Frontier Analysis

TECHNICAL SERVICE RESPONSE NO.: UT001

Subject: Analysis of Soil Samples Related to the Delphos, Kansas November 2, 1971 CE2 Event

Date: August 9, 1999

Requested By: Ted Phillips
Director
C. P. T. R.[1]

Reported By: P. A. Budinger
Analytical Scientist

Background/Objective:

The famous Delphos, Kansas CE2 encounter occurred at approximately 7:00 in the evening on November 2, 1971. 16 year-old Ron Johnson was tending sheep when he saw a mushroom-shaped object approximately nine feet in diameter with multicolored lights covering its surface. The object, about 25 yards away, was hovering about two feet off the ground. The UFO sounded like "an old washing machine which vibrates." When it took off it temporarily blinded Ronald with a bright light from its base. Ron went to get his family, and when they returned the entire family saw the object in the sky.

At the site where the UFO had hovered witnesses saw "a glowing ring on the ground" and luminescence on nearby trees. Ron’s parents experienced numbing effects on touching the ring. One investigator said that the soil "felt strange, like a slick crust, as if the soil was crystallized." On examination the soil was found to be impermeable to water and "dry to a depth of at least one foot". A foul odor has also been reported by some investigators[2].

The objective of this analysis was to build on the initial analysis done by Erol Faruk on the Delphos ring soils in the 1970s[3]. At the very least it is hoped this investigation will be a base case for reference to future analyses. Erol Faruk developed his analytical approach based on his experience as an Organic Chemist. He analyzed these materials using 1970’s technology which has

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[1] The Center for Physical Trace Research
[2] Personal Communication, Ted Phillips.
[3] Erol A. Faruk. *Journal of UFO Studies,* n.s. 1, 1989, 41-65.

advanced dramatically in 20 years. Computerization, new techniques, and instrumentation have advanced the field of analytical sciences to previously unachievable heights. Yet, Faruk's work was outstanding and provided preliminary observations and conjectures regarding unknown residues extracted from the ring soils. My approach to the analysis, as an Analytical Chemist, is different; and there is nothing to contradict his initial observations.

Both ring and control soil samples from this event were located on Thanksgiving Day 1998, and received for analyses on December 7th. Thanks to the wisdom of John Timmerman, the samples were preserved in his attic for many years after closure of the CUFOS Chicago office. Documentation/sample labeling existed attesting to their authenticity, and they were encased in their original tightly closed film containers with no sign of tampering.

Conclusions:

In reading these conclusions it should be emphasized that the soils analyzed were sampled two months after the event. Also the time that transpired before this analysis is 27 years. It is unknown if any changes may have occurred to the samples over this period of time. The following conclusions are based on the results of the current analysis.

1) There has been a definite release of material. This analyst concurs with Erol Faruk in that it was most probably deposited as an aqueous solution. The material, excluding any volatiles such as the water, coats the soil's surface, still imparting the hydrophobic 'effect' noted 27 year's ago. This non-volatile material amounts to approximately 2-3 wt.% of the ring soil. Following is its composition and a rough estimate of the amounts.

RELEASE COMPOSITION
(Non-Volatiles)

	Wt. %
•Humic Substance **-Probably low molecular weight Fulvic Acid**	**85 ±10**
•Calcium Oxalate	**5 ±2**
•Calcium Carbonate	**~1**
•Phosphate	**<0.1**
•Sulfate	**<0.1**
•Sulfide and/or Mercaptan	**<0.01**

2) The humic substance specifically appears to be fulvic acid. It has properties resembling a mull type humus which occurs under conditions of high biological

activities such as under grass vegetation and soils under cultivation. This material coats the soil surface, initially imparting a hydrophobic effect. On water addition to the ring soil, followed by agitation, it solubulizes and the soil readily loses its ‘apparent’ hydrophobic effect. There is speculation that this predominating component is actually the result of decomposition from the original release material. This cannot be confirmed. However, this analyst leans toward the hypothesis that the fulvic acid is originally part of the release. This is based on observations regarding some physical properties when the soils were sampled in 1971, e.g. the apparent hydrophobic ‘effect’ and lighter color of the ring soils. The present day samples still retain these properties.

3) Both calcium oxalate and oxalic acid are known skin and eye irritants and could account for the physical effects suffered by the witnesses. It is suspected that the calcium oxalate found in the ring soil was deposited as free oxalic acid and combined with calcium in the ground.

4) Humic substances in the presence of oxalate derivatives and a suitable catalyst, e.g. hydrogen peroxide, may possibly cause the chemiluminescence (glowing) effect.

5) The presence of sulfide/mercaptan could explain any obnoxious odor which purportedly emanated from the ring soils.

6) The ring soil was not exposed to a physical effect such as high temperature.

7) The analysis neither proves nor rules out a UFO source of the release. The above natural products have many useful properties. Specifically, humates are known for their chelation/bonding to metals and organics. “Earthside” we use them in fertilizer and for removal of toxic metals and organic pollutants. It is natural to assume intelligent extraterrestrial life forms would also use them. One speculation is they are perhaps waste products of a biological process.

8.) A speculation is offered by a colleague (Dr. J. Robert Mooney). It is based on the presence of the high concentration (5%) of oxalic acid. (The following may sound bizarre, yet isn’t the whole UFO phenomena bizarre? It is worth contemplating.) Oxalic acid is a natural product in the soil. However, such a high concentration would not be expected from the usual plant source. Exhaust from a low temperature ionization or combustion engine (whose fuel source was <u>elemental carbon</u>) could leave a high concentration of the acid along with other lower molecular weight acids. Of course the major components from such an engine would be expected to the carbon dioxide and carbon monoxide. These would be lost as gases. The acids would concentrate in the soil beneath the exhaust. Use of elemental carbon, as a fuel, seems very reasonable as it is safely transportable and contains a high energy density. It is recommended that future ring sites be carefully assayed for oxalic acid and other low molecular weight acetic components[4].

9.) Finally, others have countered that the release represents the products of “well seasoned barnyard soil”. If this were the case there should be much higher concentrations of elements such as nitrogen, phosphorus, and potassium present. Also there should be evidence of significant amounts of other components such as urea, uric acid, and ammonium components, which are typical of animal waste and its decomposition products. These are not detected. Only the fulvic acid predominates.

<u>Procedure</u>:

Samples: Six Delphos soil samples were received in a 4 x 4 x 2” box containing a 1971 Missouri road map fragment as packing. They were in tightly sealed, and apparently undisturbed, gray Kodak film canisters with black tops. The sample identifications follow:

- Ring Sample A-2, Surface to ½ inch, taken 1/11/72 (15.1 g)
- Ring Sample C-3, Surface to ½ inch (15.9 g)
- Ring Sample D-3 Surface to ½ inch (14.0 g)
- Control Sample Center Surface to ½ inch (23.1 g)
- Control Sample A-9, Surface to ½ inch (21.4 g)
- Control Sample C-8, Surface to ½ inch (23.7 g)

The “as received” ring soils and control soils were analyzed using a battery of tests which includes most of the analytical “alphabet”. These include the following: EDX (Energy Dispersive X-ray) elemental analysis; %C, %H, %N; XPS (X-ray Photoelectron Spectroscopy); XRD (X-ray Diffraction); FT-IR (Fourier Transform - Infrared) analysis; SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-ray); headspace GC/MS (Gas Chromatography/Mass Spectrometry).

Aqueous[5] extractions of the soils were done quantitatively. The following tests were done on the extracts: FT-IR; ^{1}H NMR (Proton Nuclear Magnetic Resonance)[6]; %C, %H, %N; IC (Ion Chromatography); UV (Ultraviolet Spectroscopy); SEM/EDX. GC/MS analysis was attempted on the extracts, but

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[4] There is not enough of the currently analyzed Delphos ring soil available for this analysis. The following procedure is suggested. Perform an acid extraction followed by ion chromatography. Quantitatively, this would yield very accurate amounts of the acids. Acids should then be examined by isotope Mass Spectrometry to determine the C-14 level. Natural product sources of these acids will give the expected values of 15.3 disintegrations/min/gm. Any higher level of C-14 indicates the source was non-terrestrial. Lower levels indicate the source is not of recent biological origin or is not terrestrial.

[5] Nanopure water.

[6] Unfortunately there was not enough extract for additional ^{13}C NMR analysis.

the material hung up on the GC column, attesting to the presence of very highly polar material. GC/MS was additionally done on the headspace above the extract. IR spectroscopic examination was done on a silver nitrate precipitates of the D-3 extract and an aqueous solution of the sodium salt of humic acid (Sigma-Aldrich Catalog No.: H1675-2).

Organic solvent extractions were done using progressively polar solvents (pentane, chloroform, 1:1 acetone:methanol) on the D-3 ring soil and the A-9 control soil. The fractions were examined by FT-IR.

Results:

The results of the individual tests performed on the samples follow. These results are summarized in the conclusions section on page two of this report.

Analyses of the Soils "As Received"

Ring soil samples have been reported to be much lighter in color than the control soils[7]. Subtle color differences are noted for the samples analyzed in this report. Following is a photograph of two ring soils and one control soil in front of their original containers.

Photograph of the two ring soils (C-3, left; A-2, center) and the control soil (C-8, right).

Elemental Data: The elemental data were acquired on the "as received" soils using EDX, %C, %H, %N, XPS, and SEM/EDX. Differences between the ring and control soils are clearly discerned which show a definite release of materials had occurred. The elements attributed to the release are sulfur, calcium, carbon,

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[7] Personal Communication, Ted Phillips.

and nitrogen. Additionally indicated is organic material adsorbed on the surface of the soil. A very small amount of mercaptan and/or sulfide is detected. The detailed data follow.

EDX analysis suggests slightly higher levels of sulfur and calcium. The values are displayed in the following table.

**EDX Elemental Data "As Received" Soils
(Normalized Wt. %)**

Sample	Al	Si	S	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
C-3 Ring	19.4	59.4	**1.3**	8.1	**4.0**	1.4	0.07	0.20	6.0	0.14	0.04
A-2 Ring	19.2	60.5	**0.97**	8.0	**4.0**	1.5	0.12	0.17	5.5	0.14	0.04
D-3 Ring	18.9	57.8	**1.0**	7.5	**4.9**	1.5	0.06	0.16	8.2	0.05	0.05
C-8 Control	18.8	60.6	**0.94**	8.0	**3.8**	1.5	0.08	0.16	5.9	0.15	0.04
Control Center	19.5	60.7	**0.64**	7.6	**3.6**	2.0	0.06	0.14	5.6	0.12	0.03
A-9 Control	19.4	61.4	**0.64**	7.8	**3.6**	1.1	0.09	0.17	5.6	0.12	0.02

The percent carbon, hydrogen and nitrogen analyses suggest a small increase in carbon and nitrogen in the ring soil samples. Carbon/nitrogen atom ratios are also different. They are lower for the ring samples. It is noted that all of the ratios are consistent with those found in surface soils[8]. Following are the values:

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[8] Jerzy Weber, Agricultural University of Wroclaw, Poland Web Site: www.ar.wroc.pl/%7Eweber/azot2.htm

Carbon, Hydrogen, Nitrogen Content (Wt. %)

Sample	C	H	N	C/N Ratio
C-3 Ring	2.59	0.54	0.29	10.4
A-2 Ring	2.46	0.52	0.29	9.9
D-3 Ring	4.01	0.76	0.51	9.2
C-8 Control	2.52	0.54	0.25	11.8
Control Center	2.93	0.58	0.29	11.8
A-9 Control	2.04	0.50	0.21	11.3

At first glance the above does not appear to be earth shaking. However, it is very interesting when viewed in context of the following XPS surface data.

XPS is an excellent technique for looking at the surfaces of materials. It shows a very significant increase in both carbon and nitrogen on the surfaces of all the ring soils which indicates that some of the release is organic. There is an expected decrease in soil elements, i.e. much of the oxygen, magnesium, aluminum, and silicon, because they are coated by the organic material[9]. Specifically for the D-3 ring sample, the data show a higher concentration of phosphorus and calcium. XPS also shows differences in oxidation states of the elements. Further perusal of the carbon data show more of it is associated with oxygen in the ring soils. Evaluation of the sulfur data, which is present in very small amounts, indicates more sulfur is in the form of mercaptans and/or sulfides than in the ring soils. The detailed report can be found in the addendum. Below is the table.

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[9] This had been also noted in a previous SEM analysis done in 1975 at the Oak Ridge National Laboratory.

XPS Data “As Received” Soils (Atomic Concentration)

Sample	**C 1s**	**N 1s**	**O 1s**	**F 1s**	**Mg 1s**	**Al 2p**	**Si 2p**	**P 2p**	**K 2p**	**Ca 2p**	**Fe 2p**	**S 2 SH/SC**	**SO_x**
•C-3 Ring	**27.8**	**3.4**	48.2	0.1	0.5	4.9	12.7	0.14	0.8	0.6	1.0	0.10	0.15
•A-2 Ring	**29.7**	**3.3**	47.7	0.0	0.6	4.6	11.8	0.14	0.6	0.6	0.9	0.09	0.15
•D-3 Ring	**36.3**	**4.1**	43.0	0.0	0.6	3.8	9.8	**0.29**	0.6	**0.9**	0.9	0.09	0.18
•C-8 Control	**16.5**	**1.7**	56.9	0.1	1.1	6.0	14.5	0.18	0.9	0.7	1.5	0.05	0.19
•Center Control	**15.1**	**1.3**	57.0	0.1	1.0	6.3	16.0	0.20	0.9	0.7	1.4	0.07	0.21
•A-9 Control	**16.0**	**1.3**	56.2	0.1	1.0	6.5	16.6	0.20	1.0	0.7	1.5	0.06	0.32

Very limited SEM/EDX analysis was done on two samples (D-3 Ring, and A-9 Control)[10]. Mostly soil minerals were observed. The data did indicate the ring soil contained more particulates suggestive of calcium carbonate than the control soil.

Molecular Information: The analysis done on the “as received” soils for molecular identification include FT-IR, XRD, and Headspace GC/MS analyses. Information imparted by these techniques shows the release material contains calcium oxalate, calcium carbonate and a humic substance. It is also noted that the ring soil has not been exposed to heat. Details of each test follow.

Extensive FT-IR examination was done on the total soils and individual particulates. Expectedly, infrared analysis of the “as received” soil samples shows predominant silicate absorption (mostly quartz type) from the soil for both the control and ring samples. However, there are weaker bands noted in the ring samples (between 1700 - 1300 cm^{-1}) which are not present in the controls. These are enhanced in difference spectra generated between the spectra of the ring soils versus the control soils. They are indicated to belong to materials such as calcium oxalate, carboxylic acid (chelated and/or ionic form) containing component, and possibly calcium carbonate. The carboxylic acid component is mostly part of the humic substance identified in later tests (see aqueous extracts). Figures 1a, 1b, and 1c are representative spectra of a ring soil, a control soil, and a difference spectrum.

Numerous infrared spectra were also obtained from particulates isolated from the ring and control soils. More different types of particulates were noted in the ring soils. As above, calcium oxalate is found to be unique to the ring samples and usually found as a white ‘fibrous appearing’ stratum infused in the soil

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[10] The instrument suffered down time and other work prevailed.

lumps. Calcium carbonate is also in higher amounts, especially in the D3 ring soil. (In the D-3 sample this component was visually apparent as numerous white lumps of approximately 1 mm in size.) Additionally noted was a higher concentration of a humic substance which was specifically characterized in the analysis of the aqueous extracts. The following table summarizes the identifications of all the different types of particulates observed and references the attached labeled infrared spectra.

Sample Particulates	Figure	Identification[11]
•D-3 Ring		
Light Tan	2a	Calcium Oxalate; Residual Soil Mineral (Quartz); Carbonate and/or Humic Substance.
Black	2b	Insect Droppings (Protein Amide Material); Residual Quartz.
Light Brown Cylindrical	2c	Quartz; Protein Amide Material (Possible Insect Droppings); Possible Calcium Oxalate.
Brown Fibrous Material	3a	Calcium Oxalate; Residual Soil Mineral (Quartz); Carbonate and/or Humic Substance.
White	3b	Quartz; Calcium Oxalate; Carbonate and/or Humic Substance.
Tan	3c	Quartz; Calcium Oxalate; Carbonate and/or Humic Substance.
White Stratum in Lump	4a	Calcium Oxalate.
Colorless Fiber	4b	Polystyrene.
Light Brown Stratum in Lump	4c	Celluloidal Material (Plant Origin - Probably Wood Fragment).
Black Flat	5a	Celluloidal Material (Wood Fragment); Quartz.
White	5b	Calcium Carbonate, $Ca(CO_3)_2$.
Sample Particulates	**Figure**	**Identification**
White Fines	5c	Calcium Carbonate, $Ca(CO_3)_2$.

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[11] The first component listed predominates.

More White Particulates	6a	Calcium Carbonate, $Ca(CO_3)_2$; Residual Quartz.
•A-2 Ring		
White Stratum in Lump	6b	Quartz; Calcium Oxalate; Carbonate and/or Humic Substance.
Black	6c	Humic Substance; Celluloidal Material (Plant Origin - Possible Wood).
Off-White	7a	Calcium Oxalate; Residual Soil Mineral (Quartz); Possible Humic Substance.
White	7b	Celluloidal (Wood Fragment).
Light Brown	7c	Quartz; Secondary Amide (Peptide Linkages - Insect Exoskeleton Suspected).
Off-White	8a	Quartz.
White	8b	Quartz; Calcium Oxalate; Carbonate and/or Humic Substance.
White	8c	Celluloidal Material (Plant Origin - Wood Fragment Indicated); Calcium Oxalate.
•C-3 Ring		
White Fibrous	9a	Quartz; Calcium Oxalate; Possible Celluloidal Material (Plant Origin).
White	9b	Celluloidal Material (Plant Origin); Calcium Oxalate; Quartz.
Brown Material Inside Tiny Pod	9c	Quartz.
Black	10a	Humic Substance; Quartz; Possible Celluloidal Material.
Light Tan	10b	Quartz.

Sample Particulates	Figure	Identification
White Fibrous Stratum in Lump	11c	Calcium Oxalate; Quartz.
Amber - Bug Exoskeleton	11a	Secondary Amide (Peptide Linkages - Insect Exoskeleton). Reference Spectrum.
Orange	11b	Cellulose Nitrate; Phthalate Ester (Common Plasticizer).
Black Pod	11c	Amide Material (Noted in Controls).
White Fibrous	12a	Celluloidal Material (Plant Origin - Wood).
Light Brown	12b	Quartz; celluloidal Indications; Possible Calcium Oxalate.
Spherical Light Tan	12c	Silicate (Probable Clay Type).
White Fibrous	13a	Quartz; Calcium Oxalate.
•**Center Control**		
Wood Appearing Fragment	13b	Celluloidal Material (Wood)
Insect Egg Appearing	13c	Barium Calcium Carbonate, $BaCa(CO_3)_2$.
Fine Soil	14a	Silicate Soil Mineral (Microcline)
Black	14b	Quartz; Humic Substance.
Black	14c	Quartz; Humic Substance.
•**C-8 Control**		
Wood Appearing	15a	Celluloidal Material (Wood).
Insect Egg	15b	Barium Calcium Carbonate, $BaCa(CO_3)_2$.
Black	15c	Quartz; Humic Substance.
Sample Particulates	**Figure**	**Identification**

White	16a	Silicate Soil Mineral (Illite).
White	16b	Silicate Soil Mineral (Microcline).
Soil	16c	Quartz; Humic Substance.
Woody	17a	Celluloidal Material (Wood Fragment).
White	17b	Celluloidal Material (Wood Fragment).
Amber	17c	Quartz; Humic Substance; Possible Carbonate.
Gray	18a	Quartz; Possible Carbonate; Possible Humic Substance.
•A-9 Control		
White	18b	Quartz; Barium Calcium Carbonate, $BaCa(CO_3)_2$.
Fine Soil	18c	Quartz; Possible Humic Substance.
Colorless Fiber	19a	Polystyrene.
Light Brown	19b	Quartz; Celluloidal Material; Possible Amide Material.
Black	19c	Oxidized Asphaltic Material; Silicate Mineral.
Brown Bark-Like	20	Celluloidal Material (Wood Fragment); Residual Quartz.

XRD analysis detects and identifies any crystalline material. The data show soil minerals for all samples. These are identified as mostly quartz and smaller amounts of feldspars and clays. No significant differences between the ring and control soils are detected which suggests there was no exposure to physical effects such as heat. If that was the scenario, the clays in the ring soils would have changed, i.e. they would have been dehydroxylated. Additionally, there would have been alterations to the feldspars[12] and quartz[13]. The diffraction patterns are displayed in Figures 21 - 26.

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[12] C. S. Hurlbut, Jr. “Dana’s Manual of Mineralogy”, 17th Edition, John Wiley & Sons, Inc., New York, 1966, p. 487-490.

[13] L. G. Berry et al, “Mineralogy”, Second Edition, W. H. Freeman and Company, San Francisco, 1983, p130-132.

Headspace GC/MS analysis was done on the air space over the selected soils. This was the first test performed when the tightly sealed sample containers were initially opened. It was an attempt to identify any volatiles which may have originated from the samples, because of purported reports of an odiferous emanation from the samples. No volatiles were detected in the headspace. If present, they may have dispersed over the years.

Aqueous Extracts

The samples were quantitatively extracted with nanopure water. When the water was added round globules of soil floated to the surface showing that it still retained its previously reported hydrophobic nature after all these years[14]. On agitation the soil readily dispersed and the water became clear brown in color. This indicates water soluble material coating the soil is responsible for the hydrophobic effect. The amounts of material extracted from the ring samples are substantially higher (ave. 15.6 mg/g - 1.6 wt.%) compared to the control soils (ave. 6.4 mg/g - 0.6 wt.%). These data clearly show that >1% of ring soils consist of water soluble material from a release. (The actual release content is probably closer to 2-3% if one considers the release also contains some water insoluble material, e.g. calcium oxalate and calcium carbonate previously identified by FT-IR analysis of the as received samples.) Following are the amounts extracted from each sample.

Amounts Aqueous Extracts

Sample	Weight (mg/g)	Wt.% of Soil
C-3 Ring	12.8	1.3
A-2 Ring	15.8	1.6
D-3 Ring	18.3	1.8
C-8 Control	6.1	0.6
Center Control	6.7	0.7
A-9 Control	6.4	0.6

The excessive amounts in two ring samples can be visually observed in the photograph of the extracts below. It shows 3 ml aqueous extracts of equivalent amounts (1 gram quantities) of a control soil and two ring soils. The control is notably lighter.

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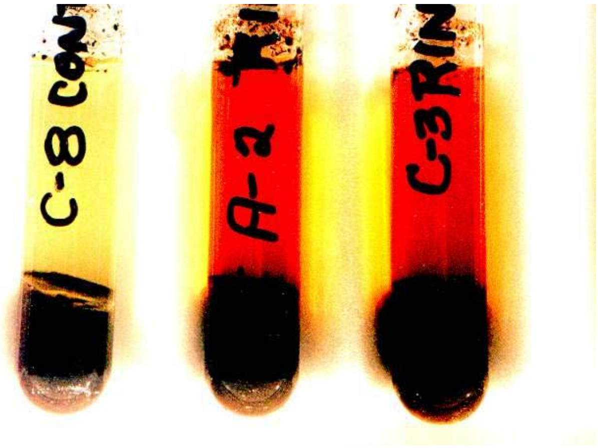
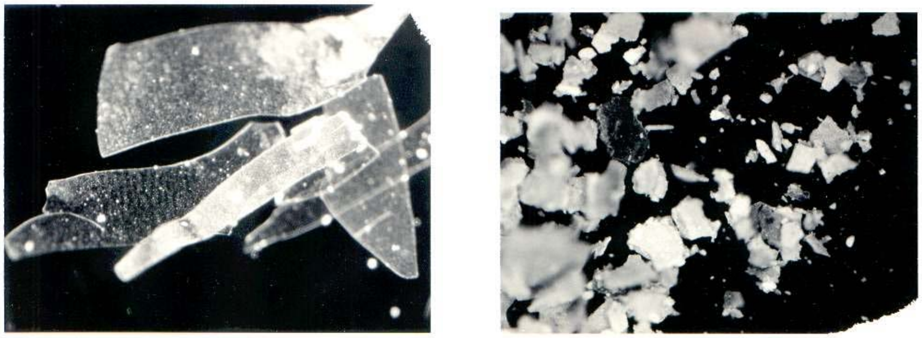
[14] Ref. 3.



Photograph of aqueous extracts of the C-8 control soil (left), and the two ring soils (A-2 center, C-3 right).

After water removal the appearance of the isolated materials from the ring extracts are also different from those of the controls. The ring extract consists of brittle, clear, amber flat particulates. The control extract contains opaque, light brown, particles in a variety of shapes.   Following are black and white microscope photographs of a ring and a control extract.



100X Microscope photographs of the C-3 ring extract (left) and the C-8 control extract (right).

Elemental Analysis: Elemental composition of the extracts was determined by the following tests: EDX; %C; %H; %N. Higher levels of carbon, hydrogen, nitrogen, sulfur, phosphorus, and potassium were detected in the ring extracts than in the control extracts. The composition of the humic substance was estimated to be 43% C, 5% H, 5% N and 42% O.   Following are the details from each test.

EDX shows increased amounts of sulfur, phosphorus, and potassium in the ring extracts. The lower level of silicon in the ring extracts is believed to be soil in association with the organic substance rather than residual soil fines. There has been extensive research which shows that very little humic substances in soil are in free states. Most is bonded to colloidal clay in various ways[15]. However, in the control soils the source of silicon is definitely from fines. (See explanation in FT-IR discussion). The data follow:

EDX Elemental Data “Aqueous Extracts”
(Normalized Wt. %)

Sample	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe
C-3 Ring	-	-	3.3	**6.7**	**19.0**	**49.1**	19.8	0.02	-	1.1	0.98
A-2 Ring	-	-	6.8	**5.3**	**15.8**	**37.7**	31.9	0.15	0.29	0.90	1.2
D-3 Ring	-	1.9	5.0	**6.4**	**9.0**	**36.0**	37.2	0.23	0.05	0.70	3.6
C-8 Control	7.5	-	2.1	**1.3**	**4.6**	**33.9**	49.8	0.11	-	0.45	0.35
Center Cont.	-	11.5	19.3	**6.0**	**5.4**	**27.9**	28.0	0.21	-	0.21	1.5
A-9 Control	7.2	8.4	18.5	**1.4**	**3.1**	**29.2**	28.1	0.23	-	0.93	2.8

The %C, %H, %N values in the table below are significantly higher for the ring soil extracts compared to the control extracts. These values indicate the predominant organic nature of the release. Additionally, the carbon/nitrogen atom ratios for the ring extracts are lower. For the most part these elements represent a humic substance which was positively identified by ^{1}H NMR and FT-IR analysis below. When the data from this analysis are examined in context with the following SEM/EDX analysis a reasonably accurate profile of the elements and their amounts is presented. It is noted that the actual C, H, N values attributed to the humate are skewed to the low side by the presence of bonded soil minerals and other inorganics. The minerals/inorganics amount to roughly 27 wt.% based on the SEM/EDX analysis. Taking this into account the actual C, H, N values for the humate are close to 43 %C, 5 %H, 5 %N. The O value determined from the SEM/EDX analysis is roughly 42 %. The humic substance is specifically suggested to be a fulvic acid because of its water solubility, color, and the low %C and O/C, H/C, N/C atom ratios[16]. It should be

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[15] Jerzy Weber, Agricultural University of Wroclaw, Poland Web Site: www.ar.wroc.pl/%7Eweber/kombi2.htm

[16] Jerzy Weber, Agricultural University of Wroclaw, Poland Web Site: www.ar.wroc.pl/%7Eweber/kwasy2.htm; O. Francioso et al, *Applied Spectroscopy*, Volume 50, Number 9, 1996, p. 1165; O. Francioso et al, *Applied Spectroscopy*, Volume 52, Number 2, 1998, p. 270; R. Ikan et al, *Analytica Chemica Acta*, 232 (1990) p11; R. L. Wershaw, *Analytica Chemica Acta*, 232 (1990) p31; J. F. Gaffney et al editors, “Humic and Fulvic Acids Isolation, Structure, and

noted that the all of these values will vary depending on the source of the humate, i.e. grassland soil, forest soil, desert soil, peat, river bottom, marine bottom, etc. It is difficult to make a confirmation regarding the humic origin, but we can conjecture at this point. Based on a C/N ratio of close to 6, the fulvic acid in the ring extract most resembles a mull type humus. This humus occurs under conditions of high biological activity. It typically occurs under grass vegetation and is noted in soils under cultivation. In this soil type fulvic acid predominates[17]. Although this is also true of the Delphos control soil, the values in the following table as noted above are different enough to show they are not from the same source. Following is a table of the results:

Carbon, Nitrogen, Hydrogen Analysis
(Wt. %)

Sample	C	H	N	C/N Ratio	N/C Ratio	H/C Ratio
C-3 Ring	32.0	4.2	6.0	6.2	0.16	1.58
A-2 Ring	31.8	4.2	5.8	6.4	0.18	1.58
D-3 Ring	31.6	4.2	6.1	6.0	0.17	1.59
C-8 Control	14.2	2.0	4.3	3.9	0.26	1.69
Center Cont.	16.2	2.2	4.7	4.0	0.25	1.63
A-9 Control	12.7	1.9	4.8	3.1	0.32	1.79

SEM/EDAX analysis was only done on the extract from the D-3 ring soil. This analysis most likely shows all the major and minor elements except carbon[18] and hydrogen present in this extract. Nitrogen and oxygen predominantly belong to the humate substance and smaller amounts to other minerals and inorganics. The minerals/inorganics probably account for almost 27% of the extract. These are indicated by the presence of Na, Mg, Al, Si, P, S, K, Ca, and Mn. Using the results from the %C, %N, %H analysis and the normalized SEM/EDX results, one can determine reasonable absolute wt.% values for the elements in the extract composition. However, one must make the reasonably valid assumption that all of the elements in the extract are detected. Following is a table of the original normalized and adjusted SEM/EDX data.

Environmental Role", ACS Symposium Series 651, American Chemical Society, Washington DC, Chapter 11 (p 151); S. A. Visser, *Environ. Sci. Technol.,* 1983, 17 p. 412.

[17] Jerzy Weber, Agricultural University of Wroclaw, Poland Web Site: www.ar.wroc.pl/%7Eweber/typy3.htm

[18] Preparation of the extract for this analysis requires carbon coating the sample, so accurate carbon values could not be determined.

SEM/EDX of D-3 Aqueous Extract

Element	Normalized Wt.%[19]	Absolute Wt.%
N[20]	17.6	11.3
O	62.2	39.3
Na	0.35	0.22
Mg	1.7	1.1
Al	1.5	1.0
Si	3.5	2.3
P	2.5	1.6
S	2.0	1.3
K	4.6	3.0
Ca	4.1	2.6
Mn	0.14	0.09
Fe	0.82	0.53

Furthermore, one can now approximate the C, H, N, O absolute elemental composition of the humic substance. But this is also based on fairly valid assumptions regarding the amount of oxygen, nitrogen and hydrogen belonging to the soil minerals/inorganics which are: 0.5% H (probably mostly hydrated water); 9% O (oxides and hydrated water); 1%N (ammonium nitrate). Once the math is performed the composition of the humic substance is estimated to be 43% C, 5% H, 5% N and 42% O.

Molecular Information: Three important tests (FT-IR, ^{1}H NMR, IC) along with the above elemental data provided pertinent information regarding the types of components comprising the extracts. The humic substance predominates the aqueous extracts. It is indicated to be different and in significantly higher levels than the substance native to the Delphos environment. Besides the previous data regarding water solubility, color, and elemental distribution, there is more evidence that the humic substance is specifically low molecular weight fulvic acid. Furthermore, there are indications that the ring extracts contain very slightly elevated levels of sulfate and phosphate. The detailed molecular investigation follows.

^{1}H NMR spectra of the extracts (Figs. 27-32) are descriptive of humic structures in both ring and control samples. All the characteristic resonance peaks prevail, which match those in literature references[21] of fulvic acids and humic acids, as

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[19] This is the average of two runs.

[20] The nitrogen value a felt to be slightly on the high side, and may be due to instrument error. The 6.1 N% value reported by the previous analysis is considered very accurate.

[21] O. Francioso et al, *Applied Spectroscopy*, Volume 50, Number 9, 1996, p. 1165; O. Francioso et al, *Applied Spectroscopy*, Volume 52, Number 2, 1998, p. 270; R. L. Malcom, *Analytica Chemica Acta*, 232 (1990), p19; Z. Wang et al, *Analytica Chemica Acta*, 232 (1990), p. 43.

well as a reference of purchased humic acid sodium salt[22]. The interpretation follows:

δ (ppm)	Interpretation of proton resonance areas
0.7 - 1.0	Terminal methyls (CH_3) on alkyl groups
1.0 - 1.7	Branch CH_3s and methylenes (CH_2) on alkyl groups
1.7 - 2.5	Methines (CH) and CH_2s alpha to carbonyls and aromatics
2.5 - 3.3	CHs and CH_2s alpha to nitrogen, some oxygen
3.3 - 5.0	Primarily CHs and CH_2s alpha to oxygen, some nitrogen
6.5 - 8.4	Aromatic and heteroaromatic
8.4	formate group -(C=O)H

Quantitation of the above resonance areas show the humates in the ring soils are different than in the control soils. Following is a table of the integrated areas of the spectra as well as a ratio of the branch CH_x/end CH_3 areas showing the differences between the humic substances. Note the humic substance from the ring extract is more aromatic, contains more branched alkyls (see ratio), and appears to contain slightly less carbonyl containing functional groups. This is additional evidence that the ring humate is not natural to the Delphos area, and is a release. The data follow.

**Hydrogen Distribution
(Mole %)**

Samples	Arom	C(H)C=O	CH α O[23]	Probable CH_x α N + Some O	CH_2 and CH α C=O + Arom.	Branch CH_3 and CH_2	End CH_3	Ratio End/ Branch
•D-3 Ring	7.2	0.6	40.9	14.5	12.5	19.2	5.0	3.8
•C-3 Ring	8.0	0.8	43.0	13	13.4	17.6	4.2	4.2
•A-2 Ring	6.4	0.7	45.6	13.3	12.8	18.3	4.2	4.4
Ring Ave.	**7.2**	**0.7**	**43.2**	**13.6**	**12.8**	**18.3**	**4.2**	**4.5**
•A-9 Control	4.0	1.4	38.9	13.8	15.8	22.4	3.8	5.9
•Center Control	3.3	1.4	40.9	13.2	16.7	21.3	3.3	6.5
•C-8 Control	3.5	1.3	42.0	13.6	15.5	20.6	3.6	5.7
Control Ave.	**3.6**	**1.4**	**40.6**	**13.6**	**16.0**	**21.4**	**3.6**	**5.9**

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[22] Sigma-Aldrich, Humic Acid, Sodium Salt, (tech.), Catalog No.: H1675-2.
[23] Solvent peak interference may cause the biggest variation in this value.

As in previous tests these data also indicate that the humic substance is specifically fulvic acid in both ring and controls extracts. This is evident because of the highly oxygenated (CH/CH_2 alpha to oxygen, 3.3-5.0 ppm) and low aliphatic nature (terminal CH_3s on alkyl groups and branch CH_3s and CH_2s on alkyl groups, 0.7-1.7 ppm) compared to the data from humic acids[24].

Infrared spectra of the ring extracts (Figs. 33a-c) also are typical of references of humic substances[25]. The data from the ring extracts show very strong absorption bands due to ionic and/or chelated carboxylic acid C=O (COO^- asymmetric stretch,1590 cm^{-1}; COO^- symmetric stretch, 1385 cm^{-1}), C-O (1100-1000 cm^{-1}) and OH/NH (H-bonded O-H and N-H stretch ca. 3600-3000 cm^{-1}). There are also bands belonging to quartz (1024, 821, 529 and 470 cm^{-1}). Since great care was taken to minimize as much as possible any insoluble fines from the soil, and the water extract was clear brown (see above), it is felt that the humic material has bonded to the quartz pulling it into aqueous solution and not residual fines. The spectra of the control extracts are different (Figs. 34a-c). The predominating infrared bands are due to soluble ammonium nitrate (3350, 2407, 1760, 1372 and 821 cm^{-1}) and residual quartz (1024, 530, and 470 cm^{-1}). (Some ammonium nitrate is also in the ring extracts but is masked by the overwhelming amount of humic material. (See organic solvent extract section below.) The humic substance is in significantly lesser amounts as exhibited by weak/moderate absorption which is now at slightly different frequencies then that in the ring samples (bonded OH contribution to the 3350 NH_4^+ absorption; COO^- asymmetric stretch, 1625 cm^{-1}). The solutions were cloudy with material that could not be centrifuged or filtered out. As previously noted, there was also significantly less of this material to examine.

UV spectra of the D-3 ring extract and an aqueous solution of humic acid sodium salt extracts are similar (Fig. 35) and compare to that reported in the literature[26]. There is a maxima at 190 nm which is consistent with C=O absorption. Broad tailing between 250 - 375 nm is due to the aromatic/heteroaromatic structure of the humate. This test lends support to the ^1H NMR and infrared analysis.

IC (Ion Chromatography) suggests subtle increases of sulfate and phosphate ions in the ring samples. Therefore, to a small extent they are indicated to be part of the release. The following ions are detected.

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[24] Ref. 21.

[25] Ref. 21; J. F. Gaffney et al editors, “Humic and Fulvic Acids Isolation, Structure, and Environmental Role”, ACS Symposium Series 651, American Chemical Society, Washington DC, Chapter 1, p. 2.

[26] J. F. Gaffney et al editors, “Humic and Fulvic Acids Isolation, Structure, and Environmental Role”, ACS Symposium Series 651, American Chemical Society, Washington DC, Chapter 1, p. 2.

Ion Identification
(ppm)

Samples	Cl	NO_3	HPO_4	SO_4
•D-3 Ring	130	74	313	287
•C-3 Ring	160	400	330	640
•A-2 Ring	160	430	330	460
•A-9 Control	115	321	43	101
•Center Control	130	1500	250	340
•C-8 Control	160	400	330	640

GC/MS analysis of the ring water extracts did not detect any components. This is because of the high polarity of the previously identified humic substance. This material would be expected to hang up on the GC column. GC/MS analysis of the headspace above the ring extracts detects a very small excess of carbon dioxide.

Silver Nitrate Precipitations from Aqueous Extracts

A precipitation using 0.1 normal solution of silver nitrate was done on the D-3 ring aqueous extract and an aqueous solution of the sodium salt of humic acid. The precipitation was similar to that performed by Erol Faruk[27]. There was not much soil extract to work with because of sample limitations. So the precipitate was not washed for fear of losing some of it. Expectedly, both the extract and the humic acid solution completely precipitated leaving clear colorless solutions. This was due to the chelation of the Ag to the humic substance. FT-IR spectra of the precipitates (Figs. 36a, 36b) show bands typical of ionic/chelated acid groups (COO^- asymmetric stretch,1550 cm^{-1}; COO^- symmetric stretch, 1370 cm^{-1}). These are shifted to lower frequencies than the humic substances before silver nitrate treatment because the acid groups are now bonded to Ag. OH (H-bonded O-H stretch ca. 3600-3000 cm^{-1}) and C-O (1100-980 cm^{-1}) modes are also noted. These spectra bands are similar to those observed by Faruk. However, Faruk's carboxylate shifts occurred at higher frequencies. This can be explained by the fact that his sample preparation for infrared analysis involved pelleting the sample in a KBr matrix. Carboxylic acid functional groups notoriously bond with potassium using this preparation, so we are predominantly seeing the potassium salt rather than the silver salt of the humate. Infrared data from the precipitates in this study were examined "au natural" using the relatively new Harrick SplitPea™ ATR (a single pass attenuated total reflectance) cell. Additionally noted in the above spectra is residual silver nitrate.

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[27] Ref. 3

Organic Solvent Extracts

Very little material was extracted from two selected soils (D-3 ring and A-9 Control) using progressively polar organic solvent systems, i.e. pentane, followed by chloroform, then 1:1 acetone:methanol. Specifically, there was no detectable amount of pentane soluble material in either ring or control soils. A small amount of oxalic acid salt and residual quartz fines was exclusively found in the D-3 chloroform extract. Small amounts of materials were found to be 1:1 acetone:methanol soluble in both samples. The ring soil extract contained oxalic acid salt, ammonium nitrate, and residual quartz fines. The A-9 control extract consisted of mostly ammonium nitrate, possibly some carbonate, and residual quartz fines. The above extracts were identified by FT-IR analysis (Figs. 37a-c).

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Phyllis A. Budinger

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