ILLINOIS STATE WATER SURVEY
ATMOSPHERIC SCIENCES SECTION


TRACE ELEMENT CHEMISTRY STUDIES


by


Donald F. Gatz
Principal Investigator


TECHNICAL REPORT NO. 7
ILLINOIS PRECIPITATION ENHANCEMENT PROGRAM
PHASE I


June 30, 1973


To


Division of Atmospheric Water Resources Management
Bureau of Reclamation
U. S. Department of Interior


Contract 14-06-D-7197
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ABSTRACT

This work was undertaken to measure background silver in Illinois precipitation in the absence of any known seeding operations in or near Illinois.  The overall rainfall-weighted mean concentration at several stations was 73 ng/liter.  This is somewhat higher than has been found in unseeded precipitation in the western United States, but probably not high enough to preclude identification of silver iodide seeded precipitation, especially if the more sensitive element ratio method is used.

INTRODUCTION

The purpose of this work was to measure "background" concentrations of silver (Ag) in the proposed seeding area, Jefferson and Marion Counties in southern Illinois.  Such an assessment of present conditions is needed 1) as a baseline for comparison against Ag concentrations in precipitation during any future cloud-seeding operations, and 2) to evaluate the feasibility of using the Ag content of precipitation to  identify precipitation treated by seeding material.

Measurements of Ag concentrations in seeded and unseeded precipitation have been reported, primarily for western North America,  by Parungo and Robertson (1969), Cooper and Jolly (1970), Warburton and Young (1972), Woodriff, et al., (1973), and Summers (1972).  These authors found Ag concentrations in unseeded precipitation to be generally less than 200 ng/liter, with seeded samples typically 5 to 50 times higher than unseeded.

EXPERIMENTAL METHODS

Precipitation was collected in precleaned wide-mouth (8.6 cm diameter) polyethylene bottles.  The bottles contained small amounts of sodium
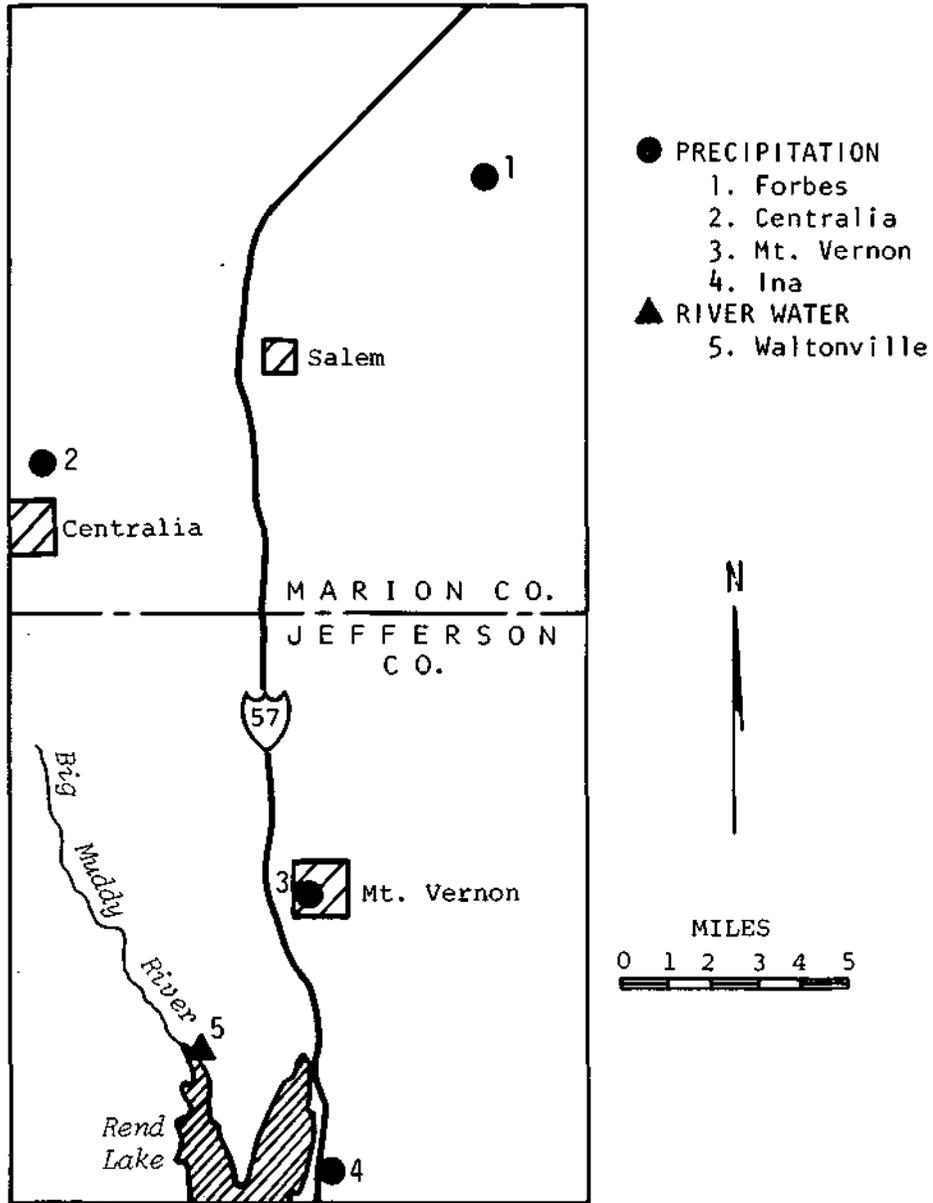
*Figure 1.     Water sampling network.*

thiosulfate crystals which were added to prevent the well-known loss of
Ag to container walls (West, et al., 1967).  Sodium carbonate was also
added to stabilize the thiosulfate.  Complete details of sample stabili-
zation and analysis procedures have been reported by Rattonetti (1973).

Four precipitation sampling sites and one river sampling site (see
map, Fig. 1) began sample collections in November 1972, and these ended
in May 1973.  Precipitation sample bottles were exposed at a height of
approximately 1 m above ground by volunteers when rain appeared imminent or
was forecast with greater than 50% probability.  Sample bottles were
capped following the precipitation and stored in semi-darkness at room
temperature.  River samples were collected at weekly intervals, and after
rains, using weighted 60-ml polyethylene bottles (precleaned and containing
$Na_2S_2O_3$ and $Na_2CO_3$ as before) lowered from a bridge.

Following our established procedures, samples were filtered through
Millipore type EH cellulose acetate membrane filters (0.5 μm pore diameter)
to separate soluble and insoluble components of the precipitation.  The Ag
was expected to be found in the soluble portion;  hence all the soluble
portions of all useable samples were analyzed.  Only enough insoluble portions
to confirm the expectation of Ag solubility were analyzed.

Analysis of the soluble portion consisted of extraction into $CCl_4$ using
dithizone (diphenylthiocarbazone) followed by flameless atomic absorption
spectrophometry.  The insoluble portion treated with $H_2SO_4$ and $H_2O_2$ to
dissolve the filter and other organic material, and HF and HNOg to dissolve
the inorganic particles, then extracted following the same procedure used
on the soluble portion.

Based primarily on replicate analyses , the overall standard error of
an individual analysis is estimated at ±5%.


RESULTS


A summary of sample collections and analytical results is given in
Table 1.  All of the river samples collected were analyzed, but only 82
of 138 precipitation samples were found suitable for analysis.  This was
caused primarily by a lack of sufficient water volume for extraction.  (The
minimum sample volume was 5 ml, which corresponds to 0.86 mm of rainfall.)

Table 1 also shows mean soluble Ag concentrations, both arithmetic and
weighted by rainfall.  Arithmetic means give equal weight to each rainfall,
and thus ordinarily yield higher concentrations , since the lighter rains
commonly contain the highest concentrations.  The rainfall-weighted mean con-
centration gives the true average concentration that would result if all
the individual rains had been accumulated in one collector (without evapo-
ration) and analyzed as a single sample.

Table 1.  Summary of Results—Ag in Precipitation and River
Samples, Jefferson and Marion Counties, Illinois

| Station | Sample Type | Number of Samples Collected | Number of Samples Analyzed | Mean soluble Ag Concentration, ng/liter | |
|---|---|---|---|---|---|
| | | | | Arithmetic | Rainfall-weighted |
| Centralia | Precipitation | 7 | 4 | 37 | 14 |
| Forbes | Precipitation | 35 | 31 | 103 | 98 |
| Ina | Precipitation | 32 | 28 | 99 | 71 |
| Mt. Vernon | Precipitation | 34 | 19 | 80 | 69 |
| TOTAL | Precipitation | 138 | 82 | 93 | 73 |
| Waltonville | River | 24 | 24 | 70 | -- |

Mean concentrations (arithmetic) range from 37 ng/liter at Centralia to
103 ng/liter at Forbes State Park.  Rainfall weighted means range from 14 to
98ing/liter, with the lowest and highest of both means at the same respective
stations.  Because of the small number of samples, however, the results for
Centralia should not be considered representative of that site.

Seasonal Variations

Silver concentrations at each sampling station have been plotted against
dates of sample collection in Fig. 2.  Although sample collection was confined
primarily to winter and spring, no particular seasonal trends are evident,
either in the river water, or at any precipitation sampling station.

Dry Deposition

The precipitation sampling method allows for the possibility that some
Ag found in the precipitation samples may actually have entered the collector
by dry deposition.  If this were the case, one should expect that Ag deposition
would be positively correlated with the duration of sample bottle exposure,
although wind speed would probably also be a strong factor.  Fig. 3 shows Ag
deposition per unit area plotted against sample duration.  The four sampling
stations are identified by separate symbols.  No overall trends are evident
from Fig. 3, but at individual stations the following correlation coefficients
were computed between soluble Ag deposition, $pg/cm^2$, and sample duration, hr.

Centralia   $r = 0.76$ ( 4 samples)

Forbes      $r = -0.04$ (31 samples)

Ina         $r = 0.14$ (28 samples)

Mt. Vernon  $r = 0.41$ (19 samples)

Only the Mt. Vernon correlation is significant at the 10% level.

SOLUBLE Ag CONCENTRATION, ng/liter

FORBES

300
200
100
0

CENTRALIA

200
100
0

MT. VERNON

200
100
0

INA

300
200
100
0

BIG MUDDY RIVER (WALTONVILLE)

300
200
100
0

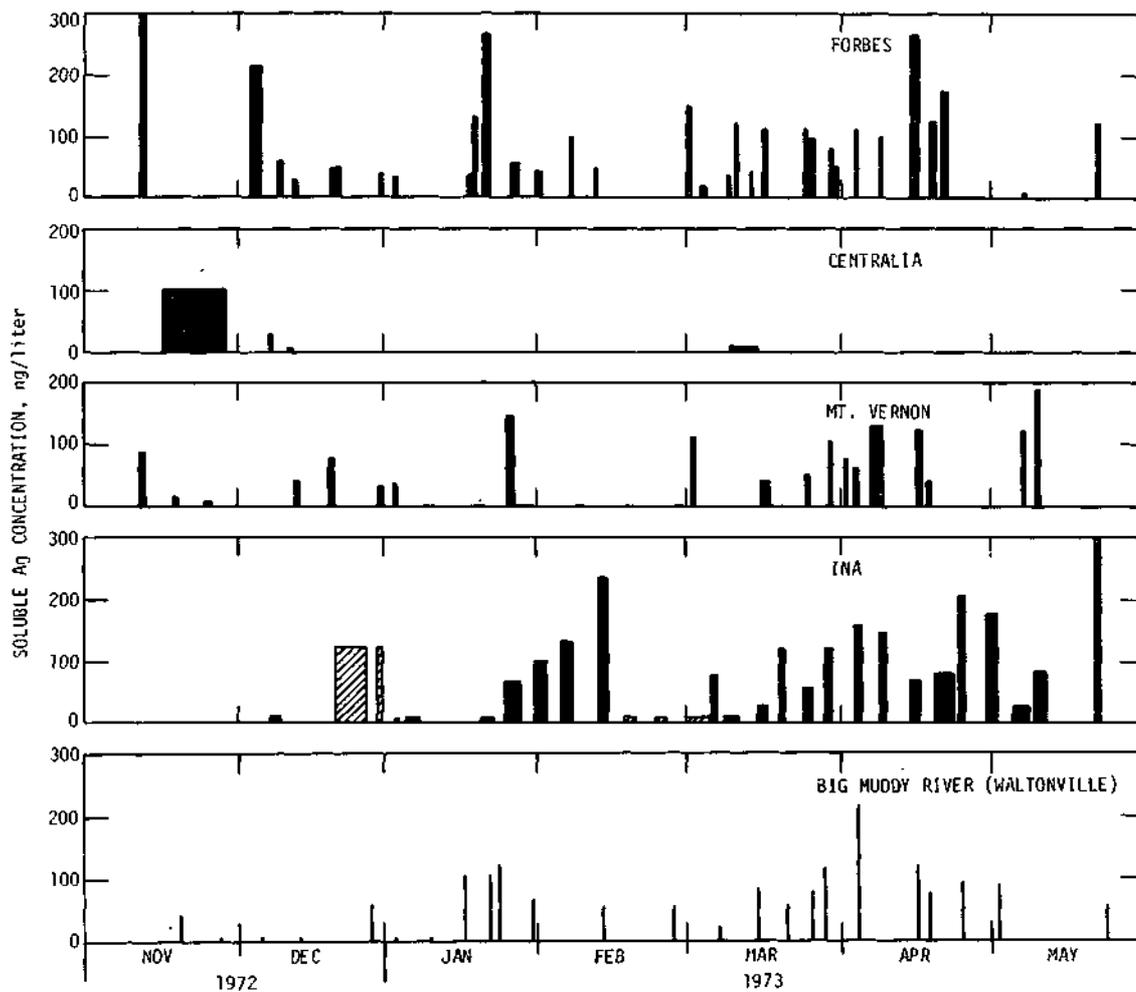NOV    DEC    JAN    FEB    MAR    APR    MAY

1972

1973

*Figure 2. Silver concentrations in relation to sampling date. Adjacent hatched bars indicate separate rain periods in same sample.*
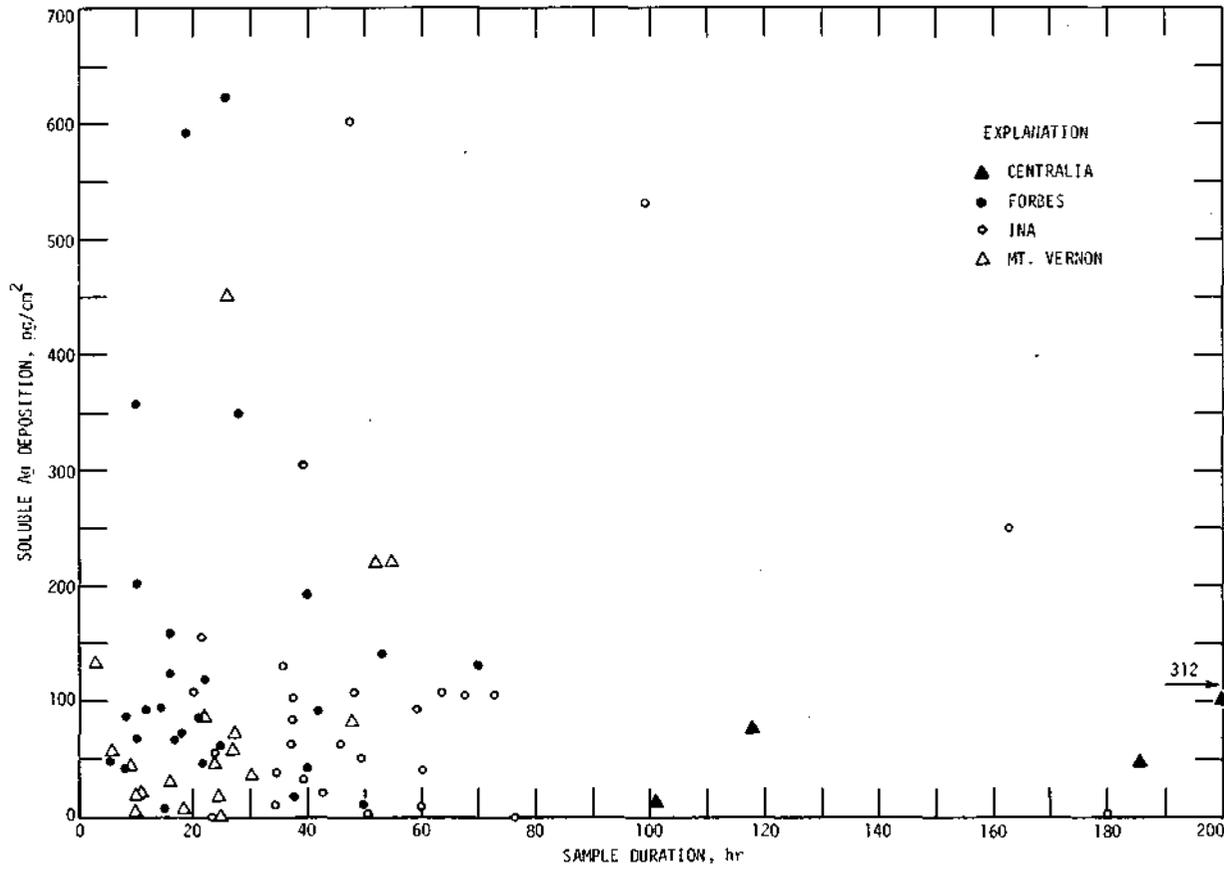
*Figure 3. Soluble stiver deposititon as a function of total length of sampler exposure.*

DISCUSSION


Aside from merely recording the observed Ag concentrations for possible later comparison against seeded precipitation, it is of interest to compare concentrations in Illinois precipitation against similar measurements else-where. In particular, it is useful to compare these results with those obtained under both seeding and non-seeding conditions elsewhere to see whether Ag analysis can be considered as a method of identifying seeded precipitation in Illinois.

Table 2, after Warburton and Young (1972), summarizes Ag concentrations observed in precipitation both during, and in the absence of, seeding opera-tions, primarily in western states. Comparison of these values with those in Table 1 shows that mean Ag concentrations in southern Illinois are generally larger than the no-seed values found elsewhere. The Illinois values even match or exceed median concentrations observed <u>during</u> seeding operations in the Sierra Nevada, Eastern Nevada, and Lake Erie areas.


Table 2. Observed Ag Concentrations in Precipitation (ng/liter), after Warburton and Young (1972)

| Area | No Seeding Operations | | Seeding Operations | | |
| --- | --- | --- | --- | --- | --- |
| | Number of Samples | Mean Concen-tration Observed | Number of Samples | Maximum Concen-tration Observed | Median Concen-tration Observed |
| Sierra Nevada | 169 | 4.2 | 60 | 400 | 20 |
| Eastern Nevada | 25 | 22.0 | 13 | 80 | 55 |
| Bridger Range, Montana | 17 | 36.0 | 35 | 20,000 | 550 |
| Rocky Mountains, Colorado | 48 | 43.0 | 186 | 1,000 | 300 |
| Lake Erie, N.Y. | 40 | 23.0 | 60 | 2,000 | 100 |


These comparisons suggest that it might be difficult to detect seeded Ag in the presence of background Ag in Illinois precipitation. However, it must be stressed that differences in storm type, as well as in seeding methods and rates must be considered very carefully when comparing data on Ag concen-trations in precipitation. Seeding operations in the western United States focus primarily on ground-based seeding of widespread storms, while the program envisioned for Illinois would concentrate on aircraft seeding of convective storms. Silver analyses of precipitation from both seeded and unseeded convective storms in Alberta have been reported by Summers (1972). Summers'.

detection limit for Ag (100-200 ng/liter) was not sufficient to detect silver in most unseeded precipitation samples.  Nevertheless, concentrations up to 4200 ng/liter were detected in convective storms seeded with approximately 1 kg of Ag.

Our experience in releasing lithium and indium tracers into Illinois convective clouds and recovering them in precipitation may also be helpful here.  Tracer injections of the order of 1 kg into thunderstorm updrafts generally result in concentrations of tracer in precipitation between 100 and 1000 ng/liter.  If the results were to be similar for Ag, the seeded Ag could not be positively identified at all times on the basis of Ag concentration. However, our experience with tracers also suggests that element <u>ratios</u> are far more sensitive indicators of the presence of tracer materials than concentration alone.  Thus, if it is possible to identify another element to serve as a tracer for the source of background Ag (perhaps K, or Ti, or Ca if the source is soil dust), then a small amount of seeded Ag might change the Ca/Ag ratio, say, by a factor of 10 or more from that typical of local soils.  The same amount of Ag might change the Ag concentration by a factor of perhaps 2, which would probably be in the normal range of variability of the background Ag.

As an example of the use of elemental ratios, we may compare the ratio Ca/Ag in Southern Illinois precipitation with that expected in local and upwind soils.  For precipitation, we take our overall weighted mean concentration of 73 ng/liter ($0.73 \times 10^{-7}$ g/1) and Junge's (1963) value of approximately 1.5 ppm ($1.5 \times 10^{-3}$ g/1).  The resulting ratio is

$$\frac{Ca}{Ag} = \frac{1.5 \times 10^{-3} \text{ g/1}}{0.73 \times 10^{-7} \text{ g/1}} \approx 2 \times 10^{4}$$

From the results for Ca in surficial materials reported by Shacklette <u>et al</u>. (1971) for Central Illinois and Missouri, we assume an approximate Ca content in soil of 0.4% (4000 ppm).  Unfortunately, Shacklette <u>et al</u>. did not report Ag values, but taking the earth's crust value of 0.1 ppm (Mason, 1952) we obtain the ratio

$$\frac{Ca}{Ag} = \frac{4000 \text{ ppm}}{0.1 \text{ ppm}} = 4 \times 10^{4}$$

Thus, the Ca/Ag ratio in Southern Illinois precipitation is within a factor of 2 of the approximate soil value, indicating that wind blown soil dust could account for the Ag observed in precipitation.

Despite the significant (10% level) correlation between deposition and sample duration at the Mt. Vernon station, there is no strong overall evidence for a large component of dry deposited Ag in the precipitation samples. However, any future sampling program should include the collection of dry deposition samples to check the validity of this indication.

CONCLUSIONS


The overall weighted mean background Ag concentrations in precipitation in Jefferson and Marion Counties of Illinois were found to be 73 ng/liter during the winter and spring of 1973.  These concentrations are somewhat higher than have been found in the absence of seeding operations in other parts of the United States, but probably not so high that Ag from convective cloud seeding operations could not be identified in precipitation.  If necessary, however, it is likely that element ratios, which are subject to considerably less natural variability than concentrations, could be used successfully to identify seeded precipitation.


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