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Factors controlling mercury contamination in Berry's Creek and downstream ecosystems

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By

Tamar Barkay & John Reinfelder
Rutgers University

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The objectives of our study were two fold:

1. To analyze the distribution patterns of mercury from Berry's Creek to the lower Hackensack River estuary
2. To investigate factors that control methylmercruy (MM) production in Berry's canal

To achieve these objectives we sampled three sites spanning the length of Berry's canal and a control site in the Hackensack River (Fig. 1). Samplings were carried out in July and September of 2002 and July of 2003. In July 2002 we also sampled sites upstream of the tidal gate. General conditions during sampling were determined (Table 1) and samples were collected for analysis of Hg specific parameters (Total Hg [Hg_T], particulate and dissolved Hg, dissolved gaseous Hg [DGM], and methylmercury [MM] and microbiological analyses (^{14}C-MM degradation and identification of $^{14}CH_4$ and $^{14}CO_2$ end-products and ^{203}Hg(II) methylation). Sediment samples were collected for all sites for Hg_T and MM analyses. Sediment analyses were performed by the staff of the MERI's research lab.

Our results and a preliminary interpretation or the data are summarized below. Included, in some cases, are results of data collected during earlier samplings in Berry's creek up stream of the tidal gate.

<u>*Mercury speciation and distribution in Berry's creek*</u>

1. The distribution of Hg_T and MM in water samples shows that concentrations of both decreased with distance from the source (Fig. 2). This clearly implicated Berry's Creek as a source of contamination to the downstream estuary.

2. The distribution of Hg_T and MM in sediment does not show as clear a pattern as that of the water samples (Table 2). In July and Sept. of 2002 the highest Hg_T and MM concentrations were observed in tidal gate sediments with much lower concentrations downstream. This pattern however was not repeated in July of 2003. In July 2002 we collected three sediment samples about one meter apart at the MW site in order to determine the within site spatial variability (Table 2). Results show that for HgT the standard deviation was 25% of the means (24$\pm$6 mg/kg) and for MM the corresponding value was 33% of the means (12$\pm$4 ng/g).

3. Analyses of dissolved and particulate Hg clearly show that most Hg_T was bound to particulate matter in the water column (Fig. 3). This result suggests that the distribution of Hg from the source of contamination in Berry's creek is controlled by the distribution of particulate matter. Particulate matter may be suspended sediment particles as well as unicellular algae that were abundant in Berry's canal waters during summer months.

4. Elemental mercury (Hg[0]) flux values at Berry's creek ranged from 0.09 to 6.25 ng/m^2/h (Table 3). These values are similar to others found in rivers and estuaries of the US (Table 4). All fluxes were positive values indicating supersaturation of the water column. The degree of saturation was then calculated as S = [(DGM*H,)/TGM] *100. This calculation returned values ranging from 216% to 3276%. In comparison, a range of 476% to 2163% of saturation values was reported for the St. Lawrence River.

A table compiling all of our mercury analyses data is provided (Table 5)

Factors affecting MM production in Berry's canal

5. The highest potential for Hg methylation was observed in sediments from the confluence (CON) between Barry's canal and the Hackensack River (Fig. 4A). This trend cannot be explained by sulfide control of the availability of Hg for methylation in Berry's Creek as has been previously suggested because sulfide concentrations were much lower in tidal gate pore water (Fig. 4D). One possible explanation to the observed pattern in methylation potentials is the toxicity of Hg as total Hg concentrations were highest in sediments of the TG (Table 2). One should also notice that the presented sulfide data is from July 2003 while methylation data is from the summer of 2002. Clearly more research is needed to understand the effects of sulfides and Hg on potential methylation in Berry's creek sediments.

6. Potential demethylation rates in both water (Fig. 4C) and sediments (Fig. 4B) declined with distance from the source of Hg in Berry's Creek. In the water column this trend clearly follow the concentration of MM the substrates for the degradation reaction (Figure 1).

7. The pathways for the degradation of MM in water and sediment differed from each other as indicated by the gaseous carbon product of the demethylation reaction. In sediment, demethylation occurred by the oxidative pathways resulting in the production of mostly CO_2 while the major demethylation product in water samples was CH_4, indicating a reductive pathway. The distinction between these two pathway may be critical because the product of oxidative demethylation is most likely Hg(II) which can be subsequently methylation in anoxic sediments, while reductive demethylation results in the production of Hg(0) which is volatile and is removed to the atmosphere.

Presentations and publications resulting from this project

1. A journal manuscript: Schaefer, J.K., J. Yagi, J. Reinfelder, T. Cardona, K. Ellickson, S. Tel-Or, and T. Barkay. The role of the bacterial organomercury lyase in controlling methylmercury accumulation in mercury contaminated natural waters. Env. Sci. Technol. In press.

2. A journal manuscript summarizing our work in Berry's canal is currently in preparation.

3. Several talks and posters describing our work have been presented in international and national meetings. These include a workshop on Hg contamination in estuaries that was held in Slovenia in 2001, the annual meetings of the American Society of Microbiology, The MERI conference in the fall of 2003, and a conference on environmental contamination held at Rutgers University in the summer of 2003.

Fig. 1: Sampling site in Berry's canal and the Hackansack River.

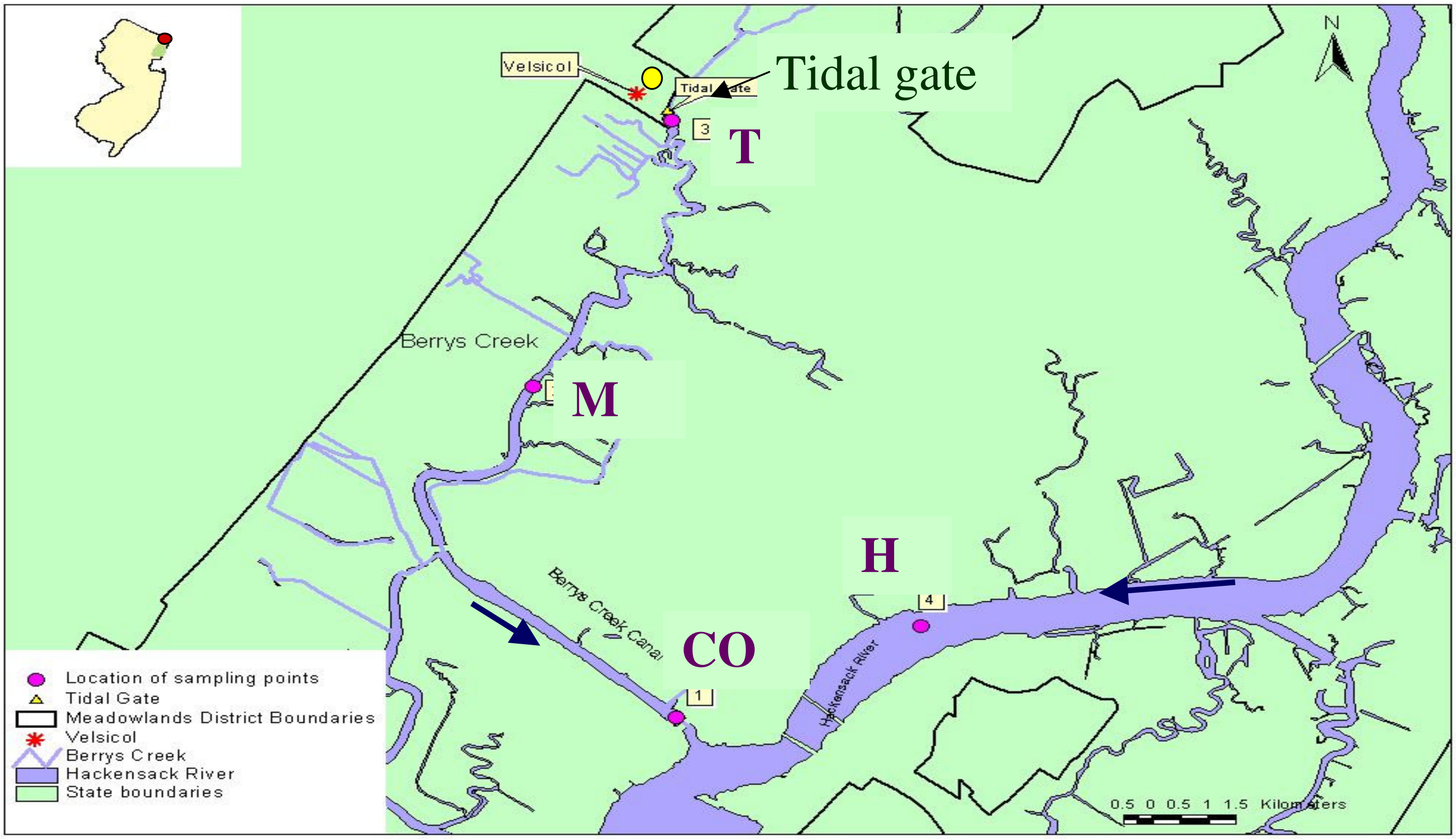

Table 1: Physical-chemical measurements during sampling in Berry's canal and the Hackensack River

Parameter	July 2002	Sept 2002	July 2003
Temp	26 - 27°C	22 - 24°C	22 - 26°C
pH	8.2 - 8.3	6.9 - 7.5	6.5 - 7.1
Salinity	9.5 - 12‰	3 - 11‰	0.8 - 4.8 ‰
Tides	Receding	Receding	Low tide

Figure 2: Distribution of HgT and MM in Berry's Creek and Berry's canal. Blue bars depict concentrations of Hg_T and yellow bars indicate concentrations of MM. MLU, MLM, and MLD are sampling sites located upstream of the tidal gate in Berry's creek. The source of mercury contamination is proximal to MLM (illustrated by a vertical black arrow). Flow directions are depicted with horizontal arrows.

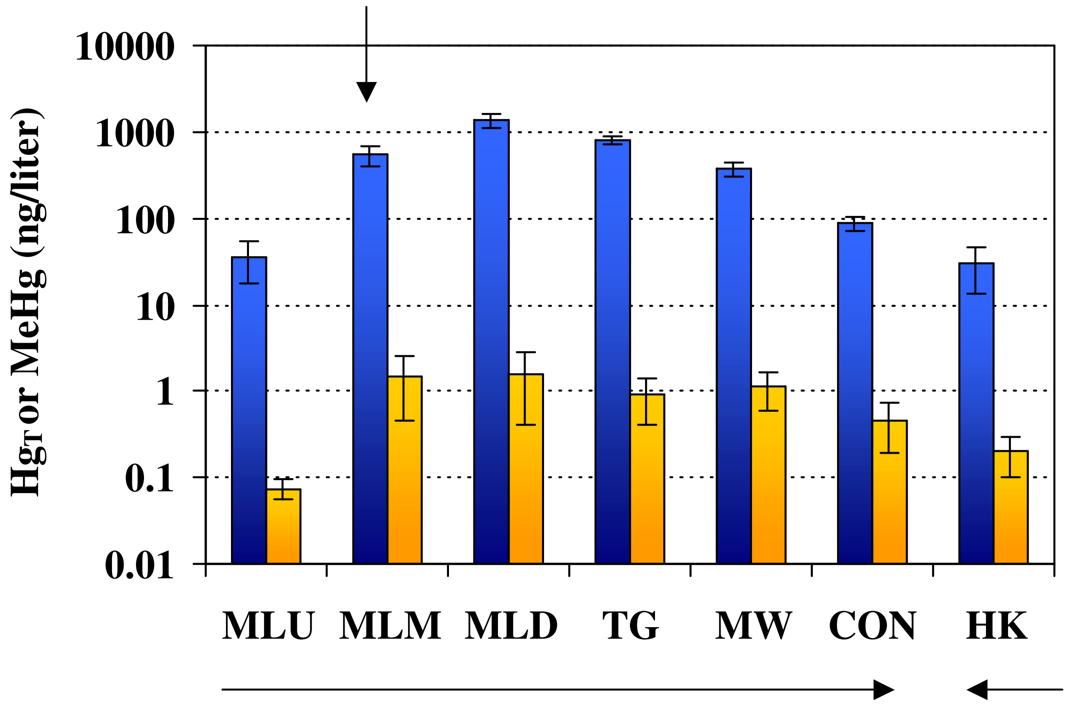

Table 2: Concentrations of Hg_T and MM in sediment samples.

Sampling Date	Site	Total Hg mg/kg	MM ng/g
18-Jul-02	CON	11.5	9.43
18-Jul-02	MW-1	29.0	7.33
18-Jul-02	MW-2	25.0	13.0
18-Jul-02	MW-3	17.3	14.9
18-Jul-02	TG	917	36.1
20-Sep-02	CON	5.79	4.62
20-Sep-02	MW	22.6	1.59
20-Sep-02	TG	519	16.1
10-Jul-03	CON	47.8	9.75
10-Jul-03	HK	14.3	1.58
10-Jul-03	MW	34.6	10.9
10-Jul-03	TG	13.0	7.67

Fig. 3: Particulate and dissolved HgT in Berry's canal and Hackensack River water samples. Light green depicts particulate-bound Hg and green depicts soluble Hg. Horizontal arrows depict flow directions.

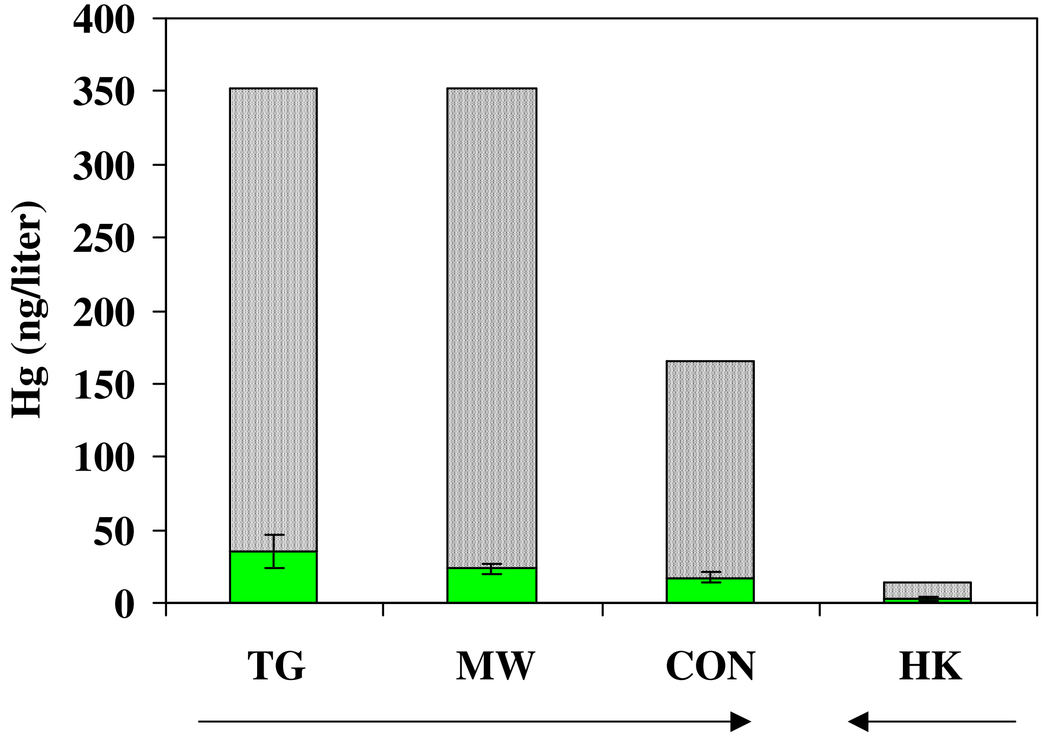

Table 3. Gaseous mercury concentrations and volatilization fluxes in Berry's Creek during sampling events.
*NA = not available

Date	Site	Wind Speed (m/s)	DGM (ng/L)	TGM (ng/m^3)	Flux (ng/m^2/h)
July 2002	TG	2.46	0.075	2.015	1.747
	MW	2.46	0.211	2.326	5.157
	CON	2.46	0.047	2.106	1.042
	HK	2.46	*NA**	2.273	*NA**
Sept. 2002	TG	2.08	0.026	2.649	0.314
	MW	2.08	0.033	2.032	0.468
	CON	2.08	0.015	1.865	0.166
	HK	2.08	0.010	1.543	0.097
July 2003	TG	2.94	0.214	2.067	6.265
	MW	2.94	0.113	2.067	3.419
	CON	2.94	0.024	2.259	0.587
	HK	2.94	0.082	1.930	2.521

Table 4: Gaseous Hg volatilization fluxes from Berry's Creek estuary and other rivers and estuaries.

Site	DGM (ng/L)	TGM (ng/m^3)	Flux (ng/m^2/h)	Reference
Berry's Creek Estuary	<0.01 to 0.21	1.54 to 2.64	0.09 to 6.25	This study
Knobesholm (small river in Sweden)	0.56 ng/L	2.61	11.0	Gardfeldt et al. 2001
St. Lawrence River	0.028 to 0.050	1.51 to 1.99	0.02 to 9.28	Poissant et al. 2000
San Francisco Bay	0.18	2.00	2.5 to 46	Conaway et al. 2003
Chesapeake Bay Estuary	0.02 ± 0.015	1.5-2.0	1.12	Mason et al. 1999

Table 5. Total mercury (THg) and monomethylmercury (MeHg) concentrations in Berry's Creek estuary surface waters. Concentrations are given for unfiltered water (THg, TMeHg), suspended particles (PHg_T, PMeHg), and filtered water (DHg_T, DMeHg). Values are means and standard deviations of replicate analyses (n = 2 to 16).
(*NA= not available)

Date	Site	THg	PHg_T (pM)	DHg_T	TMeHg (pM)	PMeHg (pM)	DMeHg
June 2002 (preliminary assessment)	TG	2083	*NA**	*NA**	*NA**	*NA**	*NA**
	S04	922	*NA**	*NA**	*NA**	*NA**	*NA**
	MW	3830	*NA**	*NA**	*NA**	*NA**	*NA**
	S02	1557	*NA**	*NA**	*NA**	*NA**	*NA**
	CON	627	*NA**	*NA**	*NA**	*NA**	*NA**
	HK	11	*NA**	*NA**	*NA**	*NA**	*NA**
July 2002	TG	4071 ± 441	2251	178 ± 57	4.5 ± 2.5	16.3	
	MW	1856 ± 377	5171	117 ± 16	5.7 ± 2.75	11.85	
	CON	430 ± 77	741	86.4 ± 19	2.3 ± 1.35	3.20	
	HK	152 ± 84	53	15.5 ± 8.2	1.0 ± 0.5	1.25	
Sep 2002	TG	59 ± 41	188	23 ± 8.5	7.5 ± 2.2	4.46	
	MW	978 ± 427	405	28 ± 5.5	11.9 ± 4.0	4.75	
	CON	329 ± 38	1206	5.2 ± 2.7	2.4 ± 0.55	0.4	
	HK	6.0 ± 6.0	59	4.3 ± 1.7	1.9 ± 0.5	1.8	
July 2003	TG	6775 ± 1585	1023	383	9.2 ± 4.6	12.85	
	MW	5087 ± 572	4958	237	15.2 ± 5.2	17.5	
	CON	694 ± 131	1062	74	7.3 ± 3.2	7.50	
	HK	77 ± 11	50	17	3.4 ± 1.3	6.6	

Figure 4: Potential first order rate constants for methylation and demethyltion in Berry's creek water a nd sediments. A. Methylation rates in sediments samples; B. Demethylation rates in sediments; C. Demethylation rates in water columns; D. Pore water sulfide concentrations.

A

C

B

D