Chapter 9

Planning Level Estimates of Heavy Metals (Pb and Cu), Total PCBs and HCB Loadings to the Buffalo River, NY, from Combined Sewer Overflows

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Pratt, E., K. Irvine, S. Marshall, B.G. Loganathan, S. Kumar and H.C. Sikka. 1995. "Planning Level Estimates of Heavy Metals, Total PCBs and HCB Loading to The Buffalo River, NY from Combined Sewer Overflows." *Journal of Water Management Modeling* R183-09. doi: 10.14796/JWMM.R183-09. © CHI 1995 www.chijournal.org ISSN: 2292-6062 (Formerly in Modern Methods for Modeling the Management of Stormwater Impacts. ISBN: 0-9697422-4-X)

9.1 Introduction

The collection, transport and disposal of dry-weather and wet-weather flow is an environmental problem for many U.S. cities (Roesner and Burgess, 1992). Combined sewer systems commonly service the older sections of U.S. cities and combined sewer overflows (CSOs) may be a source of bacterial, inorganic and organic pollutants to receiving water bodies (Meinholz EcolSciences, Inc., 1980; USEPA, 1984; Marsalek and Ng, 1989; Irvine et al., 1993a). There is a growing concern, particularly in the Great Lakes Basin, over pollutant loadings associated with CSOs. Many of the Areas of Concern (AOCs) around the Great Lakes have problems with CSOs and it is important under the Remedial Action Plan process to develop methodologies for the quantification and evaluation of pollutant inputs from this source.

The International Joint Commission (IJC) has identified the Buffalo River, NY as one of 43 AOCs around the Great Lakes. Among the several potential sources contributing to water quality degradation in the river, are 38 combined sewer outfalls (Figure 9.1). Other potential sources contributing pollutants to the river include direct industrial discharges, groundwater leachate from inactive hazardous waste sites, historically contaminated bed sediments and upstream (i.e. above the AOC) point and nonpoint sources (e.g. agricultural runoff, small municipal treatment plants).

One method for the determination of CSO impacts on the Buffalo River is to mathematically model the combined sewer system. Currently, a mass balance study for the Buffalo River is being conducted by a research team from the State University of New York (SUNY) at Buffalo and SUNY College at Buffalo (Loganathan et al., in prep; Atkinson et al., in prep; Irvine et al., 1993b). One of the intents of the study is to quantify pollutant inputs to the river from the different sources. This information can be used both as input to chemical transport and fate models and as a guide in the selection of appropriate remediation strategies. The objective of this chapter is to discuss the modeling approach used in the mass balance study to estimate pollutant loads from CSOs.

The impact assessment approach identified representative pollutant concentrations for the CSOs through a combination of sampling and review of past studies for the Buffalo River area. The representative pollutant concentrations were combined with estimated overflow volumes to determine pollutant loadings. The overflow volumes were esti-

mated, at a planning level, using a personal computer (PC) version of the Stormwater Management Model, release 4 (PCSWWM4) distributed by Computational Hydraulics Int., Guelph, Ontario. Overflow volume estimates were made both for a typical year and design storms with different return intervals. Design storms were examined in the mass balance framework, in part, as a means of assessing the hydraulics of particle-bound contaminant transport and deposition in the river. For completeness, design storm estimates were done of CSO volumes. In this chapter, total PCBs, HCB, Cu and Pb, were the pollutants selected to illustrate the loading estimate approach. Total PCBs and HCB are considered an environmental concern because of their persistence and toxic effects (Loganathan et al., 1990; Wren, 1991; Williams and Giesy, 1992; and Yamashita, 1993). The heavy metals, Cu and Pb, were selected for evaluation due to the concern of impact on the river's wildlife and available data for this study.

Figure 9.1
The location of the 38 combined sewer outfalls.

9.2 Study Area Description

The Buffalo River is located in the City of Buffalo in western New York State. The Buffalo River watershed has a drainage area of 1244 km², but the actual AOC includes only the lower 9.2 km of the river (Figure 9.1). A fuller description of the AOC is contained in Irvine et al. (1992; 1993a) and NYSDEC (1989).

Figure 9.2
South Buffalo sewer districts.

The combined sewer study area is referred to as the South Buffalo Sewer Districts (Figure 9.2) and consists only of the southern part of the city. The South Buffalo Sewer Districts are divided into 16 different areas, and there are 38 combined sewer outfalls associated with the districts (Figure 9.1). The Buffalo River is the receiving water body for these outfalls. The area of the Sewer Districts is approximately 3,879 ha and current landuses include light and heavy industry, commercial, low and medium density residential and open space. Much of the pervious land area either is vacant land or railway lines. Industries are granted permits

by the Buffalo Sewer Authority (BSA) to discharge waste and processing effluent to the South Buffalo sewer system. According to the estimates by the BSA, the average industrial waste flow in the South Buffalo Sewer Districts is 2,419,152 liters per day (LPD) (Irvine and Torok, 1991).

The entire city of Buffalo has approximately 1,287 km of combined sewers of various sizes (Calocerinos and Spina, 1988; BSA, undated). According to Sargent (1975), 60% of the sewers in Buffalo were constructed prior to 1910 and 92% prior to 1940. Most likely these percentages have diminished slightly since 1975, but the Buffalo sewer system evidently is older. Calocerinos and Spina (1988) mention that there are a total of 250 overflow structures and that these are connected to 67 sewer outfalls within the entire city of Buffalo.

9.3 Methods

9.3.1 Field Sampling Practices and Techniques

Automated sampling equipment was installed at the Babcock St. main diversion structure (Figure 9.1, site 27). A Montedoro-Whitney System Q flow device was used to measure and record the average (directional) flow velocity and flow depth for the calculation of overflow discharge. The flow data were uploaded from the datalogger using a laptop computer. The flow probe from the System Q datalogger was fastened to the top of the side weir within the main overflow chamber. The System Q was connected to a Sigma Streamline Model 700 Composite Pump Sampler. The pump sampler collected flow proportioned composite samples for quality analysis. The system was programmed to take 250 ml samples at 250 m³ overflow intervals. The pump sampler intake was attached a few centimeters in front and below the crest of the side weir. The automated system was calibrated in a 6.1 m recirculating flume (housed in the Earth Sciences Department at SUNY College at Buffalo) prior to installation in the overflow chamber.

The system was installed at the Babcock St. overflow chamber for three field seasons. The first two field seasons began 90.06.25 and 91.04.12, respectively and ended 90.12.04 and 91.11.04, respectively (Irvine et al., 1993a). The third season began 92.05.02 and ended 92.11.21.

Grab samples of wet-weather flows (i.e. runoff events that did not produce overflows) were collected using the Sigma 700 pump samplers at the Babcock St. site and three additional locations in 1990 and 1991

(Figure 9.1, outfalls 25 and 67; and a small overflow chamber contributing to outfall 26). Flow rates at the time of sample collection were determined using a Montedoro-Whitney PVM-2A electronic flow meter and measurement of flow depth. A grab sample of the sanitary flow also was collected at the Babcock St. overflow chamber.

9.3.2 Sample Analysis

The CSO and sanitary samples collected at the Babcock St. overflow chamber for the evaluation of total polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) levels were analyzed at the Great Lakes Center laboratories, SUNY College at Buffalo, following the procedures described in the Federal Register (1984) and Loganathan et al. (1990), with some modifications. Results for some of these samples have been reported previously (Irvine et al., 1993a). The HCB can be extracted by the same process as the PCBs due to their similar chemical structures. Standard reference materials (USEPA certified) were used for the extraction of the total PCBs and HCB.

The overflow and sanitary samples were homogenized in a separatory funnel and 1 liter of the sample was collected. The 1 liter of the sample was filtered through 0.45 micron Whatmann GF/C glass microfibre filters using a Millipore filter system. The filtration split the sample into two portions, a dissolved phase and a particulate phase. The separated samples were processed individually using different extraction procedures. Hexane-washed distilled water also was filtered for use as a blank. The blank was analyzed by the same procedure as the samples.

All samples were spiked with surrogate standards (2,4,5,6-tetrachloro-m-xylene and 2,2',3,4,4',5,6,6'-octachlorobiphenyl) and were subjected to the same procedures throughout the sample preparation in order to check the efficiency of the analytical procedure.

The dissolved phase samples were transferred to individual 2000 ml separatory funnels and extracted thrice with 60 ml of methylene chloride for 15 minutes. The methylene chloride solution was thrice passed through a glass funnel containing sodium sulfate and supported with a glass wool plug to prevent loss of the sodium sulfate. The dehydrated methylene chloride extracts were carefully transferred to the K-D concentrator. The methylene chloride extract was K-D concentrated to about 5 ml and transferred to hexane. The hexane solution was placed onto a silica gel chromatography column (20 cm x 1 cm bed of 80 mesh

silica gel) for separation of pesticides from PCBs. The fraction of the column eluant containing the PCBs and HCB was collected and concentrated using a K-D concentrator. The extract was treated with 5% fuming H_2SO_4 and washed with hexane rinsed water. The extract was concentrated to 1 ml using ultrapure dry N_2 gas. An aliquot of the sample was injected into the gas chromatograph equipped with an electron capture detector. If the chromatograph peaks were under detection limit, the sample was micro-concentrated by reducing the volume using a gentle stream of ultrapure N_2 to the desired volume (i.e. 0.300 ml) and then injected again.

The particulate phase was extracted for 16 hours using 300 ml of methylene chloride. The sample was transferred to clean K-D concentrator and further prepared in the same manner as the methylene chloride solutions for the dissolved phase sample.

The samples were analyzed using a Varian 3400 Gas Chromatograph equipped with a Varian 8100 Autosampler. The sample was injected into a split/splitless capillary injector maintained at 250°C. The separation was carried out on a DB-5 capillary column (J&W Scientific) 30m x 0.25mm with a 0.25 micrometer film thickness. The column carrier gas and the detector makeup gas were grade 5 nitrogen and the detector was a ^{63}Ni electron capture detector maintained at 300°C. The column oven was temperature programmed from 160°C to 230°C at a rate of 2°C per minute. Both the initial temperature and the final temperature were held for 10 minutes.

The PCBs and HCB concentrations were quantified by using specific resolved peaks with corresponding standard peaks. These peaks were selected for calculation of total PCBs by choosing five or six of the most prominent peaks within the gaussian distribution. The PCBs standard used for computation contained a 1:1:1:1 mixture of Aroclors 1242, 1248, 1254, and 1260. The recoveries of the surrogate standard were within a range of $100 \pm 20\%$. The PCBs and HCB concentrations were not corrected for the standard recoveries. The detection limit for the methodology was 3 ng/l.

The analytical method for the wet-weather and sanitary grab samples had some procedural differences from the Babcock overflow samples. The primary differences were related to a larger sample volume (20 liters) being processed. A pentaplate system with 293 mm diameter Whatmann Glass Fibre Filters was used to separate the dissolved and particulate material from the raw samples. The dissolved phase was passed through an XAD-2 resin column for extraction. The volumes of

extraction solvents were greater because of the larger sample volume. Conditions for the gas chromatograph analysis essentially were as described above. Greater detail about analytical methodology is contained in Loganathan et al. (in prep.).

The levels of Cu and Pb in collected wet-weather samples were determined by the SUNY College at Alfred laboratories. The particulate and dissolved phase concentrations were not determined separately (i.e. a total concentration was reported). The analytical methodologies followed that described under USEPA method code 239.2 for Pb and USEPA method code 220.2 for Cu. For additional details on metals sampling and analytical methodology, see Loganathan et al. (in prep.).

9.3.3 Modeling Approach

The South Buffalo Sewer Districts combined sewer system was modeled using the RUNOFF and TRANSPORT blocks of PCSWMM4. Although the EXTRAN block more accurately represents surcharging and backwater conditions, the TRANSPORT block was used in this study because

1. of its ability to route pollutants,
2. it is less computationally intensive, and
3. therefore produces results more quickly, and
4. input data are more easily derived.

Two different approaches were used to estimate and evaluate overflow volumes. First, rainfall intensities (mm/hr) were determined at five-minute intervals from a BSA tipping bucket gage at the South Buffalo Pump Station for 90.03.01 to 90.10.18 (Figure 9.1). For the periods in 1990 that were not recorded by the BSA gage, hourly rainfall intensity data were obtained from the National Weather Service site located at the Buffalo Airport. The BSA rainfall data were used to the extent possible because of the gage's proximity to the study area and the shorter timesteps. The period 90.03.01 to 90.10.18 also was the time of the most frequent overflows. The precipitation for the year 1990 was similar to the 30 year norms, particularly from the summer through fall (Figure 9.3) and 1990 therefore can be considered a typical hydrologic year.

The second approach to evaluating overflow volumes was through the use of 24-hour design storms with rainfall depths having return intervals of 1, 2, 5, 10, 25 and 100 years. The return intervals were determined from the records for the National Weather Service site located

Figure 9.3 Comparison of monthly rainfall for Buffalo.

at the Buffalo Airport. The hourly rainfall intensities for observed storms having 24-hour depths similar to the above return intervals were used as input to PCSWMM4. It is possible for storms to have similar 24-hour precipitation depths but different patterns of rainfall intensity through the 24-hour period. Different intensity patterns will result in different overflow characteristics. This variability was evaluated by running two different storms having similar 100-year depths.

It is not feasible to model all sewers and overflow structures in South Buffalo due to computational constraints. To determine surface physical parameters (e.g. slope, Manning's roughness, depth of depression storage) in the PCSWMM4 framework, a lumped approach must be used. Therefore, the entire South Buffalo area was divided into various contributing surface subcatchments and the surface flow was routed through a simplified pipe network. The spatial resolution of the subcatchments and the detail of the sewer network can vary, depending on the needs of the study. However, several researchers have found that hydrographs produced by a coarse or fine discretization can be similar (e.g. Nix, 1990; Zaghloul and Al-Shurbaji, 1990).

The schematics of the modeled South Buffalo Sewer network are shown in Figure 9.4. Much of the original discretization for this study was based on that done by Calocerinos and Spina (1988) in a modeling effort for the entire city of Buffalo. It should be noted, however, that Calocerinos and Spina (1988) used the EXTRAN rather than the TRANSPORT block and input requirements are somewhat different. Calocerinos and Spina (1988) also did not explicitly model all outfalls because of the constraints in applying the model to the entire city. The primary concern of this study was to evaluate overflow volumes to the Buffalo River and the modeling effort therefore did not consider the transportation of undiverted flow to the sewage treatment plant. As a result, several of the smaller outfalls were modeled individually and do not appear connected to the rest of the system in Figure 9.4.

The Babcock St. Sewer District (Figure 9.2, district 18; Figure 9.1, outfall 27) was modeled separately from the rest of the South Buffalo Sewer Districts. A model for this district had been calibrated previously using data from the 1990 overflow monitoring program and the network schematic is presented by Irvine et al. (1993a).

This study represents a planning level approach to pollutant loading estimates. As such, a limited amount of flow data were available for model calibration. Calibration of the Babcock St. Sewer District was

Figure 9.4a
Schematics of the modeled sewer network for the South Buffalo Districts.
Outfall numbers correspond to those in Figure 9.1.

Figure 9.4b
Schematics of the modeled sewer network for the South Buffalo Districts. Outfall numbers correspond to those in Figure 9.1.

reported by Irvine et al. (1993a). The mean absolute difference between eight modeled and observed overflow event volumes was 4% and the mean absolute difference between modeled and observed peak overflow rates was 24%. The calibration results for the Babcock St. Sewer District compared favorably with results reported in the literature (Cermola et al., 1979; M.M. Dillon Ltd., 1979; Gore and Storrie Ltd., 1980; Nix, 1990; Zaghoul and Al-Shurbaji, 1990; Warwick and Tadepalli, 1991). Model calibration and verification also were done by Calocerinos and Spina (1988) based on flow data collected at three sites for three events. The absolute difference between modeled and observed flow volumes for the various sites and events ranged between 0 and 81%, with an average of 38%. These results are reasonable, given the limited data available for calibration and the size and complexity of the system (see also Nix, 1990). The model calibrations as reported by Irvine et al. (1993a) and Calocerinos and Spina (1988) help ensure a reasonable level of accuracy for overflow volume estimates to the Buffalo River.

The pollutant loadings to the river most simply can be calculated as (after Marsalek and Ng, 1989):

$$L_j = C_j \quad V \quad (9.1)$$

where:

- L_j = the annual or design storm load of pollutant, j
- C_j = a representative concentration for pollutant, j
- V_j = the annual or design storm overflow volume.

9.4 Results

9.4.1 Overflow Volume Estimates for the Typical Year, 1990

The model results using the 1990 rainfall record as input indicated that the total overflow volume discharged to the river for the year would be in the range of 619,566 m³. It was estimated that a total of 76 overflow events may have been observed during 1990. In this case, events arbitrarily were considered independent if separated by a non-overflow period of two hour duration. In general, the south side of the river (including Cazenovia Creek) experienced more frequent, but smaller overflow events. The outfalls on the south side of the river having the most frequent or largest discharges were 58, 68, 55, 53 and 73. The outfalls on the north side of the

river having the most frequent or largest discharges were 17, 26 and 27. These outfalls could be priority targets in sewer remediation programs. The modeled overflow volumes also were tabulated on a monthly basis and the results are presented in Figure 9.5. Figure 9.5 indicates that overflows may occur throughout the year, but the maximum volumes generally are observed in late spring through early fall (a time of the highest potential for primary contact in the Buffalo River).

9.4.2 Model Results for Design Storms

The model results for the design storms having a 24-hour rainfall depth with a t-year recurrence interval are summarized in Table 9.1. In general, as the recurrence period of the storm increases, the system overflow volume and the number of outfalls discharging to the river also increases.

The shape of the hyetograph can have a major effect on the runoff characteristics in relatively small, urbanized basins. The design storms were defined on the basis of the recurrence interval for a 24-hour depth, but two rainfall events having similar 24-hour depths may have different intensity distributions. The impact of different intensity distributions on estimated overflow volume can be illustrated for two events having similar 100-year depths. The hyetographs for the two events are shown in Figure 9.6. The total overflow volume for the rainfall event of 87.06.22

Table 9.1
Results for design storms with t-year recurrence depths

Recurrence Interval (years)	Date of Event	Peak Hourly Rain (mm/hr)	Rain Event Depth (mm)	Hours of Rain in 24-Hour Period	System Overflow Volume (m ³)
1	68.09.11	14.5	50.0	12	95,528
2	71.07.12	25.4	59.2	16	119,449
5	63.07.29	27.2	85.8	8	249,095
10	86.05.19	43.4	89.4	26	269,180
25	63.08.07	44.4	101.1	6	368,195
100	87.06.22	62.2	127.2	15	614,656
100	79.09.13-14	35.0	125.5	15	382,386

Figure 9.5 Modeled monthly overflow volumes to the Buffalo River Area of Concern for the year 1990.

Figure 9.6 Observed hyetographs for storms having 100-year, 24-hour rainfall depth.

was 232,270 m³ (1.62 times) greater than the event of 79.09.13-14. These results indicate that should simple functions be developed to estimate overflow volumes from rainfall (in absence of detailed deterministic modeling), intensity characteristics should be considered.

9.4.3 Model Sensitivity

The three parameters that provide the greatest variability with respect to overflow volume are surface slope, percent imperviousness, and subcatchment width (e.g. Calocerinos and Spina, 1988; Irvine et al., 1993a). A total of eighteen sensitivity runs were made (six runs for three parameters) for all of the South Buffalo Sewer Districts. The slope, percent imperviousness, and subcatchment width were varied $\pm 30\%$ of their original values (Figure 9.7). The $\pm 30\%$ was selected because it was small enough to save computer time, but large enough to change the overflow volumes significantly. Furthermore, the $\pm 30\%$ maintained the parameter values within a realistic physical range (Irvine et al., 1993a). The value for each parameter was increased at intervals of 10%. The parameters were varied within the modeled range that would produce the minimum and maximum flow for each parameter. The other parametric values were held constant. The model sensitivity was examined using a large storm event (90.07.09) and a small storm event (90.10.04).

9.4.4 Determination of Representative Pollutant Concentrations and Loadings

The levels of total PCBs and HCB in sampled overflows for the Babcock St. Sewer District (Figure 9.1, outfall 27; Figure 9.2 district 18) are summarized in Table 9.2, along with the results of a sanitary (dry-weather) flow sample. It is worth noting that the particulate phase concentration of total PCBs in the sanitary flow is lower than particulate phase concentrations observed in the overflows. This suggests that much of the total PCBs loading in the Babcock St. Sewer District is associated with runoff events.

The representative pollutant concentrations for total PCBs and HCB were calculated by averaging the concentrations from this study (excluding the dry-weather sample) as well as those from Irvine et al. (1993a) and Loganathan et al. (in prep.). Any samples that were reported as less than detection were assigned a value that was one-half the detection limit. The Irvine et al. (1993a) samples were CSO samples and were

Figure 9.7
The sensitivity analysis for the 90.07.09 and 90.10.04 storm events.

Table 9.2
Total PCBs and HCB concentrations from the Babcock St. Sewer District CSOs
and sanitary flow.

Period	Total PCBs (ng/l)		HCB (ng/l)	
	Particulate Phase	Dissolved Phase	Particulate Phase	Dissolved Phase
Sep, 1990*	400	6	30	BDL**
Apr, 1991*	ND***	ND	20	0.045
Jul 4, 1991*	970	38	16	0.98
Jun 19, 1992	329	28	4.2	0.46
Jul 2, 1992#	43	31	2.5	1.5

* reported in Irvine et al. (1993a). The Sep, 1990 and Apr, 1991 samples represent a composite of four overflow events each

** below instrument detection limit of 3 ng/ml

*** not determined for this event

sanitary flow sample, all others in table are overflow samples

collected from the primary overflow chamber of the Babcock St. Sewer District. The Loganathan et al. (in prep.) samples were collected at four sites (including the Babcock St. chamber) during storm events that did not have enough precipitation for an overflow to occur (i.e. wet-weather samples). Data on Cu and Pb levels in the combined sewage were available from various sources (sampling by the authors, BSA, and Calocerinos and Spina, 1988) for several different locations in South Buffalo. The average concentration from all samples for each pollutant was determined as the representative concentration for use in the loading estimates. The representative (i.e. average) concentrations were: Total PCBs (particulate phase) - 221 ng/l (n=16); Total PCBs (dissolved phase) - 15 ng/l (n=16); HCB (particulate phase) - 8.7 ng/l (n=10); HCB (dissolved phase) - 0.5 ng/l (n=10); total Cu - 0.148 mg/l (n=12); total Pb - 0.144 mg/l (n=6). Using equation (9.1) and the representative concentrations, the pollutant loadings were calculated on an annual and design storm basis.

9.5 Conclusion and Recommendations

The loadings of total PCBs, HCB, Cu and Pb in CSOs to the Buffalo River were estimated on an annual basis and on a design storm basis. The loading estimates were made using modeled overflow volumes

from PCSWMM4 and representative pollutant concentrations. In particular, the estimated overflow volume for the South Buffalo Sewer Districts for the year 1990 was 619,566 m³. The annual loading for the year 1990 of total PCBs for the particulate and dissolved phase was 0.137 kg and 0.0093 kg, respectively. The annual loading for the year 1990 of HCB for the particulate phase and the dissolved phase was 0.0054 kg and 0.0003 kg. The annual loading for the year 1990 of Cu was 91.7 kg and of Pb was 89.2 kg. These loading estimates can be compared with loadings from other sources to help prioritize remediation options for the Buffalo River.

Preliminary loading estimates from other sources indicate that for a typical year, CSO input of Pb is the same order of magnitude as inputs from direct industrial discharges, but higher than groundwater input from inactive hazardous waste sites (Atkinson et al., in prep.). The input of Cu from CSOs for a typical year is lower than input from direct industrial discharges, but greater than input from inactive hazardous waste sites. The CSOs appear to be an important source of total PCBs input to the river.

The CSO volumes and loadings must be considered planning level estimates. Although studies using SWMM have shown that the model can estimate flows accurately, in this study limited flow data were available to calibrate the model. Before initiating any remediation strategies, more sewer flow monitoring should be done to calibrate and verify the model accuracy. Nonetheless, problems with combined sewer overflow discharges are observed in many of the AOCs around the Great Lakes Basin. The loading estimate approach described above could be applied to any AOC to assist in remediation decision-making.

Acknowledgements

Funding for this research was provided partially by the USEPA and the Research Foundation of SUNY. Several individuals assisted in the collection of field data and provision of background data for this study, including Dennis Torok and Mary Rossi. Special thanks to Greg McCorkhill, P.E., Calocerinos and Spina; Jim Caruso, Frank DiMascio, P.E.; Art Fisher, and other personnel at the Buffalo Sewer Authority for providing background information and field assistance.

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