The Science of Smell Part 2:
Odor Chemistry

Odor chemistry is complex and still poorly understood. More than 75 odorous compounds, in varying proportions, have been identified in livestock manures. Knowing the chemical basis of odors derived from animal manure is helpful to understand how odor develops and what can be done to design and manage manure systems and avoid nuisance complaints.

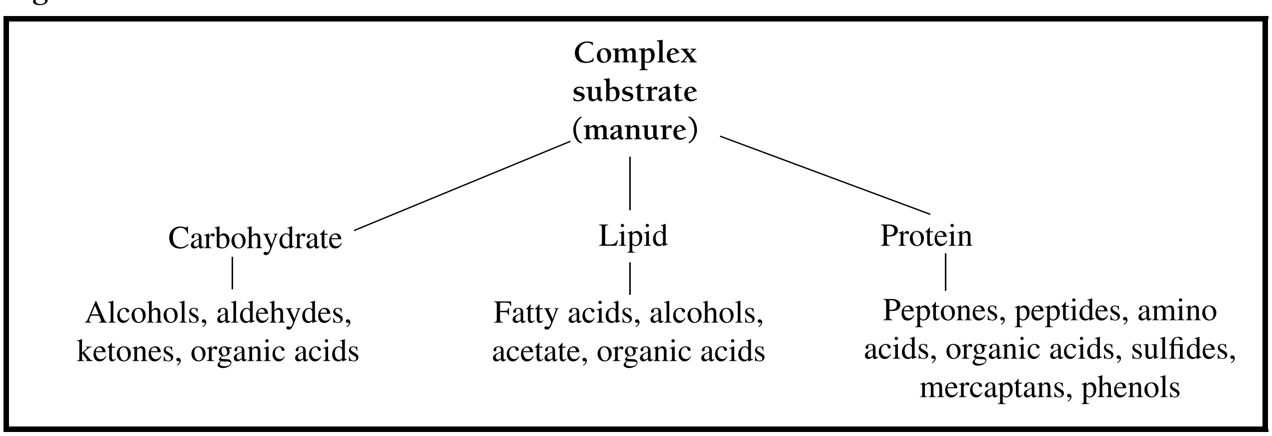
Biochemistry of manure odor

Groups of primary odorous compounds include volatile organic acids, aldehydes, ketones, amines, sulfides, thiols, indoles, and phenols. All of these groups can result from the partial decomposition of manure. Manure breakdown is accomplished by a mixed population of anaerobic bacteria, which is commonly grouped into acid-forming or methane-producing classes. Acid formers are responsible for the initial breakdown of complex molecules into short-chain compounds, including organic acids. Methane bacteria further reduce organic acids to methane and carbon dioxide.

Figure 1 provides a simple overview of the breakdown process. The breakdown of protein proceeds to ever-simpler proteoses, peptones, peptides, amino acids and finally, to ammonia and volatile organic acids such as formic, acetic, propionic, and butyric acids. Due to the presence of sulfur in certain amino acids (sulfur averages about 1 percent of most proteins), various sulfides and mercaptans can be expected as a result of protein catabolism.

Carbohydrates in animal waste include sugars, starch, and cellulose. Starch and cellulose are broken into glucose (sugar) units as the first step of decomposition. Under anaerobic conditions, sugars are broken into alcohols, aldehydes, ketones, and organic acids. These intermediate compounds are odorous and can be further metabolized and transformed into methane, carbon dioxide, and water (non-odorous end-products) if conditions allow the methane-producing microorganisms to function.

Figure 1. Manure breakdown chain.



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University Extension

PM 1963b May 2004

Fats are esters of the tri-hydroxy alcohol called glycerol. Bacteria use fats as an energy source, hydrolyzing them first to the corresponding long-chain fatty acids and alcohols. These acids, along with those produced in the deamination of amino acids, undergo further breakdown in which acetic acid is cleaved from the original acid. Acetic acid is then potentially utilized as an energy source, yielding methane and carbon dioxide as end-products.

Examination of the metabolic pathways for the breakdown of manure components indicate that the following components are expected to result in: organic acids, alcohols, aldehydes, sulfides, simple hydrocarbons, carbon dioxide, ammonia, and methane. The presence of this mixture of organic materials and ammonia in an aqueous solution leads to the formation of several other groups, as reaction products. For example, ammonia in water-- a H+ receptor -- may be expected to react with acids and alcohols to yield amides and amines. Also, hydrogen sulfide in water may combine with alcohols, aldehydes, and acids to form mercaptans, thiols, and thioacids.

An accumulation of these intermediate metabolites results in an offensive smelling product, whereas containment of intermediate compounds for sufficient time allows methane producers to act and metabolize most of the odorous compounds into non-odorous methane. Background levels of sulfur in water may also be a source of odor.

Physical chemistry

Any compound occurring in the atmosphere must have escaped the liquid phase. Thus, vapor pressure is an important factor which, within specific types of compounds, generally decreases with increasing molecular weight.

The solubility of a compound in water is another important factor in evaluating its significance as an atmospheric constituent. Insoluble gases, such as methane, escape immediately after being produced, whereas more soluble compounds, such as ammonia, are retained in solution and can engage in biological and chemical reactions. Solubility of many compounds, and hence odor, is markedly influenced by the solution pH. Hydrogen sulfide is a particularly good example of the pH effect. Under conditions of high pH, almost no odor is detected whereas under acid conditions, the H+ and HS- ions combine, escape, and produce the typical sulfide odor (H_2S). Ammonia (NH_3) is another good example of pH effect. The NH_3 in an acid medium accepts H+ to produce ammonium (NH_4^+) which stays in solution and does not volatilize. Even with a pH up to 8, ammonia remains relatively soluble in liquids and little odor is detected. Above a pH of 9, however, ammonia is rapidly volatilized.

No single compound has been identified as a good predictor of odor sensation across situations in the field. Because of this, human panelists conduct odor measurements and quantify odor intensity and unpleasantness.

Odor characterization

Based on psychological tests, seven primary classes of olfactory stimulants have been found to preferentially excite separate olfactory cells. These classes are: 1) ethereal, 2) camphoraceous, 3) musky, 4) floral, 5) minty, 6) pungent, and 7) putrid. The nervous system integrates the responses from a number of cells to determine the identity of the primary odor stimulus being received. The intensity of the perceived odor class is related to the number of receptors bound and the degree of excitation of the olfactory cells. Table 1 shows the variation in concentration needed to produce equivalent odor intensities in the seven classes. Odor intensity, as referred to in Table 1, is the strength of the odor sensation as measured on a psychological reaction scale and is not a concentration. Complex odors result from the concurrent stimulation of two or more types of receptors. This implies that a single chemical can occupy more than one receptor site.

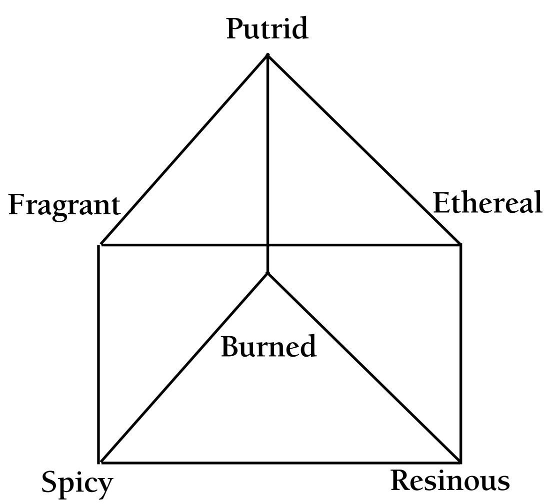
Table 1. Concentrations of the seven primary odor classes required to produce equal odor intensity.

Odor	Compound	Concentration (ppm)
Ethereal	Ethylene Dichlor	800
Camphoraceous	1,8 Cineole	10
Musky	Pentadecanlacton	1
Floral	Phenylethylmethyl ethylcarbinol	300
Minty	Methone	6
Pungent	Formic acid	50,000
Putrid	Dimethyl disulfide	0.1

The use of the seven primary odor classes is widely cited. However, it is unlikely that this list actually represents the true primary sensations of smell. More than 50 single substances have been identified in odor blindness studies, suggesting that there may be 50 or more sensations of smell.

A more flexible way of presenting the primary odors to clarify the idea of complex odors is through the use of Henning's odor prism (Fig. 2). Six primary odors are located at the corners of the prism. All other odors are mixtures of the primary odors and located on the surfaces and edges of the prism. Thus, odors consisting of two components would be represented on the edges of the prism, three-component mixtures occupy the triangular surfaces, and four-component mixtures occupy the square surfaces.

Figure 2. Henning's odor prism.



Odor interactions

Usually, an odorous stimulus is a combination of many scents. This is certainly the case in animal production facilities. The effect of one odor on another may be related to differences in the water solubility of the two odors resulting in a number of possible outcomes. Flowery, fruity odorants tend to have higher molecular weights. Aldehydes, esters, alcohols, ethers, halogens, phenols and ketones have more pleasant aromas than the lower molecular-weight carboxylic acids, nitrogenous compounds (not associated with oxygen), and sulfur-containing compounds. Blending of the two odors may occur, producing an odor with properties of both the original and properties unique to the newly-developed odors.

One odor may dominate another, or at least periodically, or the two odors may be smelled concurrently as individual odors. The complex nature of how odorants interact with each other is the primary challenge in determining how best to prevent odor formation. However, understanding that manure odors form as the result of incomplete breakdown of excreted products, and that many of these products are the result of excess protein in the diet can serve as the basis for odor management.

Resources

This publication, along with PM 1963a, Science of Smell Part 1: Odor perception and physiological response;
PM 1963c, Science of Smell Part 3: Odor detection and measurement (after 9/1/04)
PM 1963d, Science of Smell Part 4: Principles of Odor Control (after 9/1/04)
can be found on the Air Quality and Animal Agriculture Web page at:
http://www.extension.iastate.edu/airquality.

References

Powers-Schilling, W.J. 1995. Olfaction: chemical and psychological considerations. *Proc. of Nuisance Concerns in Animal Management: Odor and Flies Conference*, Gainesville, Florida, March 21-22.

Table and figures from Water Environment Federation. 1978. Odor Control for Wastewater Facilities. Manual of Practice No. 22. Water Pollution Control Federation, Washington D.C.

Prepared by Wendy Powers, extension environmental specialist, Department of Animal Science, and edited by Marisa Corzanego, extension communications intern, Communication Services, Iowa State University.

File: Environmental Quality 4-1

Issued in furtherance of Cooperative Extension work, Acts of May 8 and June 30, 1914, in cooperation with the U.S. Department of Agriculture. Stanley R. Johnson, director, Cooperative Extension Service, Iowa State University of Science and Technology, Ames, Iowa.