

Possible Roles of Transition Metals in Cloudwater Relative to the Solar Short-Wave Radiation Absorption Anomaly

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Measurements of the absorption of solar short-wave radiation by clouds exceed those predicted by theoretical calculations. In order to understand the roles of minor and trace species in this absorption anomaly, cloudwater samples were collected from individual precipitating clouds and analyzed for trace metals and anionic species. Two generalized approaches were used to assess the direct impact of the absorption of solar short-wave radiation by transition metals and/or their anionic complexes. Additionally, it was suggested that iron and manganese may act as catalyts in the formation of sulfate aerosols which efficiently scatter solar radiation.

Introduction

Variations in the delicate energy balance between the earth (including the lithosphere, hydrosphere, and biosphere) and its atmosphere can influence the world's climate and weather on regional and global scales. Solar energy absorption is one of the prime factors in this influence. Incident solar ultra-violet (UV) radiation with wavelengths shorter than 290nm is absorbed by ozone (O₃), oxygen (O₂), water (H₂O), and carbon dioxide (CO₂). These compounds are also primarily responsible for the absorption of solar radiation at wavelengths longer than 800nm. However, there are no strong absorbers for incoming solar radiation between the wavelengths of 300nm and 800nm referred, to as solar short-wave (SW) radiation. The budget for incoming solar energy to the earth is summarized qualitatively in Table 1¹. Of the 19% of incident solar energy absorbed by the atmosphere, 2% is absorbed by clouds.

Measurements of this solar absorption by clouds, however, show the existence of a solar absorption anomaly in which the measured absorption exceeds that which is predicted by theoretical calculations²⁻⁶. This cloud absorption anomaly has been known for almost four decades. Current explanations for the discrepancies focus primarily on cloud morphological properties (i.e., heterogeneous rather than homogeneous clouds). Uncertainties in cloud optical properties could be explained by morpological differences such as

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population densities, cloud droplet size distribution, and the presence of carbon-based aerosols in cloud droplets. Because absorbed solar radiation supplies the driving force for atmospheric circulation and oceanic heat transport, the consequences of this discrepancy are large in terms of the modeling of both of these systems. Thus, the question arises of what the missing absorber in clouds is, or as specifically addressed here, of whether there is some trace species in atmospheric aerosols, waters, or cloudwater, which causes the anomalous cloud solar absorption.

Table 1. Incoming Solar Energy Budget¹

Percentage Attenuation	Attenuating Medium
50%	Intercepted by clouds (25% back to space, 23% to earth, 2% absorbed by clouds)
17%	absorbed by atmospheric gaseous and particulate substances
12%	Scattered by the air
19%	Absorbed by the earth
2%	Reflected by the earth back to space
100%	Total

In order to clarify the various roles of trace elements in cloudwater physics and chemistry, cloudwater and rainwater samples were collected at Mount Washington, New Hampshire, USE (71 – 91'W, 44 – 16'N) at elevations of 1536m and 610m, respectively. The concentrations of trace inorganic species (trace elements, SO_4^{2-} , NO_3^- , H_3O^+ , and NH_4^+) in the samples were determined. These data were then used to identify their roles in aqueous-phase S(IV) oxidation chemistry, to investigate their functions in an anomalous cloud solar absorption, to chemometrically examine correlations among the measured species, and to measure concentration changes between the cloudwater and the rainwater at high and low elevations. Only the role of trace metals and anions in explaining the solar absorption anomaly will be addressed here.

Experimental

Simultaneous collection of cloudwater and rainwater from individual precipitating clouds was performed at the Lakes of the Clouds Facility of the Appalachian Mountain Club (AMC). The facility is located 1536m above sea level on the southern slope of the summit cone of Mt. the AMC's Pinkham Notch Mountain Resource Center on the eastern slope of Mt. Washington. Samples were collected during the summer months of 1988 through 1990. The ground-level cloudwater collector used was the Appalachian Mountain Club/Worcester Polytechnic Institute (AMC/WPI) Passive Cloudwater Collector. It is made of acrylic plastic and excludes sample contamination by rainwater. The collection principle and collector structure are discussed by Daube *et al.*⁷. Rainwater samples were collected by a Hubbard Brook-type bulk precipitation collector. It consists of an open polyethylene funnel, Tygon tubing, and a 2-L polyethylene container. The container is made inaccessible to the atmosphere by the employment of external water vapor barriers. Prior field tests of this sampler have found no significant sample evaporation from the system over a weekly sampling period under various environmental conditions⁸.

Trace metal concentrations were measured by Instrumental Neutron Activation Analysis (INAA) at the M.I.T. Nuclear Reactor Laboratory research reactor MITR-II. INAA has previously been employed in the analysis of a wide variety of environmental samples, including atmospheric waters. Specific procedures used in INAA and its unique features as an analytical tool are described elsewhere⁹.

Before performing INAA on these cloudwater samples, some preliminary steps were taken to ensure the precision and accuracy of the final data. All sample handling at M.I.T. was performed in a CRP laminar/flow Ultra Clean Work Station (Clean Room Products, Inc., Bay Shore, NY) to minimize contamination by ambient airborne particulate material. All pipette tips, sample bags, sample vials, and Teflon® tweezers used for sample handling were acid-cleaned prior to use. Nitric acid used for cleansing was prepared by 1:10 (V/V) dilution of concentrated nitric acid with deionized water. Since this study was only concerned with dissolved, trace inorganic species, all samples were filtered through Acrodisc® CR PTFE 1 μ m pore-size filters (Gelman Sciences, Ann Arbor, MI) to remove suspended materials from the samples.

The direct application of INAA to water samples for the analysis of trace elements is frequently impractical because many elements of interest are present only at part-per-billion (ppb) levels or lower, and direct irradiation of large enough volumes of water needed to attain the required analytical sensitivity is not feasible. In this study, each sample was freeze-dried in a small (\approx 100 mg), acid-cleaned, polyethylene bag by successive additions of 5mL aliquots of water, with each addition followed by a drying cycle. The freeze-drying unit (Freeze Dryer 3, Model 75200, Labconco Co., Kansas City, MO) was operated at a vacuum of approximately 50 torr at a temperature below 50°C. The freeze-drying process was repeated for 10 or more cycles, depending upon the volume of the samples.

Measurements of the samples' pH and anion concentrations were made at Mount Washington using a standard pH electrode, and by ion chromatography, respectively.

Results and Discussion

The frequency of observation, arithmetic mean (\bar{C}), median, (\bar{C}_m), and geometric mean (\bar{C}_g) concentrations are given in Table 2 for species which were observed in at least 70% of the samples. Based on the magnitudes of their geometric mean concentrations, the species can be classified into three groups. Species listed in Group 1 are the major anions closely related to cloudwater acidity. Group 2 species are major electroneutral balancing cations, Cl^- , and the dominant elemental species in cloudwater. The last group contains the trace elements that have both anthropogenic and crustal origins.

Group 1: SO_4^{2-} , NO_3^- ,

Group 2: NH_4^+ , Cl^- , H_3O^+ , Na, Mg, Al, K, Ca, Fe;

Group 3: Zn, Mn, Sc, V, Cr, As, Br, Sb, La, Sm, and Au.

Two facts lead to the hypothesis that these trace metals dissolved in the cloudwater are responsible for the solar SW radiation absorption anomaly. First, the concentrations of first, series transition metals, such as Fe, Mn, V, and Cr, measured in precipitating cloudwater droplets range from 10^{-5} to 10^{-8} M equivalency (most probably as complexes with dissolved organic material). However, condensing cloudwater droplet diameters are about 10 times larger than non-condensing cumulus cloudwater droplets. Therefore, it would be reasonable to expect that the concentration of transition metals in a cumulus cloudwater droplet may be 1000 times higher than concentration values measured in the precipitating cloudwater droplet. For example, a 10^{-6} M concentration in condensing cloudwater would be equivalent to a 10^{-3} M concentration in cumulus cloudwater.

Second, transition metal cations and their complexes are well known for their strong absorption of

light within the spectral range of solar SW radiation. This is adequately explained by the crystal field theory (CFT) of modern inorganic chemistry. The CFT suggests that energy level splitting of their unfilled d-orbital occurs under the influence of various ligands, such as H₂O, DOM, halogen anions (X-), etc.¹⁰.

Table 2. Summary Table of Inorganic Species Concentrations Determined in Cloudwater

Element	Observed Frequency	\bar{C} (ng/ml)	\bar{C}_m (ng/ml)	\bar{C}_g (ng/ml)
Na	1.0	97	71	62
Mg	0.81	61	38	37
Al	0.96	93	47	49
K	0.93	130	94	87
Ca	0.81	130	50	53
Sc	0.98	1.2	0.14	0.17
V	1.0	2.1	0.91	0.77
Cr	0.94	1.6	0.42	0.47
Mn	1.0	5.8	2.8	2.6
Fe	0.87	71	51	47
Zn	0.98	16	10	10
As	1.0	1.8	0.43	0.45
Br	1.0	5.6	3.4	3.4
Sb	1.0	1.2	0.13	0.16
La	0.89	1.0	0.040	0.049
Sm	0.96	0.99	0.006	0.008
Au	0.98	0.002	0.0003	0.0004
H ₃ O ⁺	1.0	120	54	61
NH ₂ ²⁻	0.81	6500	2300	2300
NO ₃ ⁻	0.81	2500	1100	1100
CL ⁻	0.81	280	130	100

The following sections present two different estimates for the increased solar SW radiation absorption by transition metals and/or their complexes, both of which are general and conceptual approaches. They were adopted with no reference to any particular transition metal or an attending organo-metallic complex.

The first approach is based on the Beer-Lambert Law as shown in the following equation:

$$\log \left(\frac{I_t}{I_o} \right) = \epsilon Cl \quad (1)$$

where I_t and I_o are the transmitted and incident light intensities, respectively, ϵ is the molar absorption coefficient (in $M^{-1} \text{ cm}^{-1}$) of an absorbing chemical species at a particular wavelength, C is its concentration in M unit), and l is the path length of the species, containing solution. The absorbed fraction of incident light $\frac{I_a}{I_o}$ can be expressed as

$$\frac{I_a}{I_o} = 1 - 10^{-\epsilon Cl} \quad (2)$$

where I_a is the absorbed light intensity. Equation 2 may be applied to estimate the fractional absorption of incoming solar SW radiation by possible absorbers in cloudwater droplets so long as relevant parameters are assigned.

A typical, fair-weather cumulus cloud is used for the estimation. Choosing nominal values of 0.5km column height (L), 1m² cross-section, and 1.0g/m³ average liquid water content (LWC), an equivalent 500 g/m² liquid water path (LWP, LWP = LWC × L) is calculated¹¹, the effective liquid water thickness (1) of this cloud column is 0.05cm. The molar absorption coefficient, ϵ , for transition metal complexes in the visible and near-visible spectrum ranges from 1 to 100 M⁻¹ cm⁻¹. Based on the measured concentration range for transition metals in precipitating cloudwater, values of $\epsilon = 10$ and $C = 10^{-3}$ M in cumulus cloudwater are chosen. The fractional absorption of incident light $\frac{I_a}{I_0}$ as calculated by this method is about 0.0012, as shown in Table III, or approximately 0.1% extra absorption by cloudwater containing transition metal complexes.

Table 3. Estimation of Solar Radiation Absorption by Cloudwater

Estimation Approach and Estimated Parameters		Pure Cloudwater	Cloudwater + Transition Metals or Complexes
Beer-Lambert's Law	Fractional Absorption	≈0	0.0012
Mie Scattering Theory	Fractional Absorption	0.0027	0.0065
	Albedo	0.6241	0.6219
	Fractional Transmission	0.3732	0.6219

The second estimation is based on the Mie Scattering Theory, and employs a model which includes multiple scattering events within clouds. Computations for this estimate were run on a Cray main-frame system using a UNIX-based combined program called Mie-Radin. The distribution of cloud droplet sizes was assumed to be a gamma distribution, as is generally adopted in cloud radiative transfer modeling. The effective average radius (r_e) of the cloud droplets was taken as 5 μ m (within the typical 1-10 μ m range for cumulus cloudwater). The thickness used for the cumulus cloud was again 0.5km. The wavelength for incident near-visible solar radiation was chosen to be $\lambda = 375$ nm. This wavelength is near the spectral region where transition metals or their complexes generally have their maximum absorption. The last required input parameter was the extinction coefficient $k(\lambda)$, which consists of the imaginary parts of the spectral complex refractive index ($\hat{n}(\lambda)$):

$$\hat{n}(\lambda) = n(\lambda) - ik(\lambda) \quad (3)$$

For pure cloudwater, $k(\lambda) \approx 10^{-9}$ at a wavelength of $\lambda = 375$ nm. The extinction coefficient $k(\lambda)$ for cloudwater with transition metals or their complexes can be estimated from following relations:

$$k(\lambda) = \frac{\lambda\alpha(\lambda)}{4\pi} \quad (4)$$

and

$$\alpha(\lambda) = 2.303\epsilon C \quad (5)$$

where $\alpha(\lambda)$ is the Lambert absorption coefficient¹². Using the same ϵ and C values as in the first approach, i.e., $\epsilon = 10$ and $C = 10^{-3}$ M, the $k(\lambda)$ was calculated as about 10^{-7} at $\lambda = 375$ nm for cloudwater containing transition metals and/or their organo-metallic complexes.

Calculations using this method show that the fractional absorption value for cloudwater containing transition metals or their complexes is 2.4 times greater than the value for pure cloudwater (Table III), and the results are very sensitive to the concentration of chemical species in cloudwater droplets. In contrast, neither the albedo nor the fractional transmission values change significantly, indicating that total reflection and transmission of clouds are insensitive to the minute or trace level substances present in cloudwater. These properties depend mainly on the overall physical parameters of the cloudwater, such as droplet size distribution.

An additional mechanism by which trace metals, specifically iron and manganese, are dissolved in cloudwater may affect the transmission of solar SW radiation by aiding in the formation of large SO_4^{2-} aerosols. Photo-oxidation of S(IV) within cloudwater forms post-cloud SO_4^{2-} aerosols that are larger and more efficient in scattering solar radiation than those aerosols formed from the oxidation of S(IV) in the gas-phase¹³. Transition metal ions or their complexes can serve as oxidants or catalysts for these oxidation reactions^{14,15}. About 40 to 80% of aqueous-phase oxidation of atmospheric SO_2 occurs in clouds, where the oxidizing species are H_2O_2 , O_3 , and O_2 ¹⁶. The oxidation of SO_2 by O_2 requires the presence of an Fe and/or Mn catalyst, and recent studies have shown that an Fe(III)-organo complex is responsible for the aqueous-phase photochemical formation of H_2O_2 ^{17,18}. In a combined Fe(III)-Mn(II) system, Martin has found the SO_4^{2-} formation rate to be 3-10 times more rapid than expected from the sum of their independent rates¹⁹, and Olmez has found an association between Mn and SO_4^{2-} concentrations in the atmosphere⁹. Laboratory studies also confirm the catalytic synergism between Mn(II) and Fe(III) in S(IV) oxidation^{21,22}.

Summary

Current models of solar SW radiation absorption by clouds, which include only absorption by pure liquid water vapor, and aerosols, do not fully account for SW absorption as it is measured. Furthermore a recent experiment indicates that the absorption and scattering properties of clouds are primarily water-like, thereby reducing the probability that carbon-based aerosols act as absorbers in cloudwater.⁵ The results presented in this study indicate that absorption by transition metals and their complexes dissolved in the cloudwater could be responsible for this discrepancy between measured and predicted solar SW absorption by clouds. Additionally, trace metals present in cloudwater may act as catalysts in the production of large SO_4^{2-} aerosols.

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