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MOUNT ST. HELENS, WASHINGTON, 1980 VOLCANIC ERUPTION: CHARACTERIZATION OF ORGANIC COMPOUNDS IN ASH SAMPLES

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Abstract. Volcanic ash samples obtained after the May 18, eruption of Mount St. Helens, Washington, were analyzed for organic compounds. Several n-alkanes, fatty acids, dicarboxylic acids, alcohols, phenols, aldehydes, aromatic acids, aromatic and polycyclic aromatic hydrocarbons and chlorinated aromatic compounds were identified by GC-MS. Pyrolysis of plants and soil organic matter is the most probable source of these compounds.

Introduction

The cataclysmic eruption of Mount St. Helens, Washington, on May 18, 1980 was a spectacular event. Volcanic ash ejected from the mountain was air-borne by prevailing winds and deposited over a large area including the states of Washington, Oregon, Montana, and Colorado.

Several lakes, rivers, and streams were contaminated

Table I. Organic compounds identified in volcanic ash from Richland, Washington

Compound Class	Compounds identified by GC/MS
Alkanes	n-alkanes (C_{15}-C_{32})
Fatty acids*	Saturated fatty acids (C_8-C_{28}) Unsaturated fatty acids (Palmitoleic and Oleic)
Dicarboxylic acids*	Straight chain (C_4,C_6,C_8,C_9,C_{10})
Benzene ring containing acids*	Benzoic; Phenylacetic; Hydroxybenzoic; Toluic isomers; 3-methoxybenzoic isomers; 3,4-Dimethoxybenzoic; 3,4-Dimethoxycinnamic
Polycyclic aromatic acids*	2-Naphthalenecarboxylic; Alkylated octahydrophenanthrene carboxylic acid isomer
Ketones	Indanone; Trimethylindanone; 1-Phenyl-1-propanone; 4-methoxyacetophenone; Ethanone, 1-(3,4-dimethoxyphenyl)-; 1-Propanone, 1-(2,4-dimethoxyphenyl)-; 2-Dodecanone; Fluorenone
Alcohols	Octadecanol; 1,3-Dimethoxy-2-propanol; 3-Methoxy-1,2-propanediol; 1-Ethyl-6-methyl-3-piperidinol; Alkyated octahydrophenanthrene-methanol isomer
Phenols* and Aldehydes	4-Methoxybenzaldehyde; Trimethoxybenzene; Trimethoxytoluene; 3,4-Dimethoxybenzaldehyde; Alkylated octahydrophenanthrenecarboxaldehyde isomer
Aromatic and Polycyclic aromatic hydrocarbons	1-Ethenyl-3,5-dimethyl benzene; 1,6-Dimethyl-4-(1-methylethyl) naphthalene; Methylphenanthrene isomer; 1-Phenylnaphthalene; Dimethylphenanthrene isomer; Trimethylphenanthrene isomer; Tetramethyl phenanthrene isomer
Chlorinated aromatics	Chlorobenzoic acid isomers; 4-Chlorophenyl-1-ethanone; 3,4-Dichlorobenzoic acid; Pentachlorobiphenyl isomers

*Identified as the methylether or methyl ester derivatives.

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by the ashfall. During the eruption, trees in the vicinity were completely pyrolized and burned, and in the outlying area, denuded of bark, branches, and leaves. Degradation or synthesis of organic compounds resulting from pyrolysis of plant and/or soil organic matter followed by condensation or adsorption led us to investigate the types of organic compounds associated with the ash. (Dissolved organic carbon levels were found to range from 6-225 mg/L carbon.) The purpose of this investigation was to characterize the types of organic materials that eventually might be leached from the ash by precipitation thus resulting in contamination of the hydrologic environment.

Experimental

Volcanic ash was collected from Richland and Spokane, WA, and Kalispell and Helena, MT. Typically 5 g of the ash was extracted with benzene: methanol (2:1) in a Soxhlet apparatus for 20 hours. The extract was concentrated to a volume of 0.5 mL, and fractionated on a column containing 3 g of activated neutral silica gel. Three elution fractions were collected; (1) 10 mL Hexane; (2) 10 mL methylene chloride; (3) 10 mL of methylene chloride-methanol (1:1). Each fraction was concentrated to approximately 100 µL in a stream of dry nitrogen and analyzed by gas chromatography-mass spectrometry (GC/MS). The gas chromatograph was equipped with a fused silica capillary column, 30 m x 0.26-mm I.D., coated with SE-54. The mass spectrometer was operated in the electron impact mode. A 15 g sample of ash from Richland, WA, was similarly extracted and methylated with ethereal diazomethane solution.

Results and Discussion

Each ash sample was found to contain similar types of organic compounds. The general classes of compounds identified in volcanic ash obtained from Richland, WA, along with selected representative compounds from each class are shown in Table I.

Examination of the data reveals several important findings. The occurrence of alkanes (C_{15}-C_{32}) with an odd/even ratio greater than 1 suggests that these compounds were derived from higher plants (Giger, 1975). In addition, oxygen containing derivatives similar to those reported as degradation products of humic material (Schnitzer, 1978) were identified. These include fatty acids, dicarboxylic acids, aromatic acids and aldehydes (Schnitzer, 1978; Kononova, 1966).

The presence of polycyclic aromatic hydrocarbons such as alkylated phenanthrenes, along with hydroxymethyl, aldehyde, and carboxylic acid derivatives of phenantharenes, suggests plants as sources of these compounds. In addition, pyrolysis of plant materials is known to produce polycyclic aromatic hydrocarbons (Youngblood, 1975).

Several chlorinated aromatic compounds were also identified. It has been reported that polychlorinated biphenyl (PCB) dibenzofurans and dioxins are formed in trace amounts in combustion processes (Rawls, 1979). In addition to chloro and dichlorobenzoic acid isomers, three pentachlorobiphenyl isomers were identified. It is well known that commercial PCB formulations are complex mixtures of isomers (Safe, 1979). The presence of only three pentachlorobiphenyl isomers suggests the possibility that these compounds were preferentially synthesized by a combustion process. It is further suggested that aromatic compounds produced as a result of degradation of plant and soil organic matter, were chlorinated in the eruption zone. Pyrolysis of these polymeric materials in the presence of inorganic chloride salts could have produced chlorinated isomers of benzoic acid and biphenyl. Analysis of the ash samples for inorganic species revealed the presence of substantial amounts of inorganic chloride salts (H. E. Taylor, unpublished data, 1980) deposited on the ash from the eruption cloud (Taylor, 1973). Our findings are consistent with the results of other researchers (Olie, 1977) concerning the de novo formation of organochlorine compounds from pyrolysis of organic material in the presence of inorganic chlorides.

The presence of such a diverse group of organic compounds, many of which are the building blocks of large bio-polymers such as lignin and humic material, leads to the assumption that the volcanic eruption of Mount St. Helens degraded and vaporized plant lignin, and humic material. Under conditions of high temperature and pressure in the eruption cloud, various chemical processes including oxidation, decarboxylation, and hydrolysis occurred breaking down these polymeric materials into simpler molecules, which were then adsorbed onto the ash from the atmosphere.

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