AIRTRACETM

FC 769

AN AIRBORNE GEOCHEMICAL TECHNIQUE

GL03836

A. R. BARRINGER

PRE-PRINT OF PAPER PRESENTED AT THE 1ST. WILLIAM T. PECORA MEMORIAL SYMPOSIUM

Applications of remote sensing to mineral and mineral fuel exploration.

October 28 - 31, 1975

Sioux Falls, South Dakota

TO BE PUBLISHED IN 1976 AS A USGS PROFESSIONAL PAPER

AIRTRACETM - AN AIRBORNE GEOCHEMICAL EXPLORATION TECHNIQUE

ABSTRACT

The AIRTRACE system is a new airborne geochemical technique for collecting and analysing atmospheric particulate material and relating this to the underlying geology and ceochemistry. The technique depends upon the existence in the atmosphere of a dispersion of particulate material which covers a broad range of particle sizes. The coarser material above 10 microns diameter tends to be localized to such an extent that if this size fraction is used the effects of man-made pollution are not a problem in most exploration areas. In temperate and tropical regions vegetation is a prime source of the particulates utilized in the system and laboratory research with radioactive tracers as well as field surveys has demonstrated the important role played by vegetation in releasing particulates carrying heavy metals and other trace elements.

Special techniques have been developed for separating particulates of local derivation from the general ambient background by specifically isolating the material in rising thermal plumes. Good results have been obtained in test surveys over orebodies covered by glacial overburden and heavy vegetation. Elements detected include Cu, Zn, Ni, Mn, Fe, Cr, Cd, Al, Ng, Ca, Ti, Si and C. Techniques for measuring uranium are under development. Tests have also been carried out over an oil and gas field and it has been demonstrated that airborne anomalies correspond with the location of the field as well as surface rock and soil anomalies in carbon isotopes and manganese. The equipment is being flown both in helicopters and fixed wing aircraft.

INTRODUCTION

In the conventional approach to geochemical exploration samples of soil, stream sediments, rocks or plant material are gathered on a reconnaissance basis or on a close grid in order to determine the regional or detailed distribution patterns of mineralization. The methods of sampling and analysis have been studied over a period of more than 25 years and have led to the establishment of geochemical exploration as a prime mineral exploration method (Hawkes and Webb 1962; Levenson 1974). Considerable research has also been carried out in hydrocarbon geochemistry, however the techniques of geochemical exploration for oil and gas appear to have found widespread application only in Russia (Kartsev 1954).

In the work reported in this paper investigations have been made of the use of atmospheric particulate geochemistry as an exploration tool for both minerals and hydrocarbons, with the aim of supplementing ground geochemical methods and providing techniques for low cost, large scale airborne reconnaissance.

An early proponent of the use of atmospheric particulates for airborne geochemical applications was Meiss (Meiss 1967 U.S. Patent). Meiss initially employed a filter method for sucking in air and an X-ray analytical technique for analysing particles on the filters. Subsequently he has used a system of towed filaments that are dragged through the air in order to collect particles on their surfaces. These filaments are periodically wiped and the material subsequently analysed. Weiss has referred to the atmospheric aerosols as containing mineral particles and has stated that the method is not applicable where the terrain is covered by heavy vegetation (Weiss 1971).

In the present investigations attempts have been made to develop new particle collection techniques that are capable of separating and collecting particles that have risen from underlying terrain and rejecting particles that have travelled substantial distances laterally. Investigations have also been carried out on the contribution of vegetation to the generation of meaningful geochemical responses in the atmosphere and in addition there has been substantial analytical chemical research to develop appropriate methods for use in atmospheric geochemistry.

SOURCES OF ATMOSPHERIC PARTICULATES AND AEROSOLS

The sources of atmospheric particulates and aerosols are both man-made (anthropogenic) and natural, the former being a source of interference in airborne geochemical studies. Anthropogenic pollutant sources associated with urban and industrial areas generate very high loadings of atmospheric particulates, the effects of which tend to be localized in the giant particle sizes (plus 10 micron), but can carry great distances under some meteorological conditions in the small particle size range. In urban environments the mean residence time in the atmosphere of sub-micron particles in the absence of precipitation is in the order of 100 to 1000 hours whereas particles in the range of 1 to 10 microns have residence times on the order of 10 to 100 hours (Esmen and Corn 1971). Pollutant particles of greater than 10 microns diameter_will therefore have mean residence times of less than 10 hours and will be generally localized to the vicinity of urban and industrial areas. Studies of easily recognized carbon and flyash spherules over the North Atlantic, confirm that these pollutant particles do not exceed 6 microns in diameter over open ocean and reach larger sizes in only a very small percentage of the total mass of particulates in ocean areas close to pollutant sources such as the Bay of Maine (Parkin, Phillips and Sullivan 1970). It has been estimated that the mean residence time of particles in the lower troposphere is about four days (Poet, Moore and Martell 1972) and it is therefore clear that in the absence of precipitation there can be widespread migration of the mean particulate burden over distances that can on occasion amount to hundreds of miles or more. The fine particle component is the fraction that migrates and it is this fraction which contains the highest concentration of trace metals (Lee, Patterson and Wagman 1967). Approximately 45% of the mass of particles in non-urban air close to the ground lies in the size range above 10 microns diameter (Noll and Pilat 1971) and it is essential to consider only this size range if the effects of urban and industrial pollution are to be minimized when studying the atmospheric geochemistry of non-urban areas.

The existence of high concentrations of heavy metals in atmospheric particulates is observed even in regions remote from civilization (Rahn and Winchester 1971) and this is frequently cited as evidence of an all pervading influence of anthropogenic pollution. However, the presence of high concentrations of heavy metals in atmospheric particulates is by no means a proven indicator of the influence of pollution, since it has been found that particulates rich in heavy metals can be released from vegetation by a phenomena that parallels the release of water by transpiration (Barber, Beauford and Barringer 1975). Once again the effects of large scale migration of particulates from vegetation sources can be minimized by considering only particles of greater than 10 microns diameter. The release of heavy metals from vegetation and particle localization will be dealt with in greater detail later.

Additional natural terrestrial sources of particulates and aerosols include the weathering of geological materials to produce soil particulates at the surface; the effects of wind erosion (Hilst and Hickola 1959); the formation of aerosol particulates derived from naturally occurring hydrocarbons produced by plants (Went 1964; 1967); the generation of condensation aerosols by homogeneous gas reactions (Walter 1973); the formation of condensation nuclei by evaporation processes in semi-arid terrains (Twomey 1960) and the production of organic particulate material by the decay, bio-degradation and weathering of plant material.

The oceans also provide a significant source of particulates in the atmosphere. Ocean derived particulates are generated by dehydration of wind blown spray and the bursting of air bubbles entrained by wave action or rain (Woodcock and Gifford 1949; Blanchard and Woodcock 1957; Junge 1972). Particulates of marine origin can contain up to 20% of organic carbon (Hoffman and Duce 1974) and in some areas can contain even higher percentages of organic material. This anomalously high concentration of organic substances in Farine particles is derived from the organic layer on the ocean surface (Garrett 1967; Barger and Garrett 1970). Aerosols generated by bursting bubbles are coated with the organic material (Blanchard 1963; 1964; 1968; 1972; Garrett 1957; Williams 1967). Micro-organisms can also be injected into the atmosphere from the ocean surface by the bubble bursting mechanism (Carlucci and Williams 1965; Blanchard and Syzdek 1972) and airborne marine micro-organisms have been observed by the author and his colleagues as well as others (ZoBell, Claude and Wathews 1939; Stevenson and Collier 1962).

- 2 -

RELEASE OF HEAVY METALS IN PARTICULATE FORM FROM NATURAL SURFACES

The transfer of elements into the atmosphere from vegetation is of special interest in relation to the application of atmospheric geochemical methods in vegetated terrain. Movement of elements into the atmosphere from coniferous trees has been studied (Curtin, King and Mosier 1974) and it has been suggested that volatile exudates are the carrier. It has also been suggested that aerosols may be formed subsequently by agglomeration processes from the volatiles and that they could be used for geochemical sampling purposes. Recent work however with laboratory plants using radioactive zinc 65 and lead 210 as tracers in the plant nutrients has indicated that the initial release takes place in particulate form (Beauford, Barber and Darringer 1975). Some of this work, as yet unpublished, has shown that particulates in small laboratory plants are released dominantly in the sub-micron range. However, in the natural environment particles labelled with radioactive tracers can be released through a size range that is collected through all stages of a multi-stage particles impactor. It is of particular significance to the present study to note that radioactively labelled particles in size ranges up to at least as large as 10 microns in diameter can be released under free convection even in the absence of any wind.

The release of radioactive materials from vegetation that has been sprayed with a solution containing Strontium 89 has been reported and it has been shown that there is a steady loss of radioactivity to the atmosphere (Moorby and Squire 1963). It was suggested that the release might be taking place during the shedding of cuticular waxes but the work was not continued by Moorby and Squire to verify this concept. Cuticular waxes abound on the leaves of most plants in the form of small wax platelets which provide the leaves with a water shedding surface. These platelets are continuously released by abrasion and the rubbing of leaves against each other, and in many instances are able to renew themselves (Eglinton and Hamilton 1967; Martin and Juniper 1970). The use of various solvents on particulates that have been released from vegetation, clearly indicates that they carry only a small wax content and an analysis of the solvent extracts also shows that the waxes do not appear to be the major carrier of metals.

In considering the mechanisms of elemental release from plant surfaces it is important to note that such surfaces contain salts that can be readily leached out by rain or dew (LeClerc and Breazeale 1908; Long, Swell and Tukey 1956; Clement, Jones and Hopper 1971). Whereas most studies are concerned with the leaching of major elements such as K, Na and Cl, the writer and his colleagues have confirmed (to be published) that the heavy metal trace elements such as copper, lead and zinc may also be leached from the surface of leaves with simulated dew or rain. It seems highly probable that the deposition of elements at the surface of leaves is related to the transpiration process in which soil solutions carrying dissolved salts are taken up by the plant roots, but the evaporation from the leaf surfaces is confined to the release of essentially pure water. Some of the salts in upward migration through the plant are utilized in the normal metabolic processes of the plant, however certain elements may be enriched in the vicinity of the leaf surfaces.

A preliminary study is being carried out using newly available equipment on the distributions of 19 elements in soils, plants and vegetative particulates on two sites in the Bancroft area of Ontario, Canada. The region is one of pre-Cambrian geology and one of the sites carries pegmatitic uranium mineralization while the other has only background values in uranium. Analyses of the A and B zone soils, bark, needles and branches of conifers and deciduous trees were studied as well as the particulates generated by this vegetation. Particulates were sampled by filling large plastic bags with vegetation material and collecting the particulate material released by agitating the bags. High volume suction sampling methods were used employing a small cyclone thereby providing sufficient material for precision multielement analysis.

Results are shown in Table 1 and indicate certain interesting features. For example the concentration of many elements in the particulates released from branches and needles is comparable with the concentration of these elements in soil. However, in the case of Fe, Al, Ti and U these elements are substantially depleted in the plants with respect to the soil concentrations but the particulates released by the plants in general are enriched in comparison with the plant concentrations. It seems as if the vegetation minimizes the uptake of these elements and at the same time tends to further eliminate them by shedding enriched particulates. These elements belong to the non-biogenic class that occupy a certain restricted area in a ionic radius/ionic charge diagram (Hutchinson 1943; Brooks 1972).

It will also be observed that uranium mineralization is more readily detected in the particulate material than in the vegetation from which it is derived.

ANALYSES OF SOILS, PLANTS AND VEGETATIVE PARTICULATES (Figures quoted are parts per million dry weight) <u>SAMPLE SITE 1</u> - URANIUM ANOMALY

3 . **7**. -

TABLE I

																		-	
	Cď	Zn	Ni	Cr	Co	Cụ	Ag.	Ио	Mn	Fe*	S٣	Ca -	Mg	ĸ	Na_	A1*	Ti*	P	U*
Soil A zone	9.4	84.2	13.7	64.1	5.5	9.7	1.6	19.7	250	32290	11.1	1695	1689	2000	353.7	10396	1500.8	472.5	4.8
Soil B zone	12.5	52.5	5.9	74.3	7.6	7.9	1.5	27.5	134	43552	5.5	727	1434	2800	375.0	13572	1932.7	503.8	13.5
Conifer Bark	. 0.9	45.9	6:0	6.6	ND	5.0	ND	ND	288	102	17.4	5437	396	1200	פא	109	0.3	310.7	< .1
Conifer Bark Particulates	2.9	35.9	7.3	ND	3.9	3.2	1.6	3.0	176	119	8.7	2746	254	1200	122.2	77	ND	205.3	< .1
Conifer Needles	1.5	74.1	24.2	56.1	1.3	3.2	0.8	3.3	716	314	30.2	10159	768	2800	149.1	199	3.4	600 .0	0.1
Conifer Needle Particulates	8.0	66.1	18.4	13.6	4.4	22.6	4.6	4.3	61	1643	5.0	532	328	800	108.0	605	32.0	382.4	0.6
Deciduous Bark	4.1	122.4	5.6	7.3	1.1	• 11.1	, 1.1	3.9	173	476	47.5	10865	435	3200	207.4	308	24.6	305.3	0.2
Deciduous Bark Particulates	0.4	126.8	ND	9.2	9.6	4.1	3.2	7.7	112	297	34.3	8169	474	3600	11.4	96	0.3	206.1.	<.1
Deciduous Branchos	1.8	58.9	37.1	71.2	6.2	2.3	2.1	4.7	92	204	12.0	2983	184	1200	130.7	ND	ND	127.5	<.1
Deciduous Branch Particulates	14.4	105.1	ND	19.5	8.7	25.8	3.4	5.9	• 117	929	23.3	6340	392	2400	137.8	469	18.5	282.4	1.5
Forest Litter	2.5	79.8	· 8.8	7.3	2.1	7.0	1.0	2.8	737	195	29.1	8804	1157	2400	81.0	135	1.7	236.6	<.1
Forest Litter Particulates.	2.0	70.5	ND	21.8	6.6	11.1	1.9	6.3	433	723	27.7	7595	940	2800	44.0	405	. 29.3	287.0	C. 8
• · · · · ·	•	.•			SAMP.	LE SITE	<u>= 2</u> - 1	BACKGR	OUND S	, ITE,	•							• •	
	-Cd	Zn .	Ni	Cr	Co	Cu	Ag	Mo	Mn	Fe*	Sr	Ca	Mg	K	Na	A1 *	Ti	Ρ	U *
Soil A zone	3.5	35.2	8.5	29.6	3.9	4.1	1.0	: 7.3	134	12445	8.5	1473	1685	1600	348.0	7056	809.1	382.4	0.4
Soil 3 zone	4.3	35.2	16.2	51.4	4.6	3.3	. 0.8	8.9	190	13944	7.6	1158	1596	2000	240.1	8436	868.7	358.8	<.2
Coniferous Bark	1.6	48.8	ND	. אם	ND	4.7	ND	2.4	190	136	25.5	5938	442	1600	СN	173	1.0	295.9	· <.1
Coniferous Eark Particulates	2.6	56.0	5.4	3.3	1.8	5.0	0.4	2.2	°223	187	27.9	6600	464	1600	76.7	185	10.4	304.6	<.1
Conifer Needles	0.9	33.8	ND	ND	3.2	2.9	1.6	10.1	261	76	18.1	4507	525	2400	39.8	135	ND	279.6	<.2
Conifer Needle Particulates	13.7	65.4	12.7	12.6	. 0.5	43.5	2.7	2.8	59	1687	6.6	702	460	ND	144.9	904	60.4	526.7	0.3
Deciduous Bark	4.0	51.0	10.5	7.3	3.4	12.0	2.6	5.5	81	451	72.4	15707	314	4000	71.0	302	8.0	229.0	0.2
Beciduous Bark Particulates	. 0.6	40.2	DN	9.2	7.1	4.7	2.1	r 7.7	98	221	97.4	18027	367	5600	2.3	167	3.0	177.1	0.1
Daciduous Branches	1.6	15.1	10.9	ND	7.8	4.1	2.6	6.7	17	סא	6.2	800	69	1200	161.9	ND	4.4	94.7	* <.2
Deciduous Branch Particulates	15.6	46.7	3.9	22.5	9.8	15.2	3.8	8.3	60	93 7	24.2	4784	342	2400	62.5	411	23.2	195.4	C.4
Forest Litter	3.2	82.0	7.6	DN	3.2	5.9	1.6	4.5	653	102	30.5	9543	1059	2300	275.6	77	1.7	232.8	<.1
Forest Litter Particulates	4.2	61.3	12.4	49.3	7.9	12.0	2.7	8.3	226	4154	23.0	4878	1212	2800	133.5	1979	243.2	318.3	.0.4

A further example of this phenomena was noted in some tests over a small deposit of massive sulphides carrying copper and zinc in the Pre-Cambrian shield of Manitoba. There was a moderate geochemical anomaly in the soils, but conventional bio-geochemistry for copper and zinc in the vegetation gave no indication of the anomaly while there was positive indication in particulates released from vegetation collected in large plastic bags. Further studies are continuing to gather more case histories on the relationship between element concentrations in soil and vegetation and the particulates released by that vegetation.

The role of vegetation is likely to be a very significant factor in any approach to airborne geochemistry, since plant surfaces cover an area many times their area as seen on an aerial photograph. Even in sparsely vegetated terrain, the total plant surface area can represent a sizable proportion of the land/air interface and in temperate regions having moderate to heavy vegetation cover, the interface is dominated by plants. Since this plant cover projects into the boundary layer and is exposed to the micro-climate of circulating convective currents and surface winds, it provides a major contribution to the total particulate burden in vegetated temperate and tropical regions. Furthermore, although some of the organic content of atmospheric particulates in the small size range is derived from the condensation and exidation of plant volatiles such as terpenes (Went 1967), twenty percent or more of the atmospheric particulate burden is normally composed of non-volatile organic material (Heumann, Fonseluis and Wanlman 1959). It is the plus 10 micron fraction of this non-volatile organic material that is the main information carrier for the AIRTRACE system in vegetated regions.

With regard to the sources of inorganic particulate material in the atmosphere in relation to metals and mineralization, it is obvious that weathered and dusty soil surfaces are a prolific source. The geochemistry of some of these surface particulates has been studied and Fig. 1 shows analyses for metal and copper in the top few millimeters of surface dust sampled in a traverse across the nickel orebody at Agnew in Western Australia.

A number of case histories have been studied of surface dust sampled across mineral deposits. Where residual soils are present there is invariably an anomaly which more or less parallels the conventional B zone geochemical anomaly. However, the problem of obtaining a ground sample, in areas of even modest vegetative cover, that is truly representative of airborne particulates is difficult because of the unknown mix between soil surface derived particles and plant surface derived particles. Furthermore even in the case where the soil surface dominates there may be a certain bias imposed by the selective winnowing of particles according to their aerodynamic shape and density.

Heavy metals are also released from the ocean surface by the bubble bursting mechanism due to the trace metal enrichment.in the sea organic surface microlayer (Piotrowicz, Ray, Hoffman and Duce 1972; Szekielda, Kupferman, Klemas and Polis 1972; Barker and Zeitlin 1972). However not all of the trace metals in the marine atmosphere are derived from the ocean surface, since the finer metal carrying particles may originate from land sources (Hoffman, Duce and Hoffman 1972). It is not known whether the trace metal content of surface organic films and of overlying atmospheric particulates will increase in the presence of mineral deposits located beneath shallow water.

METEOROLOGICAL FACTORS AND CONTROLS

When carrying out atmospheric sampling of particulates for airborne geochemical purposes it is essential to ensure that particles being collected are of local derivation and that they have not been transported long distances. This requirement can be met partially by collecting only giant particles of greater than 10 microns diameter, but this in itself is not completely satisfactory since particles can still be collected that have travelled many miles. Special techniques can be used for obtaining a highly localized sample providing that there is strong vertical mixing and the air is vigorously lifting particles from the atmospheric interface to appropriate sampling altitudes. These conditions tend to arise when there is sunshine and adiabatic or super-adiabatic conditions in which the temperature decreases adequately with increasing altitude. Low level inversions in which the normal lapse of the temperature is reversed provide very unfavorable conditions which gives rise to suppression of mixing and the trapping of atmospheric particulates at the inversion layer.

Under the correct survey conditions of sunshine and light winds, convective plumes are formed which are basically non-rotating columns of rising warm air which travel at a lower velocity than the mean wind speed (Taylor 1958; Kaimal, Bussinger 1970; Bussinger 1972). These plumes are tilted in a downwind direction and show maximum vertical flux on their leading edge (Fig. 2). Flights made with a low flying aircraft carrying equipment for measuring temperature fluctuations, vertical acceleration and particulate loading show close correlation between all of these parameters (Fig. 3). Temperatures were measured at two levels, with one sensor in the aircraft and

- 4 -







1sor 2.



the other 100 feet below in a towed bird. These sensors show the extent of vertical structure in the warm thermal peaks and they also indicate that heavy dust loading are carried aloft by these rising vertical thermal structures. It has also been noted that when flights are made over a lake the thermal structures passing with the wind from land to water, tend to smootn out within 1,000 feet of the shoreline. Clusters of dust particles however can retain coherence for distances of at least one mile. This strongly suggests that when pockets of concentrated particulates are closely associated with parcesl of warm air, then these particles have moved only a short distance from their ground source. Support for the concept that the mixing zone contains parcels of particulate matter of predominantly local origin surrounded by particulates from more distant sources is in part provided by the independent observation that the size distribution spectra of particles can vary widely in immediately adjacent air samples (Graedel and Franey 1974).

In the AIRTRACE equipment major emphasis has been placed on the development of methods for separating the particulates in rapidly rising warm air from the particulate burden in the cooler surrounding air. A very satisfactory thermal switching sampling technique has been evolved and this is outlined in the section describing the AIRTRACE airborne equipment.

When the thermal switching and sampling system is used it immediately becomes apparent that there are often pronounced differences in the chemical composition of the adjacent warm and cool air samples. Geochemical anomalies will appear on both sets of data, but there is often a displacement downwind of the anomalies derived from cool air particulates, the displacement being a function of the terrain clearance and wind velocity.

The over-riding need for some means of selectively sampling predominantly local material and rejecting the ambient background becomes obvious if one examines the mechanisms that contribute material to the near surface particulate loadings. There is a small global or continental background that occurs entirely in the minus 10 micron fraction that is derived from fallout of material that has spread in the stratosphere and upper troposphere. There is also a regional background that falls out from the middle troposphere in a size range mostly within the minus 10 micron range. Finally there is a local background generated in the zone of mixing which covers the entire size range up to 100 microns (Fig. 4). The ratio of regional to local background material is strongly controlled by meteorological conditions. In covering the climatic range from stagnant air through moderate mixing to strong mixing, the contribution of local background to the total burden increases drastically (Fig. 5). At the same time the increasing thermal plume activity creates columns of particulates rich in very local material that is sampled by the AIRTRACE equipment as described above.

In addition to day to day variations in mixing conditions there is also a marked diurnal cycle. At night time when convective mixing ceases and still air conditions prevail there is a steady settling of particulates within the lower troposphere. In the morning if the sun is shining and adiabatic or super adiabatic conditions prevail active mixing will commence, building up by mid-morning to high levels. This will raise particles into the air in thermal plumes at velocities which can amount to several metres per second and there will be a continuous increase in the particulate burden. The upward flux of particles during active mixing is much greater than the downward flux since the latter is controlled substantially by sedimentation. By early afternoon even some of the giant particles may have moved considerable distances laterally making it imperative to reject the background material if sampling resolutions of fractions of a mile are to be achieved.

In general the great variability of the conditions which effect the contribution of regional material to the local particulate burden indicates the difficulties of gathering reliable data unless a thermal plume sampling technique is employed.

Turning to the seasonal meteorological constraints placed upon the AIRTRACE system, these depend upon the region of operations. Whereas strong mixing can occur at all times of the year in warm climates, there are areas where much of the winter is unsuitable. However, satisfactory operations have been achieved in Canada at temperatures well below zero fahrenheit with total snow coverage on the ground. It appears that if sunshine is present strong mixing can occur even under these winter conditions and an adequate particulate burden for airborne geochemical surveys can be provided by evergreens and the branches of deciduous vegetation.

The meteorological constraints are of course far less onerous if the AIRTRACE system is used for assessing regional geochemistry. This approach however has only limited applications.

AIRBORNE EQUIPHENT FOR THE AIRTRACE SYSTEM

Particulate collection is carried out in the ALRTRACE system with emertial devices and both cyclones and louvred collectors are employed (Stern 1968). Light weight cyclones can be manufactured to handle several hundred cubic feet of air per minute with good collection efficiency for the requisite particle sizes and louvred collectors can readily handle air volumes of as much as 12,000 thousand cubic feet per minute in an airborne system. In one

. 5 .



AIRCRAFT TRAVERSE AT 15 METRES TERRAIN CLEARANCE FIG.5. EFFECT OF MIXING ACTIVITY ON PARTICULATE LOADING

. . .

embodiment of the system particles are concentrated into a airstream and passed to a device which transfers them into an Argon carrier gas (Barringer 1974). Spectroscopic analysis is then carried out directly in flight on the particles (Barringer 1973(a); 1973(b)). This technique is primarily applied to the measurement of volatiles such as hydrocarbons and mercury.

One of the principle methods used is to impact the particles onto a special tape and to analyse this tape on a post flight basis. The key factor in the system is the aforementioned separation of the incoming stream of particles into rising and falling air components (Barringer 1974). This selection is achieved by the use of fast response thermal detectors at the air scoop inlets in conjunction with a suitable electrical filter, a digital delay line system and solenoid valve switching. Celays are adjusted appropriately so that switching of the particle stream can be accurately tided in relation to the transit delay for the particles passing through the piping of the system. This technique enables very small air parcels to be sampled with a resolution in the order of five feet. Samples are integrated into hot and cold spots on the tape using collection intervals that can be selected at either 5 or 10 seconds.

The effectiveness and precise resolution of this plume sampling technique is a function of the choice of the lower level of particle size collected, the selection of the wave filter functions applied to the temperature sensor, and the sensitivity settings of the thermal switching thresholds. The optimization of these parameters has to be based upon extensive experimentation.

The equipment is usually mounted on a helicopter (Fig. 6) and surveys are carried out at altitudes of 20 or 30 feet above the tree tops. This altitude turns out to be quite practical and is in fact used very commonly in crop spraying operations. Navigation of standard grid surveys at a quarter mile spacing for example, can be achieved in most terrains using conventional navigation from a photo-mosaic, providing that the navigator is skilled. Alternatively electronic navigation can be employed.

The equipment is also being operated in fixed wing installations where surveys are carried out at 200 feet altitude. At this altitude the equipment is well suited for climates where there is very strong mixing such as in South Africa or Australia.

The basic AIRTRACE system is employed in conjunction with other geophysical equipment such as magnetometers in helicopters and an EM system in the case of a fixed wing installation. Inflight monitoring is provided by a multi-channel analog recorder for optical measurements of the particle stream, thermal monitoring etc.

ANALYTICAL SYSTEMS

One of the problems of airborne geochemistry is the very small amount of material that is collected. This makes it necessary to use extremely sensitive analytical techniques. Relatively simple equipment has been developed that provides inflight analysis of adsorbed hydrocarbon and mercury and there are some valuable applications for this approach. However as research on airborne geochemistry has proceeded it has become obvious that a system capable of analysing for a large number of elements would provide the optimum. Specifications for such a system include multi-element capability, very high sensitivity, wide dynamic range and high speed of operation. These requirements are extremely difficult to meet in real time analytical equipment due to the problems of weight, power consumption, complexity and the difficulties of operation and maintenance in an aircraft. It was therefore decided to develop a post-flight analytical system.

In considering possible systems, one approach that at first seems obvious would be the use of X-ray fluorescence analysis. Unfortunately however, even the most advanced of these systems have inadequate sensitivity for the particulate levels that are encountered under some climatic and terrain conditions and furthermore the time taken for sample analysis tends to be long in comparison with the time taken to collect samples.

The solution that has been employed is the use of laser vaporization in conjunction with inductively coupled plasma spectroscopic analysis. These two techniques used together provide a very wide dynamic range, high sensitivity, simultaneous multi-element capability for more than a dozen elements, good linearity and an analysis time of seconds per sample. The operational equipment is capable of functioning in a fully automatic mode and the output is on magnetic tape where it is directly available for use in the preparation of maps by computerized methods.

All readings on the equipment bear a fixed relationship to the mass of each element present on the analytical tape so that any pair of elements can be ratioed. The linearity of the system is demonstrated by Fig. 7 and 8 which show the plots of silicon versus titenium and zinc versus





titanium in a minus 200 mesh soil sample through a 40:1 range of loadings. This degree of precision is duplicated for most of the elements that are recorded and applies to both organic and inorganic matrices. Elements currently being analysed include Cu, Zn, Ni, Cr, Mn, Fe, Ti, Mg, Ca, Na, K, Cd, Si and C. It is hoped to expand this list shortly and to include uranium as well as certain volatile elements.

With regard to data handling, in a simple approach it is possible to plot the ratios of a given element pair such as copper and titanium to look for copper anomalies. However in practice a more sophisticated method is used in which linear regressions are employed to plot the variations of elements such as copper against six other pre-selected elements. In is provides a very satisfactory approach that is giving good results, but a number of other possibilities remain to be tested. These include statistical methods such as factor and cluster analysis.

FIELD RESULTS

An interesting example of the early research work carried out with the system was in a truck mounted version of the equipment which was traversed across a small orebody at Limerick, Ontario. This mineralization was substantially covered by trees with very little exposed soil present. An important feature of the area was the presence of a seepage zone located to one side of the mineralization and which provided a strong cold extractable anomaly in the soils. The truck traverse results, which were obtained with an atomic absorption analytical system, are presented in Fig. 9. It will be noted that the main AIRTRACE anomaly occurs over the seepage zone and that the anomalies were present both in the absolute concentrations of metals in the atmosphere and also in the copper/zinc metal ratio. Since the area is heavily vegetated, it seems almost certain that the anomaly must be mainly bio-geochemical in origin. Bulk collections of aerosol that were subject to sink and float separation in carbon tetrachloride (density 1.60) indicated a very high proportion of organic material being present. This substantiated the bio-geochemical nature of the particulate anomaly.

An example obtained with the current equipment operating under very difficult geochemical conditions is shown in Figs. 10 and 11. This survey was flown over a deposit recently discovered with the INPUT airborne EM system by Selco Kining Corporation and Pickens Mather Incorporated in Brouillan township in Northern Quebec. The deposit is reported to comprise 3 separate zones with an unofficial combined tonnage in excess of 50 million tons. The first zone discovered contains an estimated 35,400,000 tons of ore averaging 0.39% copper, 2.30% zinc, 1.04 oz. silver and 0.009 oz. gold and lies beneath a minimum of 30 feet of glacial overburden. Ore grades in the other two zones are reported to be much higher in copper than the first zone and they occur at greater depths.

The anomaly map was derived by a multiple regression technique carried out on a line by line basis for copper and zinc and in addition spatial filtering was employed to smooth out noise and generate a contoured map.

The area was flown twice, both times under far from ideal weather conditions, since in this region weather conditions are frequently rather poor. Nevertheless, clear cut delineation of an anomalous zone was obtained on both flights in each case somewhat displaced but clearly relating to the location of the airborne EN conductor. These results taken in conjunction with airborne geophysical data provide a definite indication of a drilling target in a region which contains large numbers of barren EM conductors that normally have to be disproven by expensive drilling.

An interesting example of the AIRTRACE system applied to a hydrocarbon target is shown in Fig. 12. This traverse was chosen to cross a geochemical anomaly in carbon isotope ratios identified by T. Donovon of the U.S. Geological Survey (Donovon 1974). The survey covered the Cement field in Oklahoma which is named for the cementation by carbonate of the surface rocks over part of the oilfield. These surface rocks not only show anomalous C^{13}/C^{12} values but also a manganese anomaly. A ground truth survey carried out by collecting fine particulate material from the surface on a traverse line indicated a definite anomaly in the manganese/iron ratio across the oilfield and this was subsequently duplicated in airborne traverses with the AIRTRACE system. Additional tests have been carried out over other oilfields using the AIRTMACE technique for hydrocarbon volatiles (Barringer 1973(a)) and strong highly localized anomalies have been observed - some apparently relating to faults and other structures over oilfields.

~ 7 ×











•

CONTINUING RESEARCH

A programme of research on botanical aspects of airborne geochemistry is continuing in the Botany Department of Imperial College, London under a post-doctorate fellowship agreement with W. Beauford, a post-graduate scholarship with M. Luton and with consulting assistance from J. Barber, Reader in the department. Current work is on the factors affecting the release of particulates from vegetation in situ as related to seasonal and diurnal factors, meteorological conditions, plant growth conditions etc.

Research is also continuing on the atmospheric geochemistry over oilfields and the application of the AIRTRACE techniques to hydrocarbon exploration. On the analytical side, new rethods of fingerprinting using spectro-fluorometric and mass spectrometric approaches, are being studied in the laboratories of Barringer Research.

OPERATIONAL PLANS

The AIRTRACE equipment is now being used operationally in parallel with continuing testing over an increasing range of environments. Certain promising applications remain to be tested, including the use of the system for uranium, coal and kimberlite exploration.

The system is being operated by Minsearch Surveys Limited for minerals and Barringer Hydrocarbons Limited for hydrocarbon exploration. Both companies are joint ventures between Anglo American Corporation and Barringer Research Limited.

CONCLUSIONS

The AIRTRACE system for airborne geochemical prospecting has been evolved over a period of years in a series of parallel research programmes on particulate collection and sampling techniques, meteorological controls near the ground, analytical methods, biogeochemical studies, and ground truth geochemical programmes. Some of the earlier field studies and case history programmes have been made obsolescent by the later development of greatly improved collection methods, thermal switching techniques, multi-element analyses, etc. There is an immediate necessity therefore to gather a great deal more data with all of the new technology. Mevertheless a scientific basis has been established for the development of multi-element particulate anomalies over areas that are partly or completely covered by vegetation as well as in the more obvious regions of soil exposure. Surveys carried out over known mineral deposits in areas covered by glacial overburden and vegetation have yielded positive results. Furthermore the possibilities for atmospheric geochemistry being of value not only for mineral exploration but also for hydrocarbons has been demonstrated and anomalous effects have been seen in both organic and inorganic parameters over known oil and gas fields.

One of the more obvious potential applications of atmospheric geochemical exploration could be in the areas having difficult access such as tropical rain forests. It will be of great interest for example to see the effects of deep tap roots and high transpiration rates on the overlying atmospheric geochemistry.

Some recent preliminary field data indicates that the principles of biogenic enrichments and depletions between plants and soil have a parallel in the enrichment factors between plants and the particulates they release. A full understanding of this phenomena should in the future allow a more fundamental approach to the interpretation of data gathered over vegetated terrain.

ACKNOWLEDGEMENTS

The writer has been associated with a number of colleagues within Barringer Research Ltd who have contributed substantially to the research reported in this paper and to the development of the operational AIRTRACE system. These persons include the following. Geochemical investigations:-P.M. Bradshaw, B. Smee, I. Thompson. Development of operation hardware and electronics:- H. Failes, M. Paul, F. Lanza. Analytical developments:- H. Silvester, F. Abercrombie, H. Zwick. Microbiological research:- A. Hurray. All of the above are members of Barringer Research except as indicated.

The writer is especially indebted to Mr. D. Macourt**who has played a very important role in many phases of the AIRTPACE development programme from its inception.

- 8 -

Research on Botanical and Biological aspects has been carried out in the Botany Department, Imperial College by J. Barber and W. Beauford.

The AIRTRACE development has only been possible through the joint efforts of all of the above together with the combined funding of Barringer Research Ltd., the Anglo American Corporation of Canada and Hudson Bay Mining and Smelting Co. Ltd.

- * M. Failes Formerly Barringer Research Limited now independent Consultant, Toronto.
- ** D. Macourt Independent Consultant, Sydney.

REFERENCES

- Barker, D.R. and Zeitlin, H. (1972). Metal-ion concentrations in sea-surface microlayer and size-separated atmospheric aerosol samples in Hawaii. J. of Geophys. Res. Vol. 27: pp. 5076-5086.
- Barger, W.R. and Garrett, W.D. (1970). Surface active organic material in the marine atmosphere. <u>J. of Geophys. Res. Vol. 75</u>: pp. 4561-4566.
- Barringer, A.R. (1973a). U.S. Patent No. 3759617. Method and Apparatus for Geochemical Surveying.
- Barringer, A.R. (1973b). U.S. Patent No. 3768302. Method and Apparatus for Sensing Substances by Analysis of Adsorbed Matter Associated with Atmospheric Particulates.
- Barringer, A.R. (1974a). U.S. Patent Pending. Method and Apparatus for Collecting atmospheric samples.
- Barringer, A.R. (1974b). Canadian Patent No. 954564. Method and Apparatus for Transferring Particles from one Fluid Stream to Another.
- Barringer, A.R. (1975) U.S. Patent No. 386822. High Resolution Geochemical Prospecting Method and Apparatus.
- Beauford, W., Barber, J. and Barringer, A.R. (1975). Heavy metal release from plants into the atmosphere. <u>Nature 256</u>: pp. 35-37.
- Blanco, A.J. and McIntyre, R.G. (1972). An infra-red spectroscopic view of atmospheric particulates over El Paso, Texas. Atmospheric Environment Vol. 6: pp. 557-562.
- Blanchard, D. and Woodcock, A.H. (1957). Bubble formation and modification in the sea and its neteorological significance. Tellus IX: No. 2, pp. 145-158.
- Blanchard, D. (1963). The electrification of the atmosphere by particles from bubbles in the sea. <u>Prog. in Oceanography Vol. 1:</u> pp. 71-202.
- Blanchard, D.C. (1964). Sea-to-Air transport of surface active material. <u>Science Vol. 146</u>: pp. 396-397.
- Blanchard, D.C. (1968). Surface active organic material on airborne salt particles. <u>Proc. of</u> <u>Int. Conf. on Cloud Physics, Toronto</u>.
- Blanchard, D.C. and Syzdek, L.D. (1970). Kechanism for water to air transfer and concentration of bacteria. Science 170: pp. 626-628.
- Blanchard, D.C. and Syzdek, L.D. (1972). Concentration of bacteria in jet drops from bursting bubbles. J. Ceophys. Res. Vol. 77: pp. 5087-5099.
- Brooks, R.R. (1972). Biobotany and biogeochemistry in mineral exploration. Harper and Row, New York.
- Bussinger, J.A. (1972). Remote Sensing of the Troposphere. U.S. Dept. of Commerce National Oceanic and Atmospheric Admin. (University of Colorado).
- Carlucci, A.F. and Williams, P.M. (1965). Concentration of bacteria from sea water by bubble scavenging. <u>J. Cons. perm. int. Explor. Mer. Vol. 30</u>; pp. 28-33.

- 9 -

- Clement, C.R., Jones, L.H.P. and Hopper, M.J. (1971). The leaching of some elements from herbage plants by simulated rain. Grassland Research Institute, Hurley, Berkshire.
- Curtin, G.C., King, H.D. and Mosier, E.L. (1974). Movement of elements into the atmosphere from coniferous trees in subalpine forests of Colorado and Idaho. <u>J.of Geochem. Exploration</u> <u>Vol. 3</u>: pp. 245-263.
- Donovon, T. (1974). Petroleum microscepage at Cement, Oklahoma: Evidence and Mechanism. The American Association of Petroleum Geologists Bulletin V.58, No. 3, pp. 429-446.
- Eglinton, G. and Hamilton, R.J. (1967). Leaf Epicuticular Waxes. <u>Science Vol. 156</u>: pp. 1322-1335.
- Esmen, N.A. and Corn, M. (1971). Residence time of particles in urban air. <u>Atmospheric</u> Envir. Vol. 5: pp. 571-578.
- Garrett, W.D. (1967). Stabilization of air bubbles at the air-sea interface by surface-active material. I. Sea surface. <u>Deep Sea Research Vol. 14</u>: pp. 661-672.
- Graedel, T.E. and Franey, J.P. (1974). Atmospheric aerosol size spectra: Rapid concentration fluctuations and bimodality. J. of Geophysical Research Vol. 79: pp. 5643-5650.
- Hawkes, H.E. and Webb, J.S. (1962). Geochemistry in mineral exploration. Harpers Geoscience Series.
- Hilst, G.R. and Nickola, P.W. (1959). On the wind erosion of small particles. <u>Bull. of</u> <u>Amer. Meteorological Soc. Vol. 40</u>: pp. 73-77.
- Hoffman, E.J. and Duce, R.A. (1974). The organic carbon content of marine aerosols collected on Bermuda. J. of Geophys. Res: Vol. 79: p. 4474.
- Hoffman, G.L., Duce, R.A. and Hoffman, E.J. (1972). Trace metals in the Hawaiian marine atmosphere. J. of Geophys. Res: Vol. 77: pp. 5322-5329.
- Hutchinson, C.E. (1943). The biogeochemistry of aluminium and of certain related elements. <u>Quart. Rev. Biology Vol.18</u>: pp. 1-29, 129-153, 242-262 and 331-363.
- Junge, C.E. (1972). Our knowledge of the physico-chemistry of aerosols in the undistributed marine environment. J. of Geophys. Res; Vol. 77: pp. 5183-5200.
- Kaimal, J.C. and Businger, J.A. (1970). Case studies of a convective plume and a dust devil. J. of Applied Meteorology Vol. 9: pp. 612-620.

Kartsev, A.A., Tabasaranskii, Z.A., Subbota, M.I. and Mogilevski, G.A. (1954). Geochemical Methods of Prospecting and Exploration for Petroleum and Natural Gas. English Translation edited by Paul A. Witherspoon and William D. Romey. University of California Press.

- LeClerc, J.A. and Breazeale, J.F. (1908). Plant food removed from growing plants by rain or dew. Yearbook of the U.S. Dept. of Agriculture. pp. 389-402.
- Lee, R.E. Jr., Patterson, R.K. and Wagman, J. (1967). Particle size distribution of metal components in urban air. Amer. Chem. Society Meeting.

Levenson, A.A. (1974). Introduction to Exploration Geochemistry. Applied Publishing, Calgary.

- Long, W.G., Swell, D.V. and Tukey, H.B. (1956). Loss of nutrients from foliage by leaching as indicated by radio-isotopes. Science Vol. 27: pp. 1039-1040.
- Nartin, J.T. and Juniper, B.E. (1970). The Cuticles of Plants. St. Martins Press, N.Y.
- Hoorby, J. and Squire, H.H. (1963). The loss of radioactive isotopes from the leaves of plants in dry conditions. Rad. Botany Vol. 3: pp. 163-167.
- Noll, K.E. and Pilat, M.J. (1971). Size Distribution of atmospheric particles. <u>Atmospheric</u> <u>Environment Vol. 5</u>: pp. 527-540.

Neumann, G.H., Fonseluis, S., and Wahlman, L. (1959). Measurements on the content of nonvolatile organic material in atmospheric precipitation. <u>Int. J. Air Pollution Vol. 2</u>. pp. 132-141.

Parkin, D.W., Phillips, D.R. and Sullivan, R.A.L. (1970). Airborne dust collections over the North Atlantic. J. of Geophys. Res. Vol. 75: pp. 1782-1793.

- 10 -

- Piotrowicz, S.R., Ray, B.J., Hoffman, G.L. and Duce, R.A. (1972). Trace metal enrichment in the sea-surface microlayer. <u>J. of Geophys. Res: Vol. 77</u>: pp. 5243-5254.
- Poet, S.E., Moore, H.E. and Martell, E.A. (1972). Lead 210, Bismuth 210, and Polonium 210 in the atmosphere: Accurate ratio measurement and application to aerosol residence time determination. J. of Geophys. Res. Vol. 77: pp. 6515-6527.
- Rahn, K.A. and Winchester, J.W. (1971). Sources of trace elements in aerosols: An approach to clean air. NTIS Report No. COO-1705-9 (U.S. Atomic Energy Commission).
- Stern, A.C. (1968). Source Control by Centrifugal Force and Gravity. Knowlton J. Caplan (author). In: Air Pollution Vol. III, pp. 359-395. Academic Press, N.Y.
- Stevenson, R.E. and Collier, A. (1962). Preliminary observations on the occurrence of airborne marine phytoplankton. Lloydia Vol. 25: pp. 89-93.
- Szekielda, K.M., Kupferman, S.L., Klemas, V. and Polis, D.F. (1972). Element enrichment in organic films and foam associated with aquatic frontal systems. <u>J. Geophys. Res: Vol. 77</u>: pp. 5278-5282.
- Taylor, R.J. (1958). Thermal structures in the lowest layers of the atmosphere. <u>Aust. J. of</u> Phys. Vol. 11: pp. 168-176.
- Twomey, S. (1970). On the nature and origin of natural cloud nuclei. <u>Bull. de L'Observatoire</u> du Puy de Dome Janvier-Mars No. 1: pp. 1-19.
- Walter, H. (1973). Coagulation and size distribution of condensation aerosols. <u>Aerosol Science</u> <u>Vol. 4</u>: pp. 1-15.
- Weiss, O. (1971). Airborne geochemical prospecting. <u>CIM Special Vol. 11</u>: Geochem. Explor. pp. 502-514.
- Weiss, O. U.S. Patent No. 3309518 dated March 1967. Method of aerial prospecting which includes a step of analysing each sample for element content, number and size of particles.
- Kent, F.W. (1967). Formation of aerosol particulates derived from naturally occurring hydrocarbons produced by plants. J. of the Air Pollution Control Assoc. Vol. 17: pp. 579-580.
- Went, F.W. (1954). The nature of Aitken condensation nuclei in the atmosphere. <u>Botany Vol. 51</u>: Proceedings of the National Acad. of Science. pp. 1259-1267.
- Noodcock, A.H. and Gifford, M.M. (1949). Sampling atmospheric sea-salt nuclei over the ocean. J. of Karine Res. Vol. VIII: No. 1-3, pp. 177-197.
- Williams, P.M. (1967). Sea surface chemistry: Organic carbon and inorganic nitrogen and phosphates in surface films and sub-surface waters. Deep Sea Res. Vol. 14: pp. 791-800.
- ZoBell, C.E. and Mathews, H.M. (1939). A qualitative study of the bacterial flora of sea and land breezes. Proc. Natl. Acad. Sci. Vol. 22: pp. 567-572.

CONCENTRATION OF ELEMENTS IN SOILS, PLANTS, AND PLANT PARTICULATES, OVER Zn MINERALIZATION, DEER LAKE, ONTARIO



· · ·

PARTICULATES, OVER Zn MINERALIZATION, DEER LAKE, ONTARIO



ø

TABLE II

AVERAGE CONCENTRATIONS OF METALS AT 7 COLLECTION SITES

IN SOIL, PLANTS AND PLANT PARTICULATES (PPM)

	(1) (2) B Horizon Conifer Branch Pa Soil and Needles C a		(3) Particulates from Conifer Branches and Necdles	(4) Enrichment Soil to Plant	(5) Enrichment Plant to Particulate	(6) Enrichment Particulate to Soil	(7) Soil/Plant/ Particulate Enrichment/ Depletion	
Calculat	ion			(2):(1)	(3) + (2)	(3)÷(1)	(3) (2) ÷ (2) (1)	
Element			•		•			
Fe	38,020	147	7,043	0.004	47.91	0.19 -	12,392	
Al	11,925	239	2,620	0.02	10.96	0.22	547	
Cr	40	2.3	44	0.06	19.13	1.10	332.7	
cđ	11	1.8	67	0.16	37.22	6.09	227.5	
Mo	29	2.4	8	0.08	3.33	0.28	40.28	
Cu	37	10	64	0.27	6.4	1.73	23.68	
Ni	13	6	32	0.33	5,33	1.78	16	
Ag	4.5	0.7	1.5	0.16	2.14	0.33	13.78	
Zn	406	77	131	0.19	1.70	0.32	8.97	
° Co	10	2.4	5.1	0.24	2.13	0.51	8.85	
κ.	2,230	299	336	0.13	1.12	0.15	8.38	
Na	264	102 .	248	0.39	2.43	0.94	6.29	
Mg	2,159	705	1,136	0.33	1.61	0.53	4.93	
Sr	8	13	15	3.25	1.15	1.88	0.71	
P	540	1,017	1,365	1.88	1.34	2.53	0.71	
Mn	375	308	119	0.82	0.39	0.32	0.47	
Ca	1,915	5,796	4,332	3.03	0.75	2.26	0.25	

. . .