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Project Summary

Phase Distributions of Low Volatilty Organics in Ambient Air

Bruce K. Cantrell, Louis J Salas, Warren B. Johnson, and James C Harper

Current strategies to control photochemical air pollution rely on abating the emission of volatile organic compounds. Primarily, these compounds exist in the vapor phase, and are those with a carbon number of ten or less. Recent attention has been given to low-volatility organic compounds (LVO) which may be partitioned between the gas and aerosol phases, and may only partially participate in smog formation. A three-part study was conducted to determine the role of such LVOs. First, a comprehensive review was made of the existing literature on atmospheric LVO to evaluate existing data and the measurement techniques used to collect the data. Second, an effort was made to develop an "estimator" for the phase distribution of LVOs in the atmosphere. While exact theoretical calculations of LVO adsorption on ambient surfaces are difficult, estimation based on the phenomenology is possible. This semi-empirical calculation has been applied to the n-alkane series with some success.

The concurrent third part of the study involved an attempt to develop and test an improved and reliable collection and analysis technique for LVO. An effective denuder device was developed which can be used to provide a sample of the aerosol fraction of LVO under laboratory conditions. Additional research is needed to perfect this device for the routine determination of the aerosol/vapor fraction in the ambient air.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Current strategies to control photochemical air pollution rely on abating the emission of volatile organic compounds. Primarily, these compounds are those with a carbon number of ten or less. Recent attention has been given to low-volatility organic compounds (LVO), which may also contribute to smog formation. To determine the role of such LVOs in smog formation, both the reactivity and the phase distribution of each compound must be known.

When these organics are emitted into the atmosphere, they can exist in either the gas or aerosol (solid/liquid) phase. Under ideal conditions, the compounds will eventually vaporize and reside solely in the gas phase until the partial pressure of the compound exceeds the vapor pressure of the pure compound. Under atmospheric conditions however, LVOs are phase distributed not only by the pure substance's thermodynamic properties, but also by the adsorption and retention properties of the myraid different surfaces which exist in the atmosphere. These include both water droplets and atmospheric aerosols. Most of these surfaces are, of themselves, extremely complex and poorly understood.

To deal with this problem, this study was conducted in three parts. First, a comprehensive review was made of the existing literature on LVO. This review covered both an evaluation of existing

data on atmospheric LVOs, and the measurement techniques used to collect the data. Following this, a selection was made of the n-alkane compounds for the study to focus upon. These compounds were selected because they represent a uniform compound structure type covering a wide range of carbon numbers.

In the second part of the study, an effort was made to develop an "estimator" for the phase distribution of LVOs in the atmosphere. While exact theoretical calculations of LVO adsorption on ambient surfaces are nearly impossible, estimation based on the phenomenology is possible. This semi-empirical calculation has been applied to the n-alkanes with some success.

The third part of the study was conducted concurrently with the other two. In this portion of the study an attempt was made to develop and test an improved and reliable collection and analysis technique for determination of the phase distribution of low volatility organics in ambient urban air. Each portion of the study is discussed separately in this report.

Conclusions

Based on the atmospheric measurements of other investigators, n-alkanes in the atmosphere are predominantly in the vapor phase for carbon numbers less than 18. This varies seasonally somewhat. In the summer, atmospheric n-alkanes up to carbon number 20 are predominantly in the vapor phase.

The assertions in the previous paragraph are supported by application of the simplification of the BET theory of adsorption. When care is taken to obtain accurate estimates of the parameters used in the BET theory, almost exact correspondence with atmospheric measurements is achieved. The critical parameters used in estimating atmospheric aerosol/vapor phase distributions are the mean temperature for the period of interest and the atmospheric aerosol surface concentration. The former is season-dependent while the latter is, for the most part, dependent on the locale where the LVO aerosol/vapor is dispersed in the atmosphere.

As a sample collection system, the SRI sampling system performs as designed. The impactor inlet provides a clean preselection cut of the sample aerosol fraction at 10 μm, and the denuder adsorbs the n-alkane test compounds vapor while passing aerosol with less than 2 percent loss. The adsorption of compounds from the atmosphere, however, is not selective so that when an attempt is made to recover the adsorbed sample by thermal desorption of the denuder, extraneous compounds (as evidenced by gas chromatographic analysis) completely obscure the compounds by interest. This occurs even when high concentrations of test vapor have been introduced into the atmospheric sample. The extraneous compounds may also cause changes in the elution times so that transferring a specific compound peak to a mass spectrometer on the basis of elution time is doubtful. Limiting sample collection time or dilution of the desorbed vapor sample does not improve the sample analysis conditions sufficiently to warrant using the denuder-derived sample to analyze for LVO in the atmosphere. Further improvements in the adhesive material and additional tests are required before this system can be satisfactorily employed in field studies.

Bruce K. Cantrell, Louis J. Salas, Warren B. Johnson, and James C. Harper are with SRI International, Menlo Park, NC 94025.
***Robert R. Arnts** is the EPA Project Officer (see below).*
The complete report, entitled "Phase Distributions of Low Volatility Organics in Ambient Air," (Order No. PB 87-129 540/AS; Cost: $13.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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