Environmental Chemistry of Animal Manure

Zhongqi He
Editor

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ENVIRONMENTAL CHEMISTRY OF ANIMAL MANURE

ZHONGQI HE
EDITOR

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PREFACE

Animal manure is traditionally regarded as a valuable resource of plant nutrients. However, there is an increasing environmental concern associated with animal manure utilization due to high and locally concentrated volumes of manure produced in modern intensified animal production. Although considerable research has been conducted on environmental impacts and best management practices, the environmental chemistry of animal manure has not developed accordingly. Accurate and insightful knowledge of the environmental chemistry of animal manure is needed to effectively utilize animal manure while reducing its adverse environmental impacts. The primary goals of this book are to (1) synthesize and analyze the basic knowledge and latest research on the environmental chemistry of animal manure, (2) stimulate new research ideas and directions in this area, and (3) promote applications of the knowledge derived from basic research in the development and improvement of applied, sustainable manure management strategies in the field. This book will serve as a valuable reference source for university faculty, graduate students, extension specialists, animal and soil scientists, agricultural engineers, and government regulators who work and deal with various aspects of animal manure.

This book consists of four parts. Part I is manure organic matter characterization. Five chapters in this part examine the chemical composition and structural environments of organic matter in animal manure and relevant compost, using pyrolysis-mass spectrometry, infrared spectroscopy, solid state ^{13}C nuclear magnetic resonance spectroscopy, ultraviolet-visible spectroscopy, and fluorescence spectroscopy. Part II is focused on nitrogen and volatile compounds in animal manure. Four chapters in Part II examine ammonia emission from animal manure, key manure odor components, manure amino compounds, and manure nitrogen availability. Part III is manure phosphorus forms and lability. The first four chapters in Part III examine solubility, enzymatic hydrolysis, forms, and metal speciation of manure phosphorus using various wet and instrumental analysis. The last two chapters in Part III then examine the models used in predicting phosphorus transformations and runoff loss for surface-applied manure and reduction of runoff potential of manure phosphorus by alum amendment. Beyond the phosphorus concern, the alum chapter also comprehensively examines the sustainability of animal agriculture by treating manure with alum. Part IV covers heavy elements and environmental concerns. The first chapter in Part IV examines sources and contents of heavy metals and other trace elements in animal manures. Although not heavy metals in strict terms, arsenic and mercury in animal and soil have been frequently investigated with other toxic heavy metals. Thus, the last two chapters in Part IV examine fate

and transport of arsenic from organoarsenicals fed to poultry and mercury in animal manure and impacts on environmental health, respectively.

Chapter contribution is by invitation only. Each chapter is designed to cover a specific topic. For each chapter to stand alone, there is occasionally some overlap in literature review, and some experiments have been used as examples in more than one chapter. All 18 chapters in the four parts were written by accomplished experts in the relevant fields, and were subject to the peer reviewing and revision processes. Positive comments from at least two reviewers were required to warrant the acceptance of a manuscript. I would like to thank all reviewers for their many helpful comments and suggestions which certainly improved the quality of this book.

ABOUT THE EDITOR

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PART I. ORGANIC MATTER CHARACTERIZATION

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Chapter 1

APPLICATION OF ANALYTICAL PYROLYSIS-MASS SPECTROMETRY IN CHARACTERIZATION OF ANIMAL MANURES

Jim J. Wang[1,], Syam K. Dodla[1] and Zhongqi He[2]*

1.1. INTRODUCTION

Analytical pyrolysis-mass spectrometry (Py-MS), principally in the format of pyrolysis-field ionization mass spectrometry (Py-FIMS) or pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), is a technique capable of providing information on complex organic matter at the molecular level. Unlike C-13 nuclear magnetic resonance (NMR) spectroscopy which provides an average structure of the whole organic material, analytical pyrolysis with mass spectrometry characterizes individual molecular composition through thermal "extraction" (pyrolysis) of the complex organic matter followed by either direct detection by MS or separation through GC then detection by MS. The technique provides a "fingerprint" that can be used to characterize a sample and statistically compare it to others. Besides the use mostly as a qualitative tool, its ability to quantitatively compare samples with similar organic and inorganic matrices makes analytical pyrolysis a powerful tool. Both Py-FIMS and Py-GC/MS have been widely used for the characterization of organic matter of various environmental matrices including aquatic and terrestrial natural organic matter (NOM), microorganisms, soils, and municipal wastes (Meuzelaar et al., 1974; Bracewell and Robertson, 1976; Saiz-Jimenez et al., 1979; Schnitzer and Schulten, 1995; Gonzalez-Vila et al., 1999; White et al., 2004; Leinweber et al., 2009). The major advantages of this technique in organic matter characterization as compared to other traditional techniques are (1) relatively small sample size (usually in the sub milligram range), (2) virtually negligible

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sample preparation except for grinding and (3) short analysis time (typically one hour or less). Also, Py-GC/MS is much more affordable as compared to solid state NMR spectroscopy. Though used widely, there have been only limited studies investigating the chemistry of animal manures using Py-FIMS or Py-GC/MS. In this chapter, we review the current literature on the use of analytical pyrolysis in organic manure characterization and present molecular composition data of cattle manure and poultry litter as characterized by Py-GC/MS.

1.2. The Principle of Analytical Pyrolysis

Analytical pyrolysis involves the chemical analysis where non-volatile organic compounds are thermally broken down at high temperature and anoxic conditions for a very short period of time. Following this process, newly formed volatile compounds are either directly detected or separated using gas chromatography followed by detection via flame ionization detector (FID), Fourier transform infrared (FTIR) spectroscopy, or MS. Among all, pyrolysis coupled with FIMS or GC/MS especially the later has been the most popular (White et al., 2004). This is attributable to the fact that MS detection is highly sensitive, specific, and reliable for many organic compounds (Schnitzer and Schulten, 1995). When a mass spectrometer shatters compounds using electron impact, the compound is fragmented in a reproducible way, the ions are separated based on mass/charge ratios, and the result is a spectrum which is both qualitative and quantitative.

The breakdown mechanism of compounds in pyrolysis is a characteristic of initial compounds and resultant low molecular weight chemical moieties compositions are indicative of specific types of macromolecule in the sample analyzed (e.g. lignin, cellulose, chitin etc.) (White et al., 2004). According to Wampler (2007), the breakdown of the compounds that occur during pyrolysis is analogous to the processes that occur during the production of mass spectrum. By applying heat to a sample that is greater than the energy of specific bonds, the molecule will fragment in a reproducible way. The fragments are then separated by the analytical column to produce the chromatogram (pyrogram) which contains both qualitative and quantitative information. The number of peaks, the resolution by capillary GC, and the relative intensities of the peaks permit discrimination among many similar formulations, making Py-GC/MS a powerful tool in the identification of unknown samples (Wampler, 2007). The heating of the sample is often carried out through flash pyrolysis, which employs rapid heating of the samples normally in an inert atmosphere. Two modes of heating, inductive (Curie-point) and resistive (filament), are commonly used in flash pyrolysis. Research has shown little difference between the results of organic material characterization using Curie-point Py-GC/MS and resistive filament Py-GC/MS (Stankiewicz et al., 1998). Besides GC separation, the sample can be pyrolyzed under vacuum directly in the ion source of the mass spectrometer, and the volatile components are identified by soft ionization (field ionization or field desorption) mass spectrometry (Py-FIMS or Py-FDMS). While Py-GC/MS is able to take the advantage of GC separation of various pyrolysis fragments for mass spectrometry, Py-FIMS emphasizes on reduced mass fragments with a wide range of mass coverage.

Analytical pyrolysis has advanced characterization of complex organic matter in many ways. Most conventional methods in identifying or quantifying individual organic compounds require the target chemical be extracted from a solid or liquid matrix. This is often done using a liquid or supercritical fluid extraction. Solvents, particularly basic solutions, can partially oxidize, or otherwise modify the organic matter being studied. In addition, organic molecules can only be identified by conventional GC/MS if they remain volatile in an inert gas stream at 300°C or less. Most organic matrices in the environment are composed of materials too large to volatilize at 300°C and cannot be analyzed by traditional GC/MS. However, pyrolysis will thermally extract intact molecules or crack large molecules into fragments that can then be separated and/or directly identified by GC/MS. As such, pyrolysis is an alternative way to "extract" organic matter from complex matrices. The major advantages of Py-GC/MS are requirement of very small sample sizes lower than few milligrams, no requirement of initial processing, reproducible results, faster analysis times, and the ability to provide information about most potential soil organic matter (SOM) precursors such as carbohydrates, lignin, amino acids and lipids (Lehtonen, 2005). Nevertheless, analytical pyrolysis has some limitations from the use of instrumentation to its interpretation (Saiz-Jimenez, C. 1994; Wampler, 2007). In particular, pyrolysis is a destructive technique that fragments organic molecules and, at the same time, can result in side reactions that form new compounds such as ring structures (White et al., 2004). Overall, analytical pyrolysis, especially Py-GC/MS and Py-FIMS, has been considered as one of premiere tools for characterizing complex organic matter (White et al., 2004; Wampler, 2007; Leinweber et al., 2009).

1.3. Application of Analytical Pyrolysis in Characterizing Natural Organic Matter

As early as 60 years ago, Zemany (1952) proposed an approach of using of Py-MS for the analysis of complex organic materials including proteins. Later, Nagar (1963) used Py-GC technique to examine the structure of soil humic acids and emphasized the importance of GC separation. Since then, there has been a great deal of work using analytical pyrolysis to investigate humic substances in soils and sediments and other natural biopolymers (Bracewell and Robertson, 1976; Saiz-Jimenez and De Leeuw, 1986; Hatcher et al., 1988; Abbt-Braun et al., 1989; Hempfling and Schulten, 1990; Fabbri et al., 1996; Stuczynski et al., 1997; Nierop et al., 2001; Chefetz et al., 2002; Buurman et al., 2007). Dignac et al. (2006) suggested that a polar (wax) column was better suited to characterize pyrolysis products originating from less humified OM, such as polysaccharides, proteins; alkanoic acids, and lignin-derived products. By contrast, the use of a non-polar column was more satisfactory to characterize the distribution of aliphatic structures producing alkanes and alkenes upon pyrolysis. Several excellent reviews on the use of analytical pyrolysis for studying organic matter can be found elsewhere (Saiz-Jimenez, 1994; Schnitzer and Schulten, 1995; Leinweber and Schulten, 1999; White et al., 2004; Leinweber et al., 2009). Analytical pyrolysis contributed significantly to the discovery of relationships between organic precursors and soil organic composition as well as between geographic origin and specific SOM constituents/soil functions (Leinweber and Schulten, 1999). In a very recent study of the SOM composition in natural ecosystems under different climatic regions using Py-GC/MS, Vancampenhout et al. (2009) found that

SOM in cold climates still resembled the composition of plant litter as evidenced by high quantities of levosugars and long alkanes relative to N-compounds and there was a clear odd-over-even dominance of the longer alkanes. On the other hand, SOM formed under temperate coniferous forests exhibits accumulation of aromatic and aliphatic moieties, whereas SOM under tropic region is generally characterized by a composition rich in N-compounds and low in lignin without any accumulation of recalcitrant fractions such as aliphatic and aromatic compounds (Vancampenhout et al., 2009). In another study that compared whole soil OM and different humic fractions in soils with contrasting land use based on pyrolysis molecular beam mass spectrometry (Py-MBMS), it was shown that agricultural cultivation generally increases the composition heterogeneity of SOM as compared to native vegetation (Plante et al., 2009). Also recently, a series of chemical parameters based on Py-GC/MS analysis were developed to better describe relations between vegetation shifts and aerobic/anaerobic decomposition of organic matter in peatlands (Schellekens et al., 2009). In a study of humic acids from different coastal wetlands, we also observed an increasing trend in the condensed domain of alkyl C, relatively more stable G-type structural unit of lignin residue, and more contribution of sulfur as a structural component in humic acids along an increasing salinity gradient (Dodla, 2009). Clearly analytical pyrolysis continues to be an important tool for researching soil and biogeochemical processes.

1.4. Animal Manure Chemistry by Analytical Pyrolysis

There has been a long history of land application of animal manures to agricultural fields as a means of waste disposal and as a soil amendment in many parts of the world. The beneficial use of animal manures has been shown to maintain the SOM status, to increase the levels of plant-available nutrients, and to improve the physical, chemical, and biological soil properties that directly or indirectly affect soil fertility (Eck and Stewart, 1995; Briceño et al., 2007). On the other hand, various studies have demonstrated that animal manure application to agricultural lands may contribute to soil, water and air contamination by emitting and releasing ammonia, greenhouse gases, excess nutrients, pathogens, and odors as well as other substances such as antibiotics (Gerba and Smith, 2005; Kumar et al., 2005, Briceño et al., 2008; Paramasivam et al., 2009; Wang et al., 2010). Chemical composition of animal manure is found to be particularly important in influencing the sorption, mobility and transport of nutrients and contaminants (McGechan and Lewis, 2002; Jorgensen and Jensen, 2009). Recently, research has also focused on possibility of using animal manure as an alternative energy source (Cantrell, 2008; Zhang et al., 2009). All these studies have generated tremendous interest in understanding the organic matter composition and structure of various animal manures (Schnitzer et al., 2007, 2008; Aust et al., 2009). A summary of the various usage of analytical pyrolysis in animal manure characterization is given in Table 1.1.

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