# Changes of Multiple Metal Accumulation (MMA) in New Orleans Soil: Preliminary Evaluation of Differences between Survey I (1992) and Survey II (2000)

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**Abstract:**  Soil metal surveys were conducted in Baltimore, MD (1976-1979), Minnesota (1981-1988) and most recently, New Orleans, LA (1989-present).  The unique characteristic of New Orleans is that it has two surveys; Survey I was completed in 1992 and Survey II was completed in 2000.  This paper seeks to determine if there is a perceptible change in the amount of metals during less than a decade that separated these surveys.  The Survey I collection was 4,026 samples stratified by 283 census tracts. All samples were collected in residential neighborhoods at least one block from a busy street.  The Survey II collection was 5,467 samples stratified by 286 census tracts (plus City Park).  The Survey II collection included busy streets as a category of samples.  For comparison, the busy street category of 1,078 samples was excluded from Survey II for a total of 4,388 samples.  The extraction methods of the two surveys used the same protocol for strength of acid (1 M $HNO_3$), shaker-time (2 hours), and room temperature (~22ºC).  However, Survey II differed in amount of sample used in extraction.  For Surveys I and II, 4.0g and 0.4g were used respectively.  The same ICP-AES was used to measure 8 metals in both surveys.  To evaluate the analytical results of the two methods, reference soi
l samples (n=36) from the Wageningen Evaluating Programs for Analytical Laboratories, International Soil-analytical Exchange (WEPAL; ISE) were used.  The relationship between the 4.0 and 0.4 g results were linear and the Survey I results were adjusted for sample:acid ratio. Further evaluation was done by creating interpolated Multiple Metal Accumulation (MMA) maps based on the median MMA for each census tract. A new map was created by dividing Survey II MMA by Survey I MMA. The ratio indicates increases of soil metals in the inner city and decreases of soil metals in the outlying areas of Metropolitan New Orleans.  Comparing fresh parent alluvium from the Mississippi River with urban soil metal quantities demonstrates that the soils of New Orleans have undergone a massive accumulation of metals.  The preliminary results provide ideas about methods needed to further evaluate the changes between these surveys.

**Key Words:** urban soil, multiple soil metals, changes over time

## Introduction

The New Orleans Soil Surveys were a natural extension of previous urban soil studies first reported for Baltimore, MD [1].  The amount of lead and other metals were measured in 454 garden soils from the entire metropolitan area.  Significant differences that could not be explained by chance (p-values as low as $10^{-23}$) were identified between soils in the inner city compared with those collected from outlying areas of Baltimore [1].

The unpainted brick buildings of Baltimore did not support the hypothesis that lead-based paint alone explained the observed pattern.  We hypothesized that the use of leaded gasoline was a major contributor to the accumulation of lead in Baltimore.  Further research was conducted in Minnesota and the pattern first observed for Baltimore was also found in the Twin Cities [2]. Another major empirical finding in Minnesota was that the amount of soil lead is directly related to size of the city [3, 4].  The larger the size of the city the larger the

amount of soil lead observed in the city. In Louisiana the studies conducted in Baltimore and Minnesota were repeated. Survey I of New Orleans was conducted between 1989 and 1992 and was the basis for several papers [5-13]. A major finding was that soil lead was a better predictor of the prevalence of childhood lead poisoning than age of housing [9, 12]. A soil lead and blood lead survey conducted in Syracuse, New York revealed a similar finding [14]. Survey II was started in 1998 and completed in 2000 and is the basis for papers on multiple metal mixtures [15-18] as well as mixtures of metals and organic hydrocarbons in the urban environment [16, 19, 20]. The purpose of this paper is to evaluate the differences between the New Orleans surveys that were separated by less than a decade. The main question is whether or not the two surveys show a perceptible change in the amount of metals accumulated in New Orleans.

## Methods

### Sample Collection

All soil samples were collected from the top 2.5 cm of the soil. Most aspects of the soil surveys were the same. The differences in treatment are described below:

### Survey I

The 1980 Census Tracts were used to stratify the samples (N = 283). Maps were prepared by hand from a New Orleans street map marking the boundaries of each census tract prior to conducting the field collection. In the field, wherever possible 15 samples per census tract were collected according to the following scheme. All samples were collected at least one block from a busy street and away from street corners. Ten samples were collected within 1 m of the street (street side), 3 samples, each matched with street side samples, were collected within 1 m of house sides (foundation), and 2 samples were collected from vacant land or parks as far as possible from streets and house sides (open space samples). The total number of samples collected for Survey I was 4,026. Soil extractions were prepared using 4.0 g of soil with 20 ml trace metal grade 1M HNO3.

### Survey II

The soil samples were stratified by 1990 Census Tracts (N = 286) plus City Park. Wherever possible, 19 samples per census tract were collected. Sampling was conducted by using U.S. Census Bureau TIGER 95 maps as a guide. Ten samples were collected within 1 m of the street (street side), 4 samples collected within 1 m of busy streets (busy street side), 3 samples, each matched with street side samples, were collected within 1 m of house sides (foundation), and 2 samples were collected from vacant land or parks as far as possible from streets and house sides (open space). The total number of samples collected for Survey II was 5,467. To compare the two surveys the busy street samples collected in Survey II were excluded as a sample category. The busy street category of 1,072 samples was removed and the

total number of 4,388 soil samples was used in this study. Soil extractions were prepared with 0.4 g of soil and 20 ml trace metal grade 1M HNO3.

### Laboratory Methods

The extraction methods of the two surveys followed the same protocol for acid pH (1 M HNO3) shaker time (2 hours) and room temperature (~ 22 °C). The two surveys differed in amount of sample, 4.0 g (Survey I) compared with 0.4 g (Survey II). ICP-AES techniques were used to measure 8 metals. The soil and acid were shaken for 2 hours in polypropylene cups and then filtered using Fisherbrand P4 paper. The extract was stored in 20 ml polypropylene scintillation vials. The ICP-AES was calibrated with NIST traceable standards and a laboratory reference, run at a rate of 1 per 15 samples. Internal laboratory references included one soil sample from City Park and one high metal sample from the junction of Elysian Fields and Highway 10. Duplicate extractions were included for every 15 samples. Further QA/QC was achieved by participation in the Analytical Products Group, Inc. laboratory proficiency environmental testing program. The same Spectro Analytical Instruments ICP-AES was used in both surveys to analyze for metals.

### Comparison of the 0.4 and 4.0 g methods

The change in extraction occurred after practical experience that indicated that student skills with pipettes were sometimes creating uneven measurements and dilutions. The dilution step was so common with urban soils that we sought to reduce this source of error by changing the amount of soil being extracted. Changing to a 1 to 10 ratio served the purpose of simplifying the extraction by eliminating the dilution step and improving laboratory productivity. For comparison of the relationship between 0.4 and 4.0 g, a group of reference samples were used. The effect of sample preparation methods was investigated with milled and thoroughly mixed soil samples purchased as part of the Wageningen Evaluating Programmes for Analytical Laboratories International Soil-analytical Exchange (WEPAL ISE).
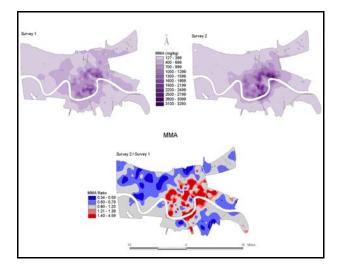
**Table 1**: The following are the WEPAL derived estimated values of parameters A (intercept) and B (slope) in $Y = A + BX$ where Y is predicted value of Survey II sample preparation data and X is observed value of Survey I data for each metal:

| Metal | A | B |
|-------|-------|-------|
| Pb | 5.650 | 0.885 |
| Zn | 1.160 | 1.202 |
| Cd | 0.590 | 1.136 |
| Mn | 0.710 | 1.112 |
| Ni | -0.050 | 1.125 |
| Cu | 3.464 | 1.010 |
| Cr | -0.027 | 1.376 |
| V | -0.384 | 1.285 |

A CIROS CCD ICP-AES (Spectro Analytical Instruments) was used for the metal analysis. The results yielded a linear relationship between the two sample extraction methods. Because of the linearity it was possible to adjust for differences for the method of Survey I to Survey II results. Table 1 shows the results of the WEPAL data that were used to adjust the results of Survey I to match the results of Survey II. The multiple metal accumulation (MMA) refers to the sum of the concentrations of metals in each sample.

*Geographic Information Science (GIS) evaluation*

The following procedures were used to make MMA maps for each survey: First, the median soil MMA was assigned to the centroid of each census tract for both surveys. Second, the centroids with their corresponding MMA value were used to create a floating-point grid by kriging interpolation in Surfer 6.0. Third, the resulting Surfer grid was imported into ArcView GIS 3.3 using the Grid Machine extension. Finally, dividing the grid of Survey II MMA by grid of Survey I MMA created a ratio MMA grid reflecting the differences between the surveys [21, 22, 23].



**Figure 1:** Preliminary MMA maps of New Orleans. Eight metals were measured in soils collected from all residential communities of New Orleans. The sum of the metals in soils is referred to as Multiple Metal Accumulation (MMA). The figure has three MMA maps. The MMA map for Survey I (1992) is shown on the upper left, the MMA map for Survey II (2000) is displayed on the upper right, and the MMA map of the ratio of Survey II/Survey I is shown below. These preliminary maps indicate that there has been an increase in the sum of metals by census tract in the inner city and a decrease in the sum of metals by census tract in the outlying areas of the city. See the text for further discussion.

**Results**

Table 2 shows the results of 8 metals measured and transformed for Survey I, metal results obtained directly from Survey II, and metal results measured in fresh

parent alluvium of the Mississippi River. Comparing Pb in the two surveys, note that the smallest amount of Pb appears below the median in Survey II and that the largest amount of Pb appears in the samples above the median of Survey II. This means that the differences between the lowest and highest amounts of Pb are larger in Survey II. The results for Survey I appear to be attenuated for lower and upper quartiles compared to the results for Survey II. This trend shows up with most of metals in the MMA map presented in Figure 1. Note especially that, with the exception of Mn, fresh alluvium from the Bonnet Carré spillway contains only a fraction of the metals that are found in the city.

**Discussion**

The current soil metals found in Mississippi River Alluvium provides the basis for comparing the amount of metals in parent materials of the Mississippi River Delta and the degree of the metal contamination of the alluvial soils of New Orleans [15]. As shown in Table 2, the Mississippi River Alluvium compared with Survey I and II soils shows a difference of median MMA by a factor 2.6-2.9. Using the Bonnet Carré Spillway samples as a baseline, the New Orleans soils exhibited the largest amounts of contamination with factors of 26 and 20 for Surveys 1 and 2 for Pb respectively, 13 for Zn, a factor of about 5 for Cu, and a factor of < 5 for Cd, Cr, and Ni. An interesting exception to the pattern is Mn which shows about the same abundance in the fresh alluvium as found in the urban alluvial soils of New Orleans. Reduced Mn is water soluble and flows with ground water to the river where it discharges and oxidizes into an insoluble compound. A biogeochemical mechanism results in the accumulation of Mn in alluvium along the banks of the river [17].

The preliminary results of the two surveys suggest that overall, during the past decade there has been a modest decrease of metals in the soils of New Orleans. The decrease is not uniformly distributed. The major decrease of metals appears in the outlying area of the city while the inner city exhibited a prominent increase of metals. The most substantial increases in the inner city are found in soil Pb and Zn.

Possible reasons for the significant increases in Pb and Zn include: New Orleans is a historic city with old wood homes dating to the 1880's through the 1950's when use of Pb-based paint was prevalent [24]. Zn is also a major constituent of paint [24]. During the 1990's, New Orleans underwent an economic revival accompanied by housing renovation where power sanding was common [24]. Automobile engine wear and tire wear also releases Zn and other metals. The annual average daily traffic (AADT) increased by 4% on U.S. Interstate 10 into New Orleans from 126,500 in 1992 to 131,123 in 2001. Thus, in 2001 each km of the highway results in over 130,000 km vehicle travel each day.

**Table 2:** Results of transformed metals of Survey I, soil metal data for Survey II, and Alluvial Parent Material of the Mississippi River Delta. All metal results are given in mg/kg.

| Survey I | | | | | | | | | Survey II | |
|---|---|---|---|---|---|---|---|---|---|---|
| *Type* | *N* | | | | | | | | *Type* | *N* |
| Street Side | 2,923 | | | | | | | | Street Side | 2,538 |
| Busy Street | NA | | | | | | | | Busy Street | 1,072 |
| Open Space | 286 | | | | | | | | Open Space | 959 |
| Foundation | 802 | | | | | | | | Foundation | 891 |
| Missing | 15 | | | | | | | | Missing | 7 |
| Total | 4,026 | | | | | | | | Total | 5,467 |
| | | | | | | | | | | |
| | | | Survey I | | | | | | | |
| *N = 4011* | *Pb* | *Zn* | *Cd* | *Mn* | *Cr* | *Ni* | *V* | *Cu* | *MMA* | |
| Min | 18 | 5 | 0.1 | 3 | 0.1 | 0.0 | 0.2 | 3 | 38 | |
| 10% | 30 | 32 | 1 | 65 | 1 | 6 | 2 | 7 | 189 | |
| 25% | 53 | 63 | 2 | 94 | 2 | 8 | 3 | 10 | 289 | |
| Median | 134 | 144 | 3 | 136 | 3 | 11 | 4 | 17 | 504 | |
| 75% | 334 | 336 | 6 | 188 | 4 | 14 | 6 | 32 | 950 | |
| 90% | 799 | 781 | 8 | 247 | 7 | 18 | 8 | 58 | 1,908 | |
| Max | 183,588 | 28,235 | 94 | 1,060 | 242 | 2,140 | 34 | 9,889 | 194,702 | |
| | | | | | | | | | | |
| | | | Survey II* | | | | | | | |
| *N = 4388* | *Pb* | *Zn* | *Cd* | *Mn* | *Cr* | *Ni* | *V* | *Cu* | *MMA* | |
| Min | 3 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 6 | |
| 10% | 12 | 32 | 1 | 60 | 1 | 4 | 2 | 5 | 150 | |
| 25% | 32 | 64 | 1 | 88 | 1 | 5 | 3 | 9 | 242 | |
| Median | 100 | 146 | 2 | 134 | 2 | 7 | 4 | 16 | 452 | |
| 75% | 390 | 378 | 4 | 191 | 3 | 10 | 6 | 32 | 1,051 | |
| 90% | 1,225 | 989 | 5 | 247 | 6 | 13 | 8 | 59 | 2,648 | |
| Max | 52,798 | 17,857 | 84 | 1,279 | 157 | 3,152 | 30 | 6,745 | 66,580 | |
| *minus busy streets | | | | | | | | | | |
| | | | Alluvium | | | | | | | |
| *N = 141* | *Pb* | *Zn* | *Cd* | *Mn* | *Cr* | *Ni* | *V* | *Cu* | *MMA* | |
| Min | 0.4 | 6 | 0.4 | 22 | 0.3 | 2 | 0.5 | 0.3 | 35 | |
| 10% | 2 | 7 | 0.5 | 50 | 0.4 | 2 | 0.9 | 0.6 | 64 | |
| 25% | 3 | 8 | 0.7 | 78 | 0.5 | 3 | 1 | 1 | 99 | |
| Median | 5 | 11 | 0.9 | 144 | 0.7 | 4 | 2 | 3 | 173 | |
| 75% | 8 | 17 | 1 | 317 | 1 | 6 | 5 | 7 | 363 | |
| 90% | 12 | 30 | 1 | 503 | 1 | 8 | 8 | 11 | 556 | |
| Max | 23 | 91 | 3 | 874 | 23 | 11 | 11 | 15 | 1,030 | |

This will result in traffic flow of 47,450,000 km (29,466,450 miles) of vehicle travel per km (mile) per year. The material consequences of this quantity of traffic would be very large in terms of the metal released by engine and tire wear per distance travelled. The suburban decreases are not easily understood. There are several possibilities: The suburbs have relatively little traffic flow. The suburbs are relatively new, many of the homes are brick, and they do not have significant surface areas with lead-based paint compared with the old wood buildings of the inner city. Perhaps clean dust from the outlying areas is being deposited into the suburbs whereas contaminated dust originating from the suburbs is being pulled and deposited by the urban heat island into the inner city. This hypothesis is supported by the observation that in three cities, Indianapolis, Syracuse, and New Orleans, children's blood lead is inversely related to seasonal changes of soil moisture indicating that the soil Pb is both a sink and a source of exposure and continuously undergoing deflation and deposition, depending on weather conditions (25).

Perhaps the comparison is biased by the method of analysis. Further study is being conducted to approach the problem with alternative methods for comparing the surveys. First, instead WEPAL ISE samples, analysis of 4.0g and 0.4g extracts is being done on archived soil samples from ten Census Tracts. Increasing the number of samples used to establish the relationship between the two extraction methods may improve the results [22]. In particular, WEPAL ISE soil samples fail to cover the upper range of contamination that is such a prominent characteristic of the soil metal results observed in New Orleans. Second, the analysis is being conducted using the Spectro FME ICP-AES instead of the Spectro CIROS ICP with axial orientation. The older Spectro FME ICP with radial orientation may have different analytical characteristics whereby it attenuates both lower and higher measurements. This characteristic was noted when we switched analysis from AAS to ICP-AES. Improved methods for statistical analysis may also be available to refine the evaluation between the two surveys [26]. Further study using alternative approaches

is being undertaken to evaluate the differences between the soil metal surveys of New Orleans.

In perspective, the issue of metal accumulation in cities is a major concern because exposure to metals may pose an enormous set of chronic problems, especially to children, which ultimately affect the wellbeing of the larger society [18, 27].

**Preliminary Conclusions**

Comparing the fresh alluvial materials of the Mississippi River Delta with the current urban soils shows that the city communities of New Orleans have undergone a massive accumulation of soil metals since the city was first settled. In the 1990's, preliminary results indicate that New Orleans soil Pb and Zn increased significantly in the inner city communities and decreased significantly in the outlying communities. These results are reflected by the MMA map. The preliminary conclusions are under review and other techniques are being used for evaluating the changes in extraction techniques between the surveys, changes in analytical instrumentation in comparing method, and the choice of GIS techniques.

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