THE QUANTIFICATION OF ATMOSPHERIC PARTICULATE DRY DEPOSITION AND ATMOSPHERIC COPPER LOADINGS TO THE BUFFALO RIVER AREA OF CONCERN

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ABSTRACT: The atmospheric deposition of particulates and contaminants can have an impact on the quality of a waterway. This paper describes the methods used to determine a planning level estimate of particle and copper loadings to the Buffalo River by way of atmospheric dry deposition. Measured dry deposition rates from an Aerochem Metrics Sampler are compared to calculated dry deposition rates from a flux equation. The Aerochem data provide a measure of 18,205 kg/yr direct deposition onto the water surface, while calculated rates range from 8,975 to 9,846 kg/yr. These estimates are in close agreement considering the calculated method does not include all coarse particles in the atmosphere. The 18,205 kg/yr value represents one quarter of one percent of the total identified sediment loadings to the river and does not seem significant. However, the amount of copper associated with this dustfall accounts for about 3 percent of the copper loadings in the river. These estimates are only for the direct dry deposition onto the water surface and do not include wet deposition or the deposition on the surrounding land surface which can enter the waterway through runoff.

INTRODUCTION

The International Joint Commission has identified 43 Areas of Concern (AOCs) in the Great Lakes basin that suffer environmental degradation. One of these AOCs is the Buffalo River in Buffalo, New York (Figure 1). The Buffalo River meanders 13.7 km through the city of Buffalo to its mouth at Lake Erie. The designated AOC extends from Lake Erie to 9.2 km upstream. The water surface area of the Buffalo River in the AOC is approximately 800,000 m^2. The three major tributaries are Cazenovia Creek, Cayuga Creek and Buffalo Creek which flow north and west from the northern Allegheny Plateau. The area of the entire drainage basin is 1155 km^2 (Torok, 1993). Historically, the lower Buffalo River hosted most of Buffalo's major industries (NYSDEC, 1989). The Buffalo River AOC presently is the focus of a multidisciplinary investigation sponsored by the Environmental Protection Agency (EPA). The goal of this study is to determine the quantity, impact and source of contaminants to the river, with the intent of developing remediation stratgies. One component absent from the current investigation is the role of atmospheric deposition as a pollutant pathway.

Atmospheric particulate deposition is the continuous fallout of particulates from the atmosphere to the earth. Atmospheric deposition occurs in two forms, through dry deposition (the gravitational settling of particles) and through wet deposition (the scavenging of particles by precipitation). Airborne particles are a subject of increasing concern in the Great Lakes area because of their contribution to chemical contamination in the basin (Arimotto, 1989). The deposition of these particles can have a major impact on ecosystems (Nater et al., 1991; Ibrahim et al., 1993) as well as human health (Paoletti et al., 1989).

While determining wet deposition loadings is considered straightforward (particle or elemental concentration times the volume of precipitation collected), the determination of dry deposition is viewed as complex and the various methods used as controversial (Hicks et al., 1991; Dolske and Gatz, 1985). The purpose of this paper is to provide a planning level estimate for the direct deposition of particles and copper (an EPA priority pollutant) to the water surface of the Buffalo River AOC and to compare the magnitudes with other sources.

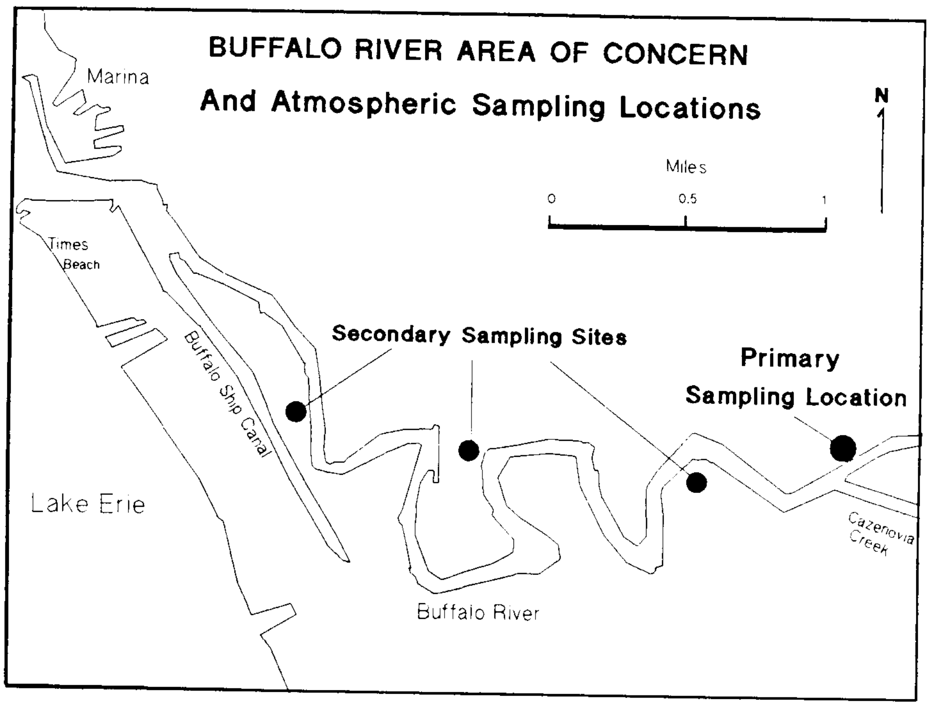

Figure 1. Buffalo River AOC and Sampling Locations

METHODOLOGY

The collection of deposition samples was performed at a field station located on the roof of the Buffalo Sewer Authority's South Buffalo Pumping Station adjacent to the river, near the upstream limit of the AOC (Figure 1). This site was chosen as the primary site because of its close proximity to the river in the AOC and it offered a secure location for equipment. The secondary sampling sites were used to determine if the primary site was representative of the AOC. The bulk of data collection occured during a 2 year study period which started in July, 1989 and ran through July, 1991. Supplemental data were collected during the summer of 1994.

QUANTIFICATION OF ATMOSPHERIC PARTICULATES

Two approaches were taken to determine dry deposition loadings to the Buffalo River AOC. One approach was to measure the dry deposition collected in a container; while the other approach was to calculate the dry deposition based on measured air concentrations and particle deposition velocities. The use of these two independent approaches provides a comparative check.

The Measurement of Dry Deposition

An Aerochem Metric Sampler was used to collect wet and dry deposition samples. The Aerochem sampler consists of two collection buckets (one for dry dustfall and one for precipitation), a precipitation sensor, a motor and a cover. The buckets are lined with polyethylene bags. One bucket is exposed to collect dry dustfall while the other is covered. At the onset of rainfall, the sensor activates the motor which moves the cover into position over the dry bucket, leaving the wet bucket open to collect precipitation. When it stops raining, the motor is activated again and the cover is moved over the wet bucket, leaving the dry bucket open for further collection.

The Aerochem Metric Sampler collected dry deposition on a weekly basis. The polyethylene bags were retrieved and processed in the Sedimentology Laboratory at Buffalo State College. The dry bags were rinsed three times with 250 ml of nanopure water to remove the particulates. The rinse water was immediately passed through dessicated, pre weighed 0.45 um Millipore filters. The filters were again dessicated and weighed to determine the mass of the particles deposited during the week. A mean dry deposition rate in $mg/m^2/day$ was determined by measuring the surface area of the dry bucket in m^2, dividing by the time the bucket was exposed to dry deposition, and multiplying by the mean mass of particulates on the filters.

The Calculation of Dry Deposition

Dry deposition rates were calculated using the following general flux equation:

$$\mathbf{D = C_a * V_d * SA * F}$$

where:	D	represents the dry deposition rate ($kg/m^2/yr$)
	C_a	represents the concentration of particulate matter in the air (ug/m^3)
	V_d	represents the deposition velocity of a particle (m/s)
	SA	represents the water surface area (m^2)
	F	represents the fraction of time not raining (%)

Data for the concentration of particulate matter in the air (C_a) were obtained using an Anderson High Volume Ambient Air Sampler (hi-vol). The hi-vol draws in a large volume of air by means of a vacuum motor and collects total suspended particulates up to 41 um (Chow and Ono, 1992) on a preweighed 20 by 25 cm cellulose fiber filter. The hi-vol was set to sample at a flow rate of 1.13 m^3/min, for a 24 hour period, on a one-in-six day cycle.

The deposition velocity (V_d) of a particle is dependent on the size and more specifically on the mass of the particle. Particle size identification was provided by a Particle Measuring Systems Classic Scattering Aerosol Spectrometer Probe (laser particle counter). The particle counter sampled for periods of 10 minutes at the primary site, twice a week for 6 weeks, and it was also used at the secondary sampling sites on two separate occasions (Figure 1). The particle counter draws in air at a rate of 12.18 cm^3/sec and passes it through a laser beam. The light scattered by a particle within the beam is a direct function of the particle size. This instrument counts and measures the size of particles in the atmosphere, reporting them in 6 um range classes. Particle size is an important factor for use in the calculation of a deposition flux, as the larger particles (greater mass) tend to be removed from the atmosphere at a faster rate than the smaller particles. Particle mass was determined by cubing the radius of the counted particles (r^3) (Stern, 1976). The deposition velocity (V_d) for the median particle (within each class) was taken from the literature (Davies, 1954), converted to a yearly deposition rate (m/yr), and weighted by the percent of mass contributed by each size class in relation to that of the overall mass.

The water surface area (SA) was calculated from the length and mean width values of the Buffalo River (NYSDEC, 1989). The fraction of time not raining (F) was determined from recordings on a Belfort raingage located at the primary site and from meteorlogic data obtained from the National Weather Service monitoring station at Buffalo International Airport.

Determination of Copper

Elemental concentrations of measured dry deposition samples were determined by Instrumental Neutron Activation Analysis (INAA). Filters and filtrate were brought to the nuclear reactor at McMaster University in Hamilton, Ontario. Short-decay Instrumental Neutron Activation Analysis (Irvine et al., 1989) was employed to provide concentrations of Br, Cu, Na, V, K, Mn, Cl and Ca reported in parts per billion. Of these elements, only copper is an EPA priority pollutant.

RESULTS AND DISCUSSION

Measurement of Dry Deposition

The average dry deposition rate, as measured by the Aerochem Metrics sampler, was 72.3 mg/m^2/day. Taking into consideration the surface area of the Buffalo River within the AOC (800,000 m^2), a particle deposition rate directly to the surface of the Buffalo River in the AOC of 18,205 kg/yr was obtained.

Weekly deposition loadings were compared with wind direction. The deposition loadings corresponded to the frequency of wind direction, with the greatest deposition occurred with winds from the southwest (prevailing direction) (Figure 2). This linkage with wind direction frequency suggests no one particular industry or area responsible for the deposition of particles to the Buffalo River AOC.

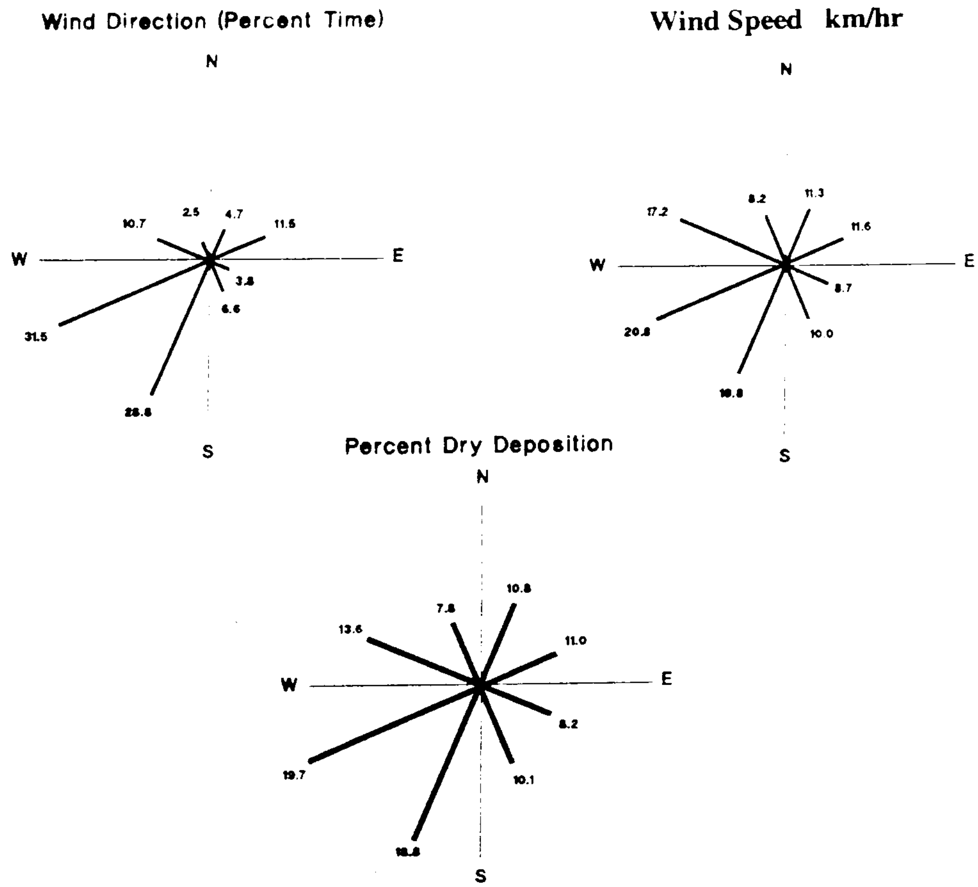

Figure 2. Wind Roses and Deposition Rose

Calculation of Dry Deposition

The New York State Department of Environment and Conservation (NYSDEC) maintains a network of hi-vol samplers throughout the city of Buffalo (NYSDEC, 1992), but unfortunately does not sample within the AOC. To obtain a particle air concentration within the AOC, three years of data (1989-91) from the NYSDEC network was used to construct isopleth contours across the city. Particle concentrations are shown to increase approaching the AOC, with the highest mean concentration (43 ug/m^3) measured on its fringe. Since landuse within the AOC is predominantly industrial, it was assumed that airborne particle concentrations would peak within the AOC. Following this assumption, an upper level estimate of 47.5 ug/m^3 was extrapolated from the NYSDEC hi-vol data (Figure 3).

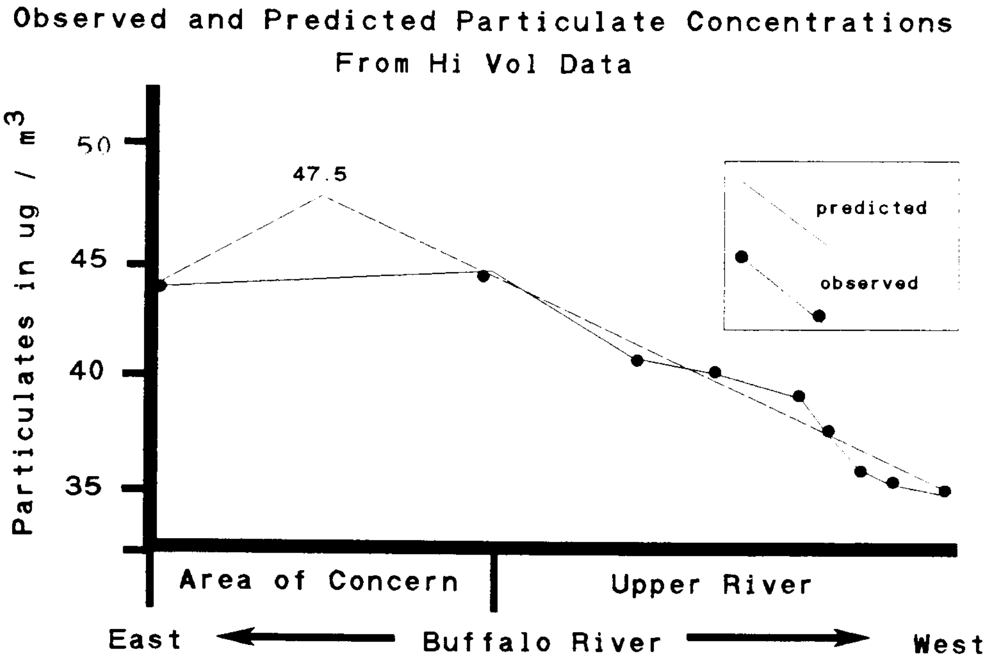

Figure 3. A Vertical Profile of Atmospheric Particle Concentrations along the Buffalo River.

Particle size distributions, obtained from the laser particle counter, showed a unimodal distribution with particle mass peaking at 8 um (Figure 4). While particles greater than 41 um were counted, calculations of dry deposition using the hi-vol sampler are restricted to particles less than the 41 um cutoff. The particle size distributions at the primary site, and the supplimental sampling at the three secondary sites, reinforced a common particle size distribution across the AOC.

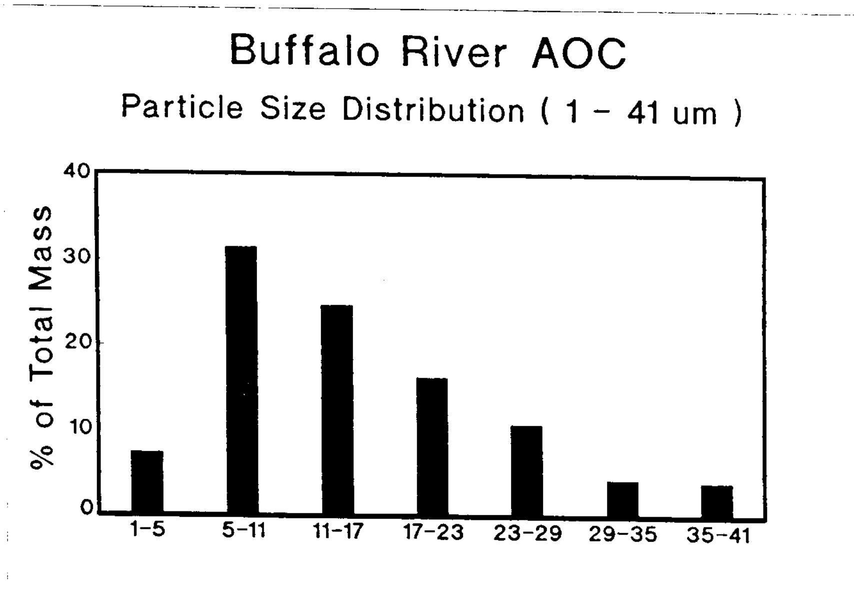

Figure 4. Adjusted Particle Size Distribution.

QUANTIFICATION OF ATMOSPHERE PARTICULATES

The National Weather Service data, in conjunction with a recording raingage at the primary site, indicate that dry deposition occured on average 88.4 percent of the time during the study period.

Using a lower (43 ug/m^3) and an upper (47.5 ug/m^3) value for the concentration of particles in the air (C_a), and a deposition velocity (V_d) determined from the particle size distribution (1 to 41 um), a particle deposition rate directly to the Buffalo River AOC of 8,975 to 9,846 kg/yr was obtained.

Dry Deposition of Copper

The measured dry deposition of copper directly to the Buffalo River AOC was 9.9 kg/yr. Five percent of this value was obtained from analysis of the filtrate, as some copper was dissolved during the bag rinsing procedure. This loss to the filtrate (alkaline water) corresponds to the low mobility rating given by Speidel and Agnew (1982) for copper in alkaline solutions.

A comparison of weekly copper loadings with wind direction do not show a linkage with the frequency of wind direction, as was the case for particle deposition. The highest copper loadings were almost exclusively associated with winds from the southeast. This relationship suggests a source of copper outside the AOC. It is interesting to note that the highest annual levels of copper measured in ambient air within the state of New York occur at a NYSDEC site located about one mile south of our primary site (NYSDEC, 1992).

Significance of Particulate Dry Deposition to the Buffalo River AOC

Examination of the data provided by the National Weather Service shows that the meteorological conditions in the Buffalo area during the study period are similar to the 30 year normal (Table 1). Airborne concentrations of particulate matter have decreased over the last 10 years (NYSDEC, 1992) and it is reasonable to assume that dry deposition rates to the Buffalo River were greater in the past. In contrast, copper concentrations have increased almost four-fold since 1982 and thus the dry deposition of copper to the Buffalo River AOC is greater now than in the past ten years.

Estimates of annual particle and copper loading to the Buffalo River AOC from upstream inputs and combined sewer outputs have recently been reported (Atkinson et al., 1993). The annual inputs of particulate dry deposition account for about 0.25 percent of all the inventoried inputs. In contrast, the annual inputs of copper attributed to dry deposition account for 3 percent of all the inventoried inputs. These estimates represent only the direct deposition onto the surface of the Buffalo River in the AOC, and do not include dry deposition over the watershed, nor do they include inputs directly to the river and watershed attributable to wet deposition.

CONCLUSION

Planning estimates of dry deposition falling directly to the Buffalo River AOC range from 8,975 to 18,205 kg/yr. There is close agreement between the measured and calculated loading, considering the calculated loading (lower value) does not include all of the larger particles and the Aerochem Metrics sampler has a high collection efficiency for large particles (Feely et al., 1985). This apparent agreement between the two independent methods reinforces the data credibility. Even though the direct measure of dry deposition, using an Aerochem Metrics sampler may be viewed in the literature as somewhat simplistic, it is our belief that the deposition loading obtained from the direct measure of dry deposition are superior to the calculated method (given the size cutoff constraints of the latter), or to the application of a simple adjustment "factor" to the wet deposition loading, and suitable for use in planning level estimates.

Table 1. Meteorlogical Conditions for Buffalo, New York

	30 year normal	Study Period 1989-1991
Mean Annual Temperature (°C)	8.7	10.2
Annual Precipitation (cm)	110.6	121.7
Mean Wind Speed (kph)	19.3	18.8
Prevailing Wind Direction	SW	SW

Future research is required to better address the large particles in our calculation of dry deposition, to identify the particle sizes associated with copper, and to develop a better understanding of the impact to the Buffalo River AOC associated with dry deposition loadings to the entire watershed.

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