suggest that DGM production in the lake engaged certain photochemical processes, either primary or secondary, but the DGM loss was probably driven by some dark processes.

1. Introduction

Air/water exchange plays an important role in global biogeochemical cycle of mercury (Hg) (Fitzgerald et al., 1991; Schroeder and Munthe, 1998). Mercury exchange at air/water interface of an aquatic system such as a lake depends on concentration of dissolved gaseous mercury (DGM), which in turn is controlled by its photochemical redox transformation in the water body (Amyot et al., 1994; Gardfeldt et al., 2001; Nriagu, 1994; Zhang, 2006; Zhang and Lindberg, 2001). To understand the photochemodynamics of freshwater Hg, one may quantify Hg evasion flux and determine DGM production separately in controlled simulation systems. Alternatively, one can gain inference by inspecting in situ temporal change of DGM concentration (O'Driscoll et al., 2003). This registers both Hg evasion and redox transformation in a lake, serving as a comprehensive index in a sense. The in situ DGM concentration change rates are valuable particularly for modeling aquatic Hg photochemodynamic cycle and verifying the models. The rate information can also provide useful insights into the mechanisms of aquatic photochemical redox cycle of Hg, especially the chemical nature of daily and seasonal rise and fall of DGM levels in a lake (e.g., Dill et al., 2006; Zhang et al., 2006). The rate information can also assist to assess the relative significance of chemical transformation vs. air/water exchange in the Hg cycle in a lake. Despite their importance

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and value, the data of DGM concentration change rates has remained deficient in the literature, especially out of long-term studies.

Changes of DGM concentrations in an open lake system occur inevitably under ever-changing environmental conditions (e.g., solar insolation, water temperature, wind speed, humidity, etc.). As a result, only apparent kinetic rates are readily obtainable, which may be empirically collected by the following approach:

$$R_a = \Delta[\mathrm{DGM}]/\Delta t = \left([\mathrm{DGM}]_2 - [\mathrm{DGM}]_1\right)/(t_2 - t_1) \quad (1)$$

where R_a is the apparent DGM concentration change rate, and $([\mathrm{DGM}]_2-[\mathrm{DGM}]_1)$ is the DGM concentration change over the time interval of (t_2-t_1). The positive rate values thus represent an apparent net production of DGM while the negative ones indicate an apparent net loss of DGM in a lake. Hence, the value and sign of the DGM kinetic rates jointly provide valuable chemodynamic information.

We here report an investigation of the apparent rates of DGM concentration changes in a southern reservoir lake, Cane Creek Lake at Cookeville (Tennessee, USA). An analysis was conducted of the apparent rates of DGM concentration changes in the lake obtained in a 12-month consecutive study from June 2003 to May 2004. The main purposes of this investigation were (1) to provide a rate profile of DGM concentration changes over a one-year period in a southern reservoir lake, (2) to quantify the apparent rates of the DGM concentration changes on various temporal scales, and (3) to compare the rates in the morning DGM production phase and afternoon DGM loss phase so as to gain insights into the possible underlying mechanisms of photochemical redox cycling of aquatic Hg in the lake. The primary focus of this article is the pertinent rate analysis and mechanistic inference. The daily and seasonal changes of DGM levels in the lake were characterized in details elsewhere (Dill, 2004; Dill et al., 2006; Zhang et al., 2006).

2. Site and methods

The apparent rates of DGM production and loss were obtained using the data of the DGM concentrations collected during a 12-month study on temporal variations of DGM concentration conducted at Cane Creek Lake (Cookeville, Tennessee, USA). A detailed description of the basic characteristics of the lake and the sampling site is available elsewhere (Dill, 2004; Dill et al., 2006).

Lake water was sampled each month from June of 2003 to May of 2004, usually twice a month; more intensive sampling campaigns were conducted in the summer of 2003. Sampling went generally from early morning till late evening, as frequently as possible (approximately one sample per hour). The DGM data reported here include those generally spanning the period of ~8:00 am–~7:30 pm (~9:00 am–~5:30 pm for winter time). The analysis of the results was thus based on the data sets obtained within the timeframe studied.

Fresh water samples were taken by surface grab primarily at a nearshore master site. Upon each sampling, field measurements were also carried out in situ to follow water temperature, global solar radiation (R_g), and UVA radiation. The water samples were promptly transferred to our laboratory on campus where the DGM in a sample was immediately purged (generally within ~0.5 h after sampling) and collected on a gold–sand trap, and then the trap was analyzed for total Hg by means of cold vapor atomic fluorescence spectroscopy (CVAFS). The detailed procedures for the field operations and laboratory analyses were documented elsewhere (Dill, 2004; Dill et al., 2006).

All the apparent kinetic rates were computed using Eq. (1). with the DGM data obtained in the field study. It is no surprise that the DGM levels in the lake were slightly or mildly fluctuating from time to time along the general temporal variation trends because of natural change or operational error, resulting in occasional DGM data inconsistent with the general trends, e.g., occasional negative rates in the morning and positive rates in the afternoon. To facilitate the rate analysis aimed at inspecting the general kinetic trends on various temporal scales and inferring the possible mechanisms of aquatic photochemical redox cycling of Hg in the lake, a simplification was adopted by appropriately excluding the irregular rates from the rate data pool (i.e., excluding the negative rate data for the morning phase and positive rate data for the afternoon phase). Consequently, all the trend descriptions and mechanistic speculations were drawn based on the data set thus appropriately processed to remove the fluctuation noise. The trade-off of this practice is a slight reduction in the size of the rate data set, but refined rate analysis and better inference can be obtained. In addition, the lack of a sufficient number of the rate data for November 2003 and February 2004 led us to exclude these two months in the analysis of the monthly apparent DGM kinetics. Nevertheless, a solid monthly rate analysis based on the data of the 10 months resulted with a satisfied data set.

3. Results and discussion

3.1. *Daily trends of apparent rates of DGM production and loss*

Distinct changes of DGM concentration in Cane Creek Lake were observed (Dill et al., 2006; Zhang et al., 2006), exhibiting the diurnal patterns in agreement with the previous findings for other freshwater aquatic systems (e.g., see Amyot et al., 1997; Krabbenhoft et al., 1998; O'Driscoll et al., 2003; Vette, 1998; Zhang and Lindberg, 2000, 2002; Zhang et al., 2002). Fig. 1 provides representative examples of the daily rate profiles of DGM concentration changes in Cane Creek Lake in various seasons. A general feature is the positive apparent rates indicating net DGM production in the morning phase and the negative rates indicating net DGM loss in the afternoon phase post the around-noon peak of DGM level. This pattern parallels the trends of insolation variation in the morning and afternoon, respectively. However, in any particular morning or afternoon phase, the trend of the rate distribution shows no clear pattern, reflecting the variable nature of the DGM kinetics on a small time scale (e.g., hourly). These kinetic characteristics seemed quite prevalent (data not shown).

On the daily scale, interestingly, both the daily mean morning apparent DGM production (DMAP) rates and the daily mean afternoon apparent DGM loss (DMAL) rates varied

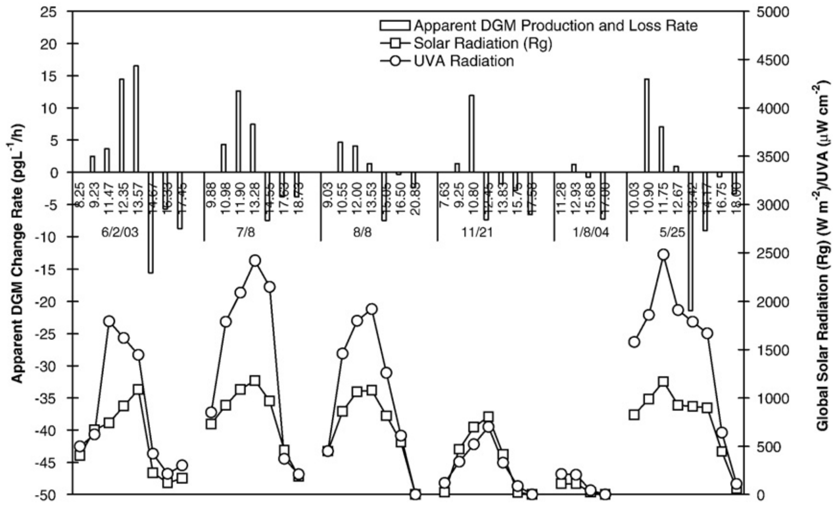

Fig. 1 – Representative examples of the daily rate change profiles of morning production and afternoon loss of DGM in Cane Creek Lake (Cookeville, Tennessee, USA) in various seasons.

remarkably from day to day, as naturally did the daily mean morning and afternoon solar radiations in terms of both global solar radiation and UVA radiation. This observation is well demonstrated by Fig. 2a and b. In each month, various values of the DMAP and DMAL rates were found. For instance, in June of 2003 among the 10 days of field sampling, the DMAP rates ranged from 3.0 to 17.4 pg L^{-1}/h and the DMAL rates from 2.0 to 10.0 pg L^{-1}/h, and in July of 2003 among the 6 days of field sampling, the DMAP rates varied from 5.0 to 14.7 pg L^{-1}/h and the DMAL rates from 1.7 to 5.0 pg L^{-1}/h. Similarly, in the two days of March of 2004, the DMAP rate was 4.4 pg L^{-1}/h on one day and 2.4 pg L^{-1}/h on the other, and the DMAL rate was 6.7 and 2.0 pg L^{-1}/h, respectively. The variations of the daily mean kinetic rates are detailed in a summary table (Table 1). Generally, these DMAP rates are comparable to those found in some northern lakes, (e.g., a study for Ranger Lake, see Amyot et al., 1997).

Although the daily mean rates of DGM concentration changes in the lake exhibited marked variations, a general trend, recognizably, still seemed to emerge in terms of the apparent DGM production with the high DMAP rates in the summer months, the low rates in the winter months, and the intermediate rates in the months in between the two seasons; and moreover, this discernable trend closely followed the trend of the monthly mean morning solar radiation variations for both global solar radiation and UVA radiation (Fig. 2a and Table 1). Yet, the same does not hold true for the apparent DGM loss kinetics, i.e., the trend for the apparent DGM loss rates in the afternoon over the different days throughout the 12-month was vague, although the daily mean afternoon solar radiation exhibited the typical seasonal trend. It is also worth noting that generally, the DMAL rate values were perceivably lower than the DMAP rate values. It is of interest to see if these kinetic features and differences would manifest on the monthly scale as the transformation of the daily rates to the monthly mean rate values would remove the noise of the daily kinetics and generate refined kinetic trends.

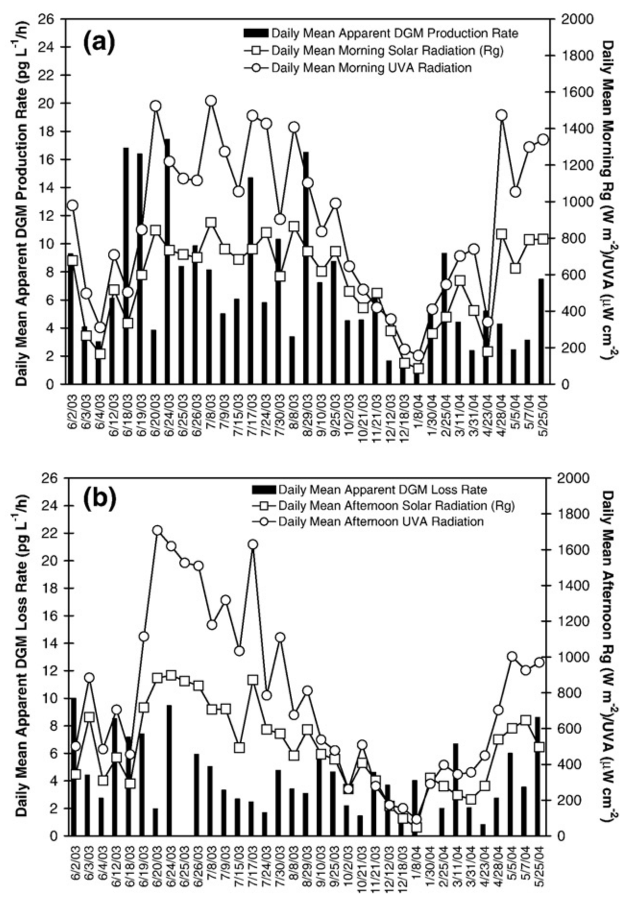

Fig. 2 – Rate profiles of (a) the daily mean apparent DGM production rates and (b) the daily mean apparent DGM loss rates for Cane Creek Lake (Tennessee) from June 2003 to May 2004 compared to the daily mean values of morning and afternoon global solar radiation (Rg) and UVA radiation, respectively.

Table 1 – Summary of mean morning DGM production rates and mean afternoon DGM loss rates and pertinent solar radiation data for Cane Creek Lake (Cookeville, TN)

Date	Mean morning DGM production rates (pg L^{-1}/h)	Mean morning global solar radiation (R_g) (W m^{-2})	Mean morning UVA radiation (μW cm^{-2})	Mean afternoon DGM loss rates (pg L^{-1}/h)	Mean afternoon solar radiation (R_g) (W m^{-2})	Mean afternoon UVA radiation (μW cm^{-2})
06/02/03	9.3	677	979	−10.0	345	502
06/03/03	4.1	266	497	−4.4	664	885
06/04/03	3.0	165	311	−2.8	309	485
06/12/03	6.1	517	708	−8.5	438	706
06/18/03	16.8	333	504	−7.2	292	456
06/19/03	16.4	598	846	−7.4	717	1115
06/20/03	3.9	843	1523	−2.0	883	1708
06/24/03	17.4	733	1220	−9.5	898	1620
06/25/03	8.4	711	1126	---	866	1527
06/26/03	9.9	694	1116	−5.9	840	1510
07/08/03	8.1	886	1552	−5.0	707	1180
07/09/03	5.0	741	1273	−3.3	710	1318
07/15/03	6.1	684	1055	−2.7	494	1034
07/17/03	14.7	739	1470	−2.5	872	1630
07/24/03	5.8	830	1427	−1.7	595	786
07/30/03	10.3	591	904	−4.8	572	1110
08/08/03	3.4	864	1408	−3.4	450	677
08/29/03	16.5	727	1103	−3.1	594	813
09/10/03	7.2	618	836	−6.0	456	538
09/25/03	8.7	727	990	−4.7	429	479
10/02/03	4.5	510	645	-2.2	262	263
10/21/03	4.6	417	519	−1.5	409	509
11/21/03	6.6	499	420	−4.6	310	279
12/12/03	1.7	293	356	−3.7	168	173
12/18/03	1.4	116	191	−1.2	97	155
01/08/04	1.2	86	157	−4.0	48	93
01/30/04	5.2	277	411	---	324	292
02/25/04	9.3	368	546	−2.0	279	397
03/11/04	4.4	568	702	−6.7	227	345
03/31/04	2.4	403	740	−2.0	205	355
04/23/04	5.2	178	341	−0.8	280	450
04/28/04	4.3	821	1473	−2.7	539	704
05/05/04	2.4	635	1054	−6.0	602	1003
05/07/04	3.1	791	1298	−3.5	647	926
05/25/04	7.5	795	1340	−8.6	496	970

3.2. *Monthly trends of apparent rates of DGM production and loss*

The monthly mean apparent DGM production (MMAP) rates were computed by averaging all the apparent DGM production rates collected in a particular month, and likewise for the monthly mean apparent DGM loss (MMAL) rates. Fig. 3 presents the monthly profiles of the MMAP and MMAL rates for Cane Creek Lake from June 2003 to May 2004 compared to the monthly mean values of morning and afternoon global solar radiation (Rg) and UVA radiation, respectively, arranged in the order of a normal calendar year from January–May of 2004 to June–December of 2003 (the monthly mean rates for November 2003 and February 2004 were excluded because of too small a size of the monthly data set for the two particular months). A detailed summary of the monthly rates is given in Table 2.

Clearly, as demonstrated in Fig. 3a, the MMAP rates rose gradually from January at 3.2 pg L^{-1}/h, peaked in the summer months (June–August, 8.9, 8.0, 8.6 pg L^{-1}/h, respectively), and then fell consistently to the lowest in December at 1.6 pg L^{-1}/h. Moreover, this general trend intimately followed the monthly insolation march in terms of both global solar radiation and UVA radiation (the low monthly mean insolation level in June was due to exceptional wet weather with many cloudy and rainy days). The monthly kinetic curve appears to be in a “bell” shape. The mean of the MMAP rates is 5.5 pg L^{-1}/h (SD = 2.6 pg L^{-1}/h, RSD = 47%).

The monthly apparent DGM loss kinetics, however, failed to show the trend similar to that for the monthly apparent DGM production as described above, and no consistent, distinct patterns seem to be recognizable (Fig. 3b). Although the MMAL rate values in May and June (6.0 and 6.6 pg L^{-1}/h, respectively) seemed to approach a summer peak, this seemingly emerging trend was immediately disrupted in July and August (3.7 and 3.2 pg L^{-1}/h, respectively), which shared the similar rate values with January and March (4.0 and 4.4 pg L^{-1}/h, respectively). However, the MMAL rate values of October and December (1.8 and 2.0 pg L^{-1}/h, respectively) and of January and March were noticeably lower than those of May, June, and September (5.2 pg L^{-1}/h). The lack of distinct consistent monthly kinetic trend is accompanied by the fact

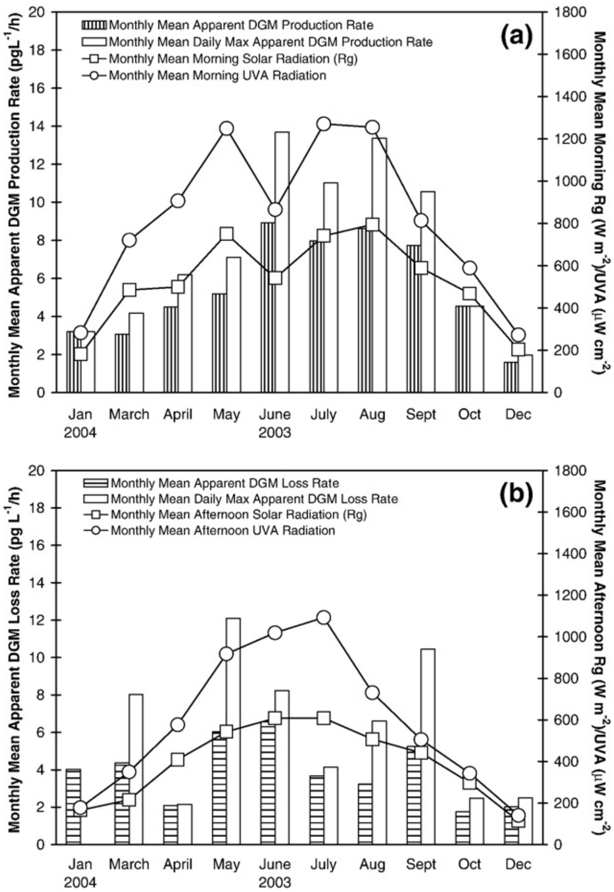

Fig. 3 – Monthly profiles of (a) the monthly mean apparent DGM production rates and the monthly mean daily maximum DGM production rates and (b) the monthly mean apparent DGM loss rates and the monthly mean daily maximum DGM loss rates for Cane Creek Lake (Tennessee) from June 2003 to May 2004 compared to the monthly mean values of morning and afternoon global solar radiation (Rg) and UVA radiation, respectively.

that overall, the MMAL rate values were smaller than those of MMAP since the average of the MMAL rates is 3.9 pg L^{-1}/h (SD=1.7 pg L^{-1}/h, RSD=44%). However, for the months of December of 2003 and January and March of 2004, the MMAL rate values appear to be close to those of the MMAP rates (Fig. 3 and Table 2).

The monthly kinetics of DGM concentration changes in Cane Creek Lake in terms of the MMAP and MMAL rates as characterized above is also echoed by the monthly kinetics in terms of the monthly mean daily maximum apparent DGM production and loss rates (Table 2), which are defined as the average of all the daily maximum apparent DGM production or loss rates for a particular month of interest. The monthly mean daily maximum apparent DGM production rates shared the same trend as the MMAP rates with a "bell" shape, while the monthly mean daily maximum apparent DGM loss rates exhibited irregular variations similar to those for the MMAL rates. The monthly mean daily maximum apparent DGM production rates were the highest in June (13.7 pg L^{-1}/h) and August (13.4 pg L^{-1}/h), but the monthly mean daily maximum DGM loss rates were the highest in May (12.1 pg L^{-1}/h) and September (10.5 pg L^{-1}/h).

3.3. *Seasonal trends of apparent rates of DGM production and loss*

The manifestation of the daily kinetics of DGM concentration changes in Cane Creek Lake on the monthly scale as presented above promotes the speculation that the monthly kinetics should be reflected by the kinetics on the seasonal scale. This notion is supported by the analysis of the seasonal rate data of DGM level changes. Fig. 4 and Table 3 summarize the seasonal apparent rates of DGM production and loss in the lake for the period of June 2003–May 2004.

Two features can be recognized about the seasonal kinetics of the apparent DGM production in the lake (Fig. 4a): First, the spring and summer had distinctively higher seasonal mean apparent DGM production rates (i.e., SMAP rates, defined as the mean of all the apparent DGM production rates collected in a particular season) than the fall and winter (6.8, 9.0, 3.9, 5.0 pg L^{-1}/h, respectively); second, the winter and fall had similar values of the SMAP rates while the SMAP rates in the summer were higher than those in the spring. Clearly, the summer season had the highest SMAP rates (32%, 131%, 80% higher than the rates of the spring, fall, and winter, respectively). Moreover, the seasonal trends appeared to closely follow the variation of the seasonal mean solar radiation. The same trend can be found for the seasonal kinetics in terms of the seasonal mean daily maximum apparent DGM production rates (i.e., average of all the daily maximum apparent DGM production rates for a particular season) (Table 3).

In contrast to the seasonal trend of the apparent DGM production rate, the seasonal kinetics of the apparent DGM loss in the lake featured quite similar rate values shared by all seasons (Fig. 4b). The seasonal mean apparent DGM loss rates (i.e., SMAL rates, defined as the mean of all the apparent DGM loss rates collected in a particular season) were 5.5, 4.3, 3.3, and 3.9 pg L^{-1}/h for spring, summer, fall, and winter, respectively, although the SMAL rate of the spring season may arguably appear to be the highest (28%, 67%, and 41% higher than the rates of the summer, fall, and winter seasons, see Table 3). Clearly, the summer season did not exhibit a significantly higher SMAL rate than the fall and winter as did with the rates in terms of the apparent DGM production. Incidentally, there was no clear parallel readily recognizable between the seasonal SMAL kinetics and seasonal mean solar radiation variation. The features of the SMAL rates were also shared by the seasonal mean maximum daily DGM loss rates (Table 3).

An overall comparison can be made of the monthly and seasonal rates with the yearly mean apparent DGM production or loss rates (YMAP or YMAL rates, i.e., the mean of all the apparent DGM production or loss rates for the period of June 2003–May 2004). Across the monthly spectrum, the summer months of June, July, August, and September all had the MMAP rates higher than the YMAP rate (7.1 pg L^{-1}/h) and the rest had the rates significantly lower than the YMAP rate. On the other hand, January, March, May, June, July, and September all had the MMAL rates close to or higher than the YMAL rate (4.5 pg L^{-1}/h), which distinctively differs from the case for the

Table 2 – Summary of monthly mean morning DGM production rates and monthly mean afternoon DGM loss rates and pertinent solar radiation data for Cane Creek Lake (Cookeville, TN)

Month	Monthly mean morning DGM production rates (pg L^{-1}/h)	Monthly mean morning global solar radiation (Rg) (W m^{-2})	Monthly mean morning UVA radiation (μW cm^{-2})	Monthly mean afternoon DGM loss rates (pg L^{-1}/h)	Monthly mean afternoon global solar radiation (Rg) (W m^{-2})	Monthly mean afternoon UVA radiation (μW cm^{-2})
June 2003	8.9	541	866	−6.6	608	1019
July	8.0	741	1270	−3.7	609	1092
Aug	8.6	795	1255	−3.2	507	731
Sept	7.7	589	814	−5.2	441	506
Oct	4.5	469	589	−1.8	298	343
Dec	1.6	204	273	−2.0	114	141
Jan 2004	3.2	181	284	−4.0	166	178
March	3.1	486	721	−4.4	216	350
April	4.5	500	907	−2.1	409	577
May	5.2	751	1250	−6.0	543	918

apparent DGM production. On the seasonal scale, the spring and summer had the SMAP rates close to or higher than the YMAP rate, while the spring, summer, and winter all had the SMAL rates close to or higher than the YMAL rate.

3.4. *Relationship between solar radiation and apparent rates of DGM level changes*

An inspection of the relationship between the rates of the apparent DGM production and loss and the solar radiation variation may offer some mechanistic inference about the aquatic cycling of Hg in a lake. This can be approached by analyzing the relationships between the apparent rates and solar radiation variation (global solar radiation and UVA radiation).

It was pointed out previously that the DGM levels and their apparent change rates varied quite largely at times within the timeframe of a particular morning or afternoon, deviating from the general trends of morning rise and afternoon fall of DGM levels. It is thus no surprise that the correlation of the apparent DGM production and loss rates with solar radiation (both global solar radiation and UVA radiation) was poor for a particular morning or afternoon. On the daily scale, the *r* value is 0.3007 between the DMAP rate and the daily mean morning global solar radiation and 0.2627 between the DMAP rate and the daily mean morning UVA radiation. Low *r* values were also found between the DMAL rate and the daily mean afternoon global solar radiation (0.1869) and between the DMAL rate and the daily mean afternoon UVA radiation (0.1909).

However, the *r* values are clearly higher on the monthly scale. The value is 0.7522 ($p<0.02$) between the MMAP rate and the monthly mean morning global solar radiation and 0.7167 ($p<0.02$) between the MMAP rate and the UVA radiation (Fig. 5a), while the *r* value is 0.7538 ($p<0.02$) between the monthly mean daily maximum apparent DGM production rate and the monthly mean morning global solar radiation and 0.7323 ($p<0.02$) between the production rate and the UVA radiation. But, low correlation values were found between the MMAL rate and the monthly mean afternoon global solar radiation as well as UVA radiation (0.5138 and 0.5307, respectively, Fig. 5b). The *r* values are also low between the monthly mean daily maximum apparent DGM loss rate and the monthly mean afternoon global solar radiation (0.4092) and between the loss rate and the UVA radiation (0.3730). The striking difference in correlation with solar radiation between

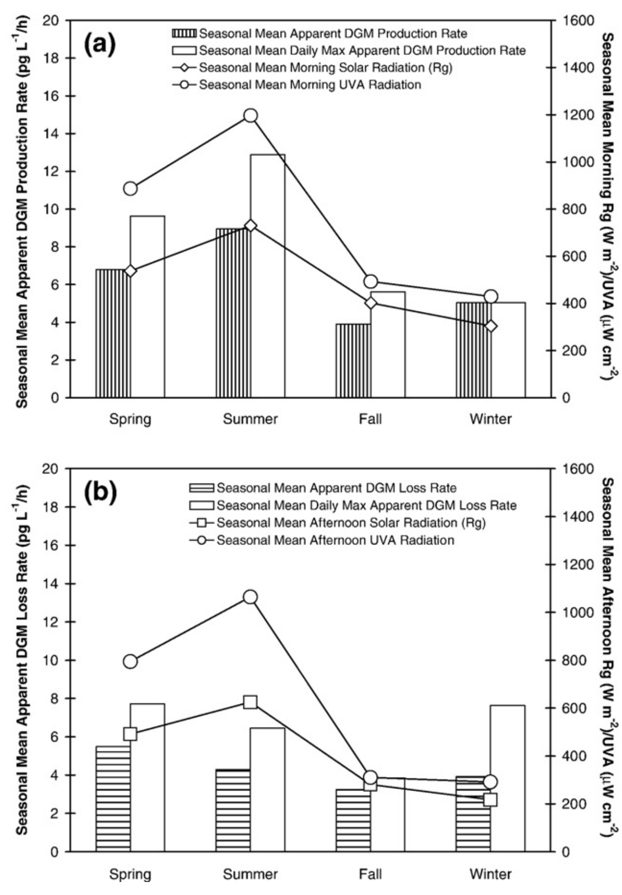

Fig. 4 – Seasonal profiles of (a) the seasonal mean apparent DGM production rates and the seasonal mean daily maximum DGM production rates and (b) the seasonal mean apparent DGM loss rates and the seasonal mean daily maximum DGM loss rates for Cane Creek Lake (Tennessee) from June 2003 to May 2004 compared to the seasonal mean values of morning and afternoon global solar radiation (Rg) and UVA radiation, respectively.

Table 3 – Summary of seasonal mean morning DGM production rates and seasonal mean afternoon DGM loss rates and pertinent solar radiation data for Cane Creek Lake (Cookeville, TN)

Season	Seasonal mean morning DGM production rates (pg L^{-1}/h)	Seasonal mean morning global solar radiation (Rg) (W m^{-2})	Seasonal mean morning UVA radiation (μW cm^{-2})	Seasonal mean afternoon DGM loss rates (pg L^{-1}/h)	Seasonal mean afternoon global solar radiation (Rg) (W m^{-2})	Seasonal mean afternoon UVA radiation (μW cm^{-2})
Spring	6.8	538	887	−5.5	491	794
Summer	8.9	730	1197	−4.3	625	1064
Fall	3.9	402	493	−3.2	280	310
Winter	5.0	304	429	−3.9	217	291

the monthly apparent DGM production and loss kinetics is of high interest concerning the mechanism of the aquatic Hg redox cycling.

Interestingly, on the seasonal scale, with an enlarged sample size and much of the kinetic noise removed, high *r* values emerged between the SMAP rate and the seasonal mean morning solar radiation (0.9084, $p<0.01$) and between the SMAP rate and the seasonal mean morning UVA radiation (0.9582, $p<0.01$), suggesting a strong control of the solar radiation over the apparent DGM production kinetics. It is worth pointing out that the correlation with UVA radiation appears better than with the global solar radiation. This seems to implicate that the UVA radiation may be more favorable as more active photo energy in inducing DMG production. Even higher *r* values were found between the seasonal mean daily maximum apparent DGM production rate and the seasonal mean morning global solar radiation (0.9849, $p<0.01$) and between the maximum production rate and the UVA radiation (0.9999, $p<0.01$).

However, contrary to the above case with respect to the seasonal apparent DGM production kinetics, the correlation between the seasonal apparent DGM loss kinetics and the solar radiation appears to be nearly as vague as the kinetics on the monthly scale. The *r* value is 0.5686 for the SMAL rate vs. the seasonal mean afternoon global solar radiation and 0.6098 for the SMAL rate vs. the UVA radiation. The *r* value is 0.2082 for the seasonal mean daily maximum apparent DGM loss rate vs. the seasonal mean afternoon global solar radiation and 0.3117 for the maximum loss rate vs. the UVA radiation. This is a revisit to the situation regarding the monthly apparent DGM loss kinetics.

3.5. *Comparison between morning production and afternoon loss of DGM and related mechanistic implications for aquatic photochemical redox cycling of Hg*

Our data analysis has provided some interesting findings with respect to apparent rates of DGM production and loss in Cane Creek Lake on daily, monthly, and seasonal scales and their relationship to solar radiation variation (both global solar radiation and UVA radiation). An incisive comparative analysis of the apparent DGM production and loss rates can help to shed some light on the mechanism of the aquatic photochemical redox cycling of freshwater Hg in lakes.

Attention can be drawn first to the correlation between the apparent DGM production and loss rates. The correlation between the monthly mean apparent DGM production and loss rates was found to be poor ($r=0.4709$), the one between the monthly mean daily maximum apparent DGM production and loss rates is similar ($r=0.3892$), and the one between the monthly maximum apparent DGM production and loss rates is also similar ($r=0.4716$) (plots not shown). These results provide a piece of evidence that may suggest that the DGM production and loss were undergoing probably along different mechanistic routes.

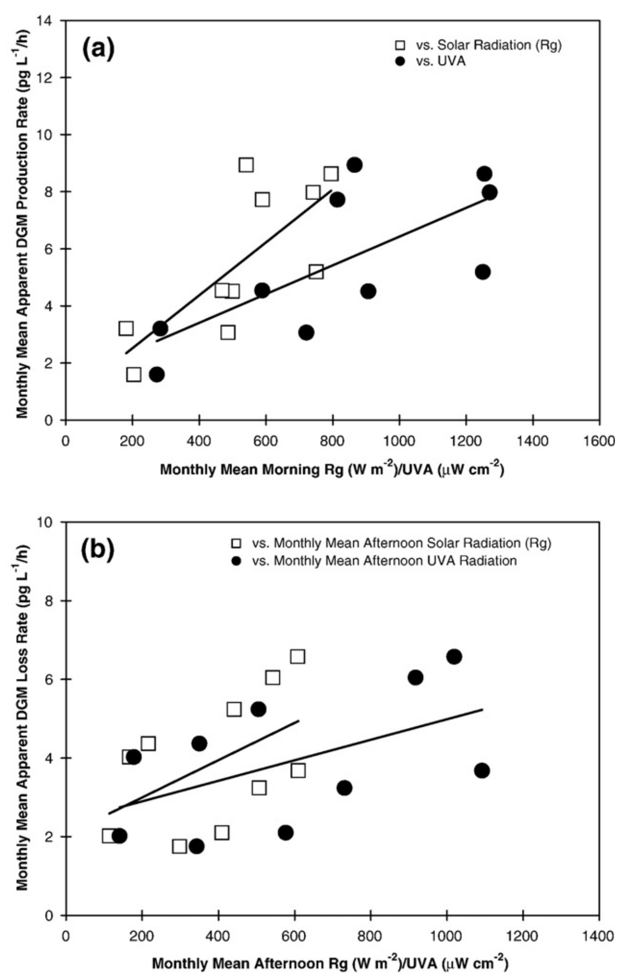

Fig. 5 – Relationships (a) between the monthly mean apparent DGM production rate and the monthly mean morning solar radiation (Rg and UVA) and (b) between the monthly mean apparent DGM loss rate and the monthly mean afternoon solar radiation (Rg and UVA).

The correlation between the apparent DGM production and loss rates and the corresponding DGM concentrations on the monthly scale was then explored. Interestingly enough, we found that the monthly mean apparent DGM production rates closely correlate to the monthly mean DGM concentrations in the lake ($r=0.8645$, $p<0.01$), but this is not the case for the monthly mean apparent DGM loss rates and the monthly mean DGM concentrations ($r=0.5572$). This reinforces the previous finding that the apparent DGM production and loss do not share similar characteristics.

To quantify the difference between the apparent DGM production and loss rates, the arithmetic difference in absolute values between the monthly mean apparent DGM production and loss rates and the arithmetic difference between the seasonal mean apparent DGM production and loss rates for Cane Creek Lake from June 2003 to May 2004 were plotted against the relevant time scale (data not shown). An interesting trend seems to emerge that in the summer and early fall months when the solar radiation was usually strong, the apparent DGM production rates were obviously higher than the apparent DGM loss rates with July and August boasting the largest differences. On the other hand, except for April for some unknown reason, in the winter and early spring months (December, January, and March), the very opposite occurred, i.e., the apparent DGM loss rates were higher than the apparent DGM production rates. On the seasonal scale, the fall and winter seasons all exhibited slight differences in the rates while the summer season showed a remarkable large difference. Moreover, as pointed out previously, the monthly and seasonal apparent DGM loss rates varied merely to a small degree, compared to the large variations of the apparent DGM production rates among the months and seasons (see Figs. 3 and 4). This seems to imply that the DGM loss was undergoing probably at certain rates poised throughout the year. Consequently, when the apparent DGM production was undergoing at high rates in the months of summer and early fall, the production was much stronger than the loss, but when the apparent DGM production was abating in the months of fall and winter, the loss could be more visible. This explains the observations of a nearly flat curve for DGM concentration change in the wintertime (Dill et al., 2006), since the DGM loss was able to catch up with the production even in the morning as a result of weak winter solar radiation.

To further speculate on the nature of the kinetic differences between the apparent DGM production and loss in addition to the differences in their absolute values, a revisit to the relationship between the apparent DGM production and loss rates and solar radiation proved interesting. We have demonstrated that the apparent DGM production rates strongly related to the solar radiation (see Fig. 5), while the apparent DGM loss rates failed to exhibit any recognizable relationship on either the monthly or seasonal scale for Cane Creek Lake. It thus reasonably follows that the DGM production in the lake probably engaged photochemical processes, either primarily or secondarily, strongly mediated by sunlight (Amyot et al., 1994; Costa and Liss, 1999), but the DGM loss in the lake was likely to be involved in some dark processes, chemical (e.g., Amyot et al., 1997, 2005; Zhang and Lindberg, 2001) or mechanical, or both. This hypothesis is in agreement with the observation mentioned before that the DGM loss rates for the lake varied only to small extents over the year. One of the dark processes of DGM loss could be dark oxidation of DGM (Amyot et al., 2005; Zhang, 2006).

By ignoring the effect of Hg evasion, profiles were constructed (plots not shown) of the monthly mean of the ratios of the apparent DGM loss rates to the corresponding DGM concentrations (assuming an apparent first-order kinetics, i.e., rate$=k$[DGM]) vs. time as compared to the monthly mean of the ratios of the apparent DGM loss rates to the square of corresponding DGM concentrations (assuming an apparent second-order kinetics, i.e., rate$=k[\mathrm{DGM}]^2$) vs. time. We found that the second-order plot seems to exhibit some higher values of the ratios for the fall and winter than for the other months. But, interestingly, overall, both types of the ratio values for the apparent DGM loss fluctuate without any clear variation feature related to the temporal scale under both the first-order and second-order kinetics assumptions (with exclusion of the January data, which showed sharp high ratios for both cases), and no regular seasonal trends were recognizable (i.e., the higher ratio values for the warm or hot months). This is inconsistent with the dependence of rate constant on temperature, since higher rate constants would be expected for higher temperatures in the warm or hot months. We thus speculated that the overall dark DGM loss process might be apparent first-order. Needless to say, more data with increased sampling frequency and an analysis using a model considering both Hg evasion and DGM production and loss would yield better inference regarding the nature of the DGM removal processes.

A rather simplified model for the aquatic photochemodynamic redox cycling of Hg in a lake may be enlisted as depicted below under the pseudo-first-order process assumption:

$$r_\mathrm{p} = k_\mathrm{p}[\mathrm{Hg(II)}],\ \text{where}\ k_\mathrm{p} = f(I_\mathrm{s}) \quad (2)$$

$$r_1 = k_1[\mathrm{DGM}] \quad (3)$$

$$R = r_\mathrm{p} - r_1 + I - O \quad (4)$$

where r_p is the apparent rate of DGM production, k_p is the apparent pseudo first-order rate coefficient, which depends on solar radiation (I_s), r_1 is the apparent rate of DGM loss with k_1 as the insolation-independent pseudo first-order rate coefficient, R is the overall apparent DGM kinetic rate, and I is the input of DGM into the lake system and O is the output of DGM (i.e., evasion) from the lake system of concern. In a small shallow lake like Cane Creek Lake, the magnitude of O can be small (e.g., ~0.5 and ~1.2 ng $\mathrm{m^{-2}\,h^{-1}}$ for mean daytime flux in winter and summer, respectively, see Crocker, 2005), but in large lakes such as the Great Lakes, O can be fairly or significantly large. The unsymmetrical feature of the daily diurnal curves of DGM in Cane Creek Lake (rapid rise of DGM level in the morning vs. gentle fall of DGM level in afternoon, see Dill et al., 2006) is probably caused by the absence of a large evasion forcing (Lindberg and Zhang, 2000). The mechanism of the DGM loss remains to be uncovered unequivocally although some mechanistic speculations have existed such as oxidation of DGM in addition to its evasion. Yet, other mechanisms for DGM loss in lakes may also be possible and more research along this line would certainly be valuable.

4. Conclusions

A clear feature of the daily DGM concentration changes in Cane Creek Lake is the regular occurrence of positive apparent rates for morning indicating net DGM production and negative rates for afternoon indicating net DGM loss. The monthly mean apparent DGM production rates rose gradually from January, peaked in the summer months, and fell to the lowest in December; this trend followed the monthly insolation march for both global solar radiation and UVA radiation. The monthly apparent DGM loss rates, however, failed to exhibit the similar trend, with no consistent pattern recognizable. The monthly mean apparent DGM loss rates were smaller than the monthly production rates. The spring and summer had distinctively higher seasonal mean apparent DGM production rates than the fall and winter, which had the similar rates, while the summer rates were clearly higher than the spring rates; the seasonal trend for DGM production appeared to follow the variation of the solar radiation. On the contrast, the seasonal apparent DGM loss rates featured similar values for all seasons. The correlation of the monthly and seasonal mean apparent DGM production rates with the corresponding morning global solar radiation and UVA radiation seems to be indicative of a strong mediation of solar radiation in the DGM production. No significant correlations were found between the monthly and seasonal mean apparent DGM loss rates and the corresponding afternoon solar radiation. These results suggest that the DGM production engaged certain photochemical processes, either primarily or secondarily, strongly mediated by sunlight, but the DGM loss was probably driven by some dark processes, chemical or mechanical, or both.

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