POLLUTANT ASSOCIATIONS WITH PARTICULATES IN STORMWATER

by

RENEE E. MORQUECHO

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Submitted by Renee E. Morquecho in partial fulfillment of the requirements for the degree of Doctor of Philosophy specializing in Civil Engineering.

Accepted on behalf of the Faculty of the Graduate School by the dissertation committee:

Pauline Johnson, Ph.D.

Derek Williamson, Ph.D.

Shirley E. Clark, Ph.D.

Melinda Lalor, Ph.D.

Robert E. Pitt, Ph.D.
Chairperson

Kenneth J. Fridley, Ph.D.
Department Chairperson

6/9/05
Date

Ronald W. Rogers, Ph.D.
Dean of the Graduate School

7/28/05
Date

LIST OF ABBREVIATIONS AND SYMBOLS

Al	Aluminum
ASV	Anodic Stripping Voltammetry
BOD_5	5-day Biological Oxygen Demand
Ca	Calcium
Cd	Cadmium
CGME	Controlled Growth Mercury Electrode
cm	Centimeter
Co	Cobalt
Cr	Chromium
CSO	Combined Sewer Overflow
Cu	Copper
d	particle diameter
DOC	Dissolved Organic Carbon
EMC	Event Mean Concentration
Fe	Iron
filt.	Filterable
GFAAS	Graphite platform Furnace Atomic Adsorption Spectrometry
H+	Hydrogen ion
HDPE	High density polyethylene

Hg	Mercury
HNO_3	Nitric acid
hr	Hour
IC_{50}	Approximate concentration required for 50% inhibition of bacterial fluorescence.
K	Potassium
KCl	Potassium chloride
kg	Kilogram
L	Liter
LDPE	Low density polyethylene
m	Meter
M	Molar
MDL	Method Detection Limit
Mg	Magnesium
mm	Millimeter
Mn	Manganese
MS4	Municipal Separate Storm Sewer System
mV	Millivolts
N	Nitrogen
na	Not available or too few detectable observations for calculation
Na	Sodium
NaOH	Sodium hydroxide
nd	not detected

Ni	Nickel
NO_3	Nitrate
NPDES	National Pollution Discharge Elimination System
NTU	Nephlometric Turbidity Units
NURP	National Urban Runoff Program
OAS	Osmotic Adjusting Solution
ORP	Ortho-reactive phosphorous
P	Phosphorus
PAH	Polyaromatic Hydrocarbon
part.	Particulate
Pb	Lead
PCB	Polychlorinated biphenyls
PO_4^{3-}	Phosphate ion
sec	Second
Si	Silicon
SPLITT	Split-Flow Thin-Cell
SS	Suspended solids
St.	Street
STORET	STORage and RETrieval database.
TSS	Total suspended Solids
µA	Microamperes
µg	Microgram
µm	Micrometer

USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultraviolet
WIDNR	Wisconsin Department of Natural Resources
Zn	Zinc
<	Less than
>	Greater than
%	Percent

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ABSTRACT

Many studies have identified metals in urban runoff as a major contributor to the degradation of urban streams and rivers. Metals of most concern are copper, cadmium, chromium, lead, mercury, and zinc. Metals in urban runoff can occur as dissolved, colloidal, and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects.

The objectives of these tests were to determine the associations of heavy metals and nutrients with different-sized particulates using cascade sieves and filters. Sequential extraction experiments were also conducted to examine the treatability and other characteristics of the filterable (<0.45 μm) portion of the heavy metals using Chelex-100 resin, UV-light exposure, and Anodic Stripping Voltammetry (ASV).

A decrease in concentration with sequential removal of particulates was obtained for total solids, turbidity, chemical oxygen demand, and total phosphorus. Total solids, turbidity, and total phosphorus were reduced by more than 50% with removal of particulates. Heavy metals were generally found more in the filterable fraction and not greatly removed by reduction in particulates. Less than 50% of Zn, Cu, Cd, or Pb were associated with particulate fraction. New toxicity testing procedures were developed. Results showed that toxicity was not associated with the particulates in these samples.

The use of ASV was also developed to measure the ionic forms of heavy metals in the filterable fractions. Good sensitivity was obtained by using Square Wave Stripping Voltammetry with a 5 minute deposition time. The use of ASV with samples exposed to an ion exchange resin were unsuccessful. Colloidal analysis showed that most of the Zn, Cd, and Pb were not present in the free ionic form, but were bound to the colloids or organic matter whose bonds could be broken by exposure to UV light. Only Cu occurred in mostly the ionic form.

Recommendations for future research include work with the new toxicity test system, decreasing the detection limit of Zn measured by ASV, and developing the use of ASV for samples digested in nitric acid and for those exposed to the Chelex-100 ion exchange resin.

CHAPTER I

LITERATURE REVIEW

1.1 Heavy Metal Pollution of Stormwater

Many studies have identified heavy metals in urban runoff as a major contributor to the degradation of urban streams and rivers (Pitt et al. 1995; Drapper, Tomlinson, and Williams 2000). Metals of most concern are copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), and zinc (Zn). Of these metals, copper and zinc are currently receiving the most attention due to their effects and their occurrence and concentrations in urban runoff. Metals in urban runoff can occur as dissolved, colloidal and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects. If possible, associations of the metals with different particle sizes should also be determined. Finally, to obtain the most meaningful data on either bioavailability or toxicity, it is important that chemical speciation techniques be applied (Florence and Bately 1980). Chemical speciation is the determination of the individual concentrations of the various chemical forms of an element that together makes up the total concentration of that element in a sample. Speciation of metals is dependent upon chemical and physical parameters such as pH, temperature and the presence of ligands and particulates. Depending upon the chemical form of the metal, a water with a high

total metal concentration may be less toxic than another water with a lower total metal concentration (Florence and Batley 1980).

The threat from metals to humans and aquatic life is due to their toxicity, persistence and bioaccumulation (Pitt 2003). It is important to determine the speciation of a metal because of the toxicity of many metals is related to their speciation and valence state. Most metals are essential nutrients for living cells, but only in small quantities. When metals are present in excess, they can become cumulative toxins. Some metals, such as mercury and lead, have no nutritional value and are considered dangerous, even in small concentrations.

1.2 Characteristics of Stormwater Affecting Treatability of Heavy Metals

1.2.1 Dissolved and Particulate Forms of Pollutants

Table 1 summarizes the filterable fraction of heavy metals found in stormwater runoff sheet flows from many urban areas (Pitt et al. 1995). Constituents that are mostly in filterable forms have a greater potential of affecting groundwater and are more difficult to control using conventional stormwater control practices that mostly rely on sedimentation and filtration principles. Luckily, most of the metals are associated with the non-filterable (suspended solids) fraction of stormwater. Likely exceptions include zinc which may be mostly found in the filtered sample portions. However, dry weather flows in storm drainage tend to have much more of the heavy metals associated with filtered sample fractions.