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Gerald L. Hoffman, and Robert A. Duce

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# Copper Contamination of Atmospheric Particulate Samples Collected with Gelman Hurricane Air Samplers

## Gerald L. Hoffman[1]

Dept. of Chemistry, University of Hawaii, Honolulu   96822

## Robert A. Duce

Graduate School of Oceanography, University of Rhode Island, Kingston, R.I.   02881

■ Atmospheric particulate samples collected with Gelman Hurricane high-volume air samplers can be seriously contaminated with copper if special precautions are not taken to isolate the filter holder from the pump. This copper contamination can easily be observed when samples are collected in the unpolluted marine atmosphere. The source of the copper contamination is probably brush wear on the copper armature of the pump. Copper contamination may also occur with other types of high-volume samplers used to collect atmospheric particulate matter and may make much of the previous data on atmospheric copper concentrations doubtful.

C ollection of atmospheric particulate matter for trace metal analysis has been accomplished for many years by various types of high-volume (hi vol) samplers. The major user of this sampler type, for collecting particulate matter in urban and nonurban areas of the United States, has been the National Air Sampling Network (USPHS, 1958, 1962, 1965, 1967, 1968). Several U.S. companies manufacture this type of pump for the specific purpose of collecting atmospheric particulate matter on filters. A typical hi vol sampler is the Hurricane (Gelman Instrument Co., Ann Arbor, Mich.).

It has come to our attention that a serious contamination of the filter with copper may occur when particulate matter is collected with Gelman Hurricane samplers. This contamination probably occurs with other types of hi vol samplers as well. Ludwig et al. (1970) have reviewed selected data collected by the NASN for the following elements: Cr, Cu, Fe, Mn, Ni, Pb, Sn, Ti, V, and Zn. Of these elements, only Cu does not show some geographical variation. Furthermore, Cu is the only element that had higher concentrations in nonurban air than in urban air. Ludwig et al. (1970) point out that the high nonurban Cu concentrations are probably due to mining and smelting of ores, as well as re-entrainment of soil particles. However, the average Cu and Fe concentrations reported at the 30 nonurban sites from all over the United States are approximately equal ($\sim$0.2 and 0.3 $\mu g/m^3$, respectively). The average crustal ratio of Cu to Fe is approximately $10^{-3}$ (Mason, 1960). If one makes the conservative assumption that all the Fe in nonurban areas is from the soil and that the effect of local smelting and mining is largely removed in the national nonurban averages, it is apparent that the mean Cu/Fe ratio in the NASN nonurban particles is approximately 1000 times too high to be from crustal material.

## Experimental

**Sampling.** In order to examine the possibility of pump contamination, the following studies were conducted during the summer of 1969. Two sets of samples were collected from a 20-m high tower at Bellows Air Force Station on the windward coast of Oahu, Hawaii. The Gelman Hurricane samplers were modified (i.e., the pump handles and leg supports for the motor were removed) and mounted in wooden shelters. The two sets of samples were obtained with different collection configurations. In one configuration (designated mode *A*) the pump was used in the normal manner recommended by the manufacturer and used by the NASN (i.e., the filter holder was attached directly to the pump). In the second configuration (designated mode *B*), the pump was attached to the filter holder by means of a 10-m length of 5-cm i.d. flexible plastic tubing, thus placing the filter a considerable distance away from the pump. Samples in modes *A* and *B* were not collected simultaneously in this study. The two sets of samples, however, were collected under similar meteorological conditions (i.e., onshore trade winds with similar speed and low precipitation level). Each sample was collected during a period of 24 hr on Delbag Microsorban polystyrene filters, type 99/97. Results of the analyses of these samples for Cu and Na are given in Table I.

A further test of pump contamination was conducted at

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[1] To whom correspondence should be addressed.

| Sample no. | Mode A | | Mode B | |
| --- | --- | --- | --- | --- |
| | Na, $\mu$g/m$^3$ | Cu, $\mu$g/m$^3$ | Na, $\mu$g/m$^3$ | Cu, $\mu$g/m$^3$ |
| 1 | 2.30 ± 0.07 | 0.197 ± 0.006 | 2.94 ± 0.09 | 0.0011 ± 0.0006 |
| 2 | 2.51 ± 0.08 | 0.173 ± 0.005 | 1.95 ± 0.06 | 0.0010 ± 0.0005 |
| 3 | 2.00 ± 0.06 | 0.186 ± 0.006 | 1.48 ± 0.04 | 0.0033 ± 0.0017 |
| 4 | 1.92 ± 0.06 | 0.291 ± 0.009 | 2.00 ± 0.06 | 0.0011 ± 0.0006 |
| 5 | 2.94 ± 0.09 | 0.320 ± 0.010 | 1.32 ± 0.04 | 0.0051 ± 0.0026 |
| 6 | 3.58 ± 0.11 | 0.260 ± 0.008 | 2.25 ± 0.07 | 0.0027 ± 0.0014 |
| 7 | 3.24 ± 0.10 | 0.188 ± 0.006 | 4.45 ± 0.13 | 0.0011 ± 0.0006 |
| 8 | 3.87 ± 0.11 | 0.210 ± 0.006 | 3.53 ± 0.11 | 0.0032 ± 0.0016 |
| Mean | 2.79 ± 0.68 | 0.228 ± 0.054 | 2.49 ± 1.08 | 0.0025 ± 0.0015 |

[a] The uncertainties reported represent only analytical uncertainties and blank corrections.

the top of the tower. While a Gelman Hurricane pump was operated in mode A, two simultaneous Millipore filter samples (47 mm, type EH, with a 0.5-$\mu$ diam pore size) were collected. One Millipore filter holder was located inside the pump shelter (mode A) while the other Millipore filter holder was 2 m to the side of the shelter (mode B). Both Millipore filter holders were connected to one Gelman low-volume vacuum pump (Model no. 25002) by means of a T-joint. This pump was located at the base of the tower, approximately 20 m from either filter holder. Two sets of samples were collected in this manner. These results are given in Table II.

**Analytical.** The Delbag polystyrene samples were dry ashed at 400°–425°C. The particulate matter was dissolved in 5 ml of 30% HCl (ultra pure) and was allowed to stand for 5 hr in a laminar-flow clean bench. Then 2 ml of 65% HNO$_3$ (ultra pure) was added and the mixture was allowed to stand for 3 hr more. This acid solution was diluted to 25 ml and analyzed for Na and Cu by atomic absorption.

The particulate matter on the Millipore filter samples collected on the tower in Hawaii was dissolved in 5 ml of 65% HNO$_3$ (ultra pure) and then diluted to 25 ml with distilled demineralized water. Only Cu was determined in these samples by atomic absorption.

The analyses of all the above samples were performed on a Perkin-Elmer Model 303 atomic absorption unit using Intensitron hollow-cathode single element lamps. All samples collected with Delbag polystyrene filters had <1% blank corrections for Na. Cu blank corrections for Delbag mode A filter samples were <1%, but were as high as 50% for mode B samples. No Cu could be detected in the blank Millipore filters.

*Results and Discussion*

The data in Table I show strong evidence of copper contamination when high-volume samples were collected in mode A. Since these samples were not collected simultaneously, they cannot be compared directly. It is obvious, however, that mode A samples are approximately 100 times higher in Cu than mode B samples. The atmospheric Na concentrations (which are due to airborne sea salt) are not affected significantly by either mode of collection.

In the second study, reported in Table II, Millipore filters inside the shelter (samples 1A and 2A) showed Cu concentrations at least 40 to 50 times those on Millipore filters outside the shelter (samples 1B and 2B).

### Table II. Copper Concentrations for Simultaneous Millipore Filter Samples Collected at Bellows A.F.S. Tower Site, Hawaii[a]

| Sample and mode | Cu, $\mu$g/m$^3$ |
| --- | --- |
| 1A | 0.24 ± 0.02 |
| 1B | <0.006 ± 0.003 |
| 2A | 0.33 ± 0.03 |
| 2B | <0.006 ± 0.003 |

[a] The uncertainties reported represent only analytical uncertainties and blank corrections.

A minimum pump production rate of particulate copper can be calculated from the data in Table I for samples collected in mode A. To make this calculation the following assumptions are necessary: all the copper collected in mode A came from the pump, and the filter collected 100% of all the copper produced by the pump. The results in Table I indicate that the first assumption is probably valid. The second assumption is obviously not valid but is made to estimate the minimum Cu production rate. The average Cu concentration for mode A samples was calculated to be 0.23 $\mu$g/m$^3$. Since the average collection rate was approximately 130 m$^3$/hr, the minimum production rate for copper can be calculated to be 30 $\mu$g/hr for the mode A samples in Table I. The average Cu concentrations reported by Ludwig et al. (1970) were ~0.1 $\mu$g/m$^3$ in urban areas and ~0.2 $\mu$g/m$^3$ in nonurban areas. These copper concentrations are similar to the contaminated copper values given in Table I.

Several Gelman Hurricane pump armatures were visually inspected. The oldest pump (used extensively for over 2 years) had a 3-mm deep and 10-mm wide groove worn in the armature, undoubtedly caused by brush wear. The copper armatures of two other types of hi vol samplers (a Unico Model 500 and a Staplex Type TF1A) were also visually inspected. Both of these pump armatures were also worn considerably where the brushes made contact with the copper. It is probable that brush wear on copper armatures of hi vol samplers is the source of the anomalously high Cu concentrations observed in this study.

Contamination of hi vol samples with copper has probably been overlooked by most workers, since the vast majority of samples is collected in areas with large amounts of industrial activity or a high population density. All Cu values become suspect, however, when hi vol samples collected in the relatively unpolluted marine atmosphere give Cu concentrations similar to those values found for urban samples.

The degree of Cu contamination would depend on several factors: type of hi vol sampler used, use of a shelter in sample collection, and meteorological conditions at the sampling site (e.g., stagnant air could cause higher copper contamination). Gelman Hurricane samplers have also been tested to determine the possibility of sample contamination for the following elements: Fe, Cr, Pb, Mn, Co, Zn, V, Al, Ni, Na, Mg, Ca, K, and Sr. This study was performed by a combination of neutron activation analysis and atomic absorption analysis. No sample contamination by the Gelman Hurricane samplers was found for the elements above.

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# Method for the Storage of Samples for Dissolved Gas Analyses

## W. C. Weimer and G. Fred Lee[1]

Water Chemistry Program, University of Wisconsin, Madison, Wis. 53706

■ A bottle for the storage of water samples prior to analysis for dissolved gas concentrations has been designed to eliminate contact between the sample and the atmosphere. Analyses of water samples for dissolved nitrogen and methane content indicated that the concentrations of these gases remained unchanged during a two-day storage period and that the samples could, potentially, be stored for longer time periods. Precision of the overall sampling and analytical technique was ±5–7%.

Many analyses of dissolved gas concentrations in water samples have been reported since Swinnerton et al. (1962a,b) published their initial work in this area involving the use of a Fisher Model 25 gas partitioner. However, few reports describe the methods of sample collection and storage preceding the actual analysis. Early in the investigation of the dissolved gas content of Lake Mary water (Weimer, 1970), it was found that the method of sample collection and storage greatly affected the reproducibility of dissolved methane concentration measurements. Samples stored in 250-ml, glass-stoppered reagent bottles gave variable results. Generally, succeeding analyses from the same sample bottle indicated decreasing amounts of methane. Because of the poor reproducibility obtained with this storage method, a dissolved gas sampling bottle was designed to eliminate contact of the water sample with the atmosphere after the initial sample collection was completed.

*Experimental*

Analyses for nitrogen and methane dissolved in water samples were performed with a Fisher Model 25 gas par-

[1] To whom correspondence should be addressed.

titioner and a modification of the analytical procedure employed by Swinnerton et al. (1962a,b). This analytical procedure involves: (1) introduction of the water sample into a specially designed gas stripping chamber, (2) removal of the dissolved gases from the water sample by stripping with an inert carrier gas (He was used in this study), (3) separation of the gases from each other through gas–solid chromatography, and (4) analysis of the components of the gas mixture via thermal conductivity measurements. The sample was introduced into this system from the dissolved gas sampling bottle shown in Figure 1. This bottle was designed so that the water sample in it would not be exposed to the atmosphere before completion of the dissolved gas analysis.

Water from a modified Van Dorn sampler (Hydro Products, 1967) was added through the neck of the dissolved gas sampling bottle; three bottle volumes were first allowed to flush through the neck and the stopcock. The stopcock was closed, allowing water to fill completely the neck of the bottle. The plunger was inserted (about 0.5–1 in. into the neck) with the stopcock of the bottle open to expel some of the water from the exit port. The stopcock was then closed.

The dissolved gas sampling bottle was fitted with a male Leur tip at the stopcock. For sample injection, this tip on the bottle was fitted into a female Leur tip (a hypodermic needle) attached to an Aerograph two-position, six-way linear valve that contained six entrance or exit portals. Two were connected to the sample loop (a $^1/_8$-in. o.d. polypropylene tube that could be adjusted to hold any desired water volume), two served as inlet and outlet valves for the sample loop, and the remaining two were connected directly into the gas-flow system. The valve was arranged so that the flow of the carrier gas could be directed through the valve, bypassing the sample loop, or through the sample loop and exit from the valve. This arrangement allowed a fresh sample to be placed into the sample loop after the preceding sample had