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STUDY OF ODOROUS COMPOUNDS PRODUCED BY PUTREFACTION OF FOODS

V*. FATTY ACIDS, SULPHUR COMPOUNDS AND AMINES

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SUMMARY

An investigation was made of the relationship between odour and odorous compounds in solid waste. A variety of foods were kept separately in 20-l polyethylene bottles at 23°C for 3 months and chemical analyses of the headspace gas and leachate were performed at regular intervals. In addition, the offensive odours were characterized by sensory tests. It was found that fatty acids and sulphur compounds were the main components producing the offensive odour of domestic waste and amines do not play an important role.

INTRODUCTION

Offensive odours are important problems in environmental studies, but the nature of these odours is not fully understood. In order to clarify the relationship between putrefaction and offensive odours in solid waste, the volatile compounds produced by putrefaction of foods have been investigated. We have previously isolated alcohols, esters, ketones, hydrocarbons, fatty acids, amines and sulphur compounds from solid wastes, and shown that alcohols, fatty acids and sulphur compounds are the major components.

Studies of the relationship between odour and odorous compounds in various materials have been carried out by several workers. Burnett[1] concluded that sulphur compounds, organic acids and skatole were important malodorous components of accumulated liquid poultry manure. Barth and Hill[2] reported that the odour intensity of cattle excrement was correlated with the volatile fatty acid, ammonia and hydrogen sulphide contents.

Yasuhara[3] found that fatty acids and sulphur compounds were the main com-

* For Part IV, see ref. 7.

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ponents with regard to malodour of solid swine manure, and Funasaka *et al.*[4] that volatile fatty acids, aromatic hydrocarbons and phenols were responsible for the offensive odour of living fish.

Little information has been obtained on the chemical nature of the odour of solid waste. In most of the reports on the odour of solid waste, the results of sensory tests were not discussed. Previous data[5–7] indicate that most of the odorous compounds concerned are probably fatty acids and sulphur compounds. However, it is not apparent whether there is relationship between odorous substances and the observed odour intensity. We have not previously elucidated the quantitative variation of the offensive odour produced by the putrefaction of foods.

This work was performed in order to attempt to explain these problems. A variety of foods were kept separately in 20-l polyethylene bottles for 3 months and the volatile organic compounds produced by anaerobic decomposition were identified by gas chromatography–mass spectrometry (GC–MS) and determined by GC at regular intervals.

In addition, the offensive odour was characterized by sensory tests. We report the quantitative variation of amines, fatty acids and sulphur compounds that were determined in high concentrations in previous work and possess unpleasant odours and very low threshold values.

EXPERIMENTAL

Sample preparation

A variety of foods, including fish, potato, cabbage, rice and apple, were kept separately in 20-l polyethylene bottles, each equipped with a glass tube and a thermometer. Each food was finely cut and kept at constant temperature (23°C) and relative humidity (38%) under anaerobic conditions. GC analysis of sulphur compounds and amines in the headspace gas and fatty acids in the leachate was performed at regular intervals.

Analytical method

Headspace gas analysis by GC with flame photometric detection was carried out for the determination of sulphur compounds using the cold trap method with liquid oxygen. The GC conditions were the same as in previous work[5].

Headspace gas analysis using a Shimazu GC 7A instrument with a flame thermionic detector was carried out for the determination of amines by the cold trap method with liquid oxygen. The GC conditions were as follows: column temperature, 70°C; injection temperature, 150°C; column, 2 m × 3 mm I.D. glass tube packed with 4% PEG + 0.8% potassium hydroxide on Carbopak B; and carrier gas (nitrogen) flow-rate, 50 ml/min.

To be able to quantify fatty acids in gases, it is necessary to take a large sample. A strong correlation between fatty acid concentration in the gas and the leachate has been reported[8]. Therefore, the fatty acid analyses reported here were performed using the leachate from putrid foods. Leachate (50–100 ml) was acidified with concentrated sulphuric acid to pH < 1.0, then steam-distilled. The distillate (300 ml) was collected in 5% sodium hydroxide solution (10 ml). After concentration, the fatty acids were liberated by the addition of phosphoric acid and examined by GC. The necessary distillation volume and the efficiency of the distillation technique were measured by adding known masses of each acid to 5% sodium hydroxide solution. The former was found to be about 200 ml and the fatty acid recovery was 85–90%. The GC conditions were the same as previously reported.

Sensory test

In addition to GC analysis, sensory tests[9] on odour concentration and acceptability were carried out by smelling the headspace gas. The term "odour concentration" was represented by the dilution of the headspace gas using the syringe dilution technique, the headspace gas being diluted with odourless air to the point at which panellists could not longer detect an odour. Acceptability is represented by the degree of pleasantness and unpleasantness on a nine-step scale.

RESULTS

Sulphur compounds

Figs. 1 and 2 show the variation of the concentration of sulphur compounds from each putrid food during 9 weeks.

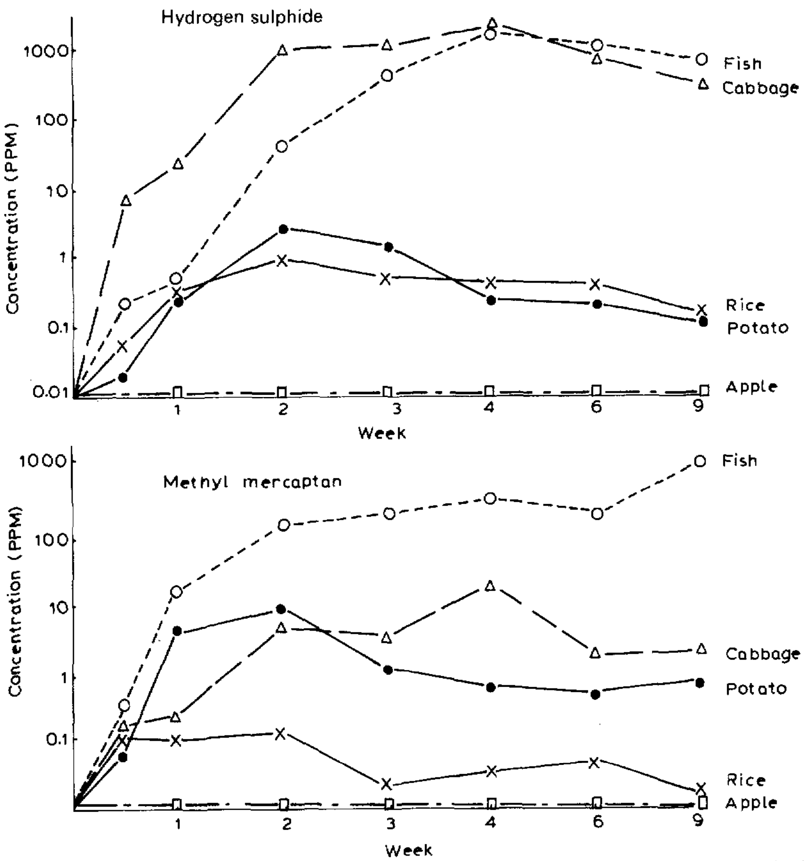

Fig. 1. Variation of concentration of hydrogen sulphide and methyl mercaptan in the headspace gas from putrid foods.

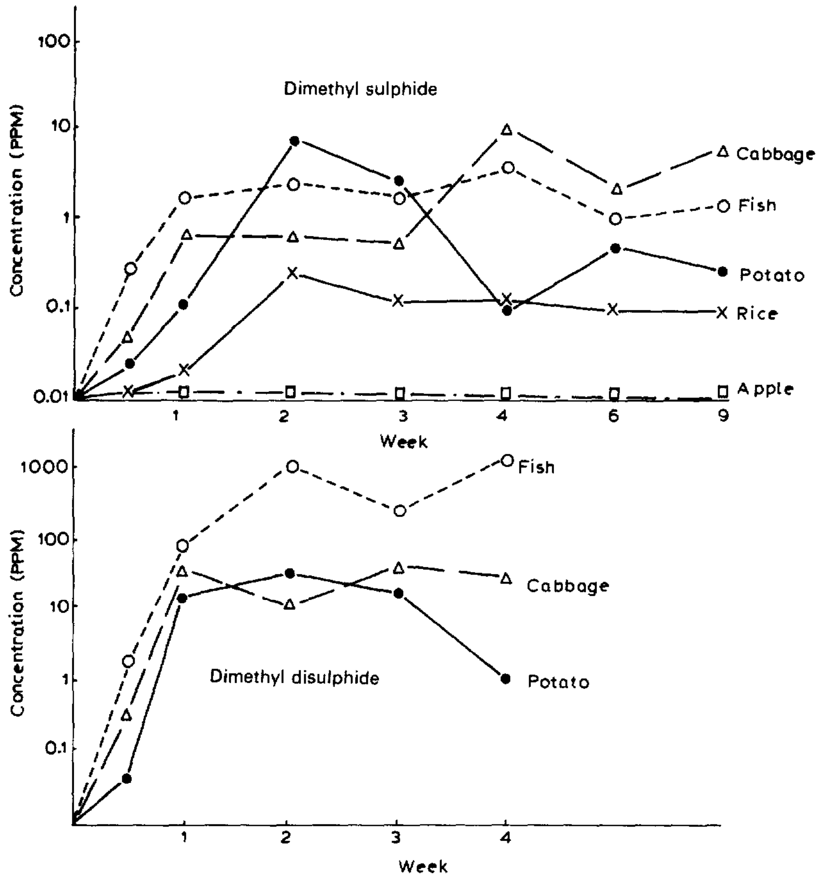

Fig. 2. Variation of concentration of dimethyl sulphide and dimethyl disulphide in the headspace gas of putrid foods.

The hydrogen sulphide concentration in the headspace gas from putrid fish increased continuously for 4 weeks and reached 1000 ppm; for putrid cabbage the level was 8 ppm after 3 days, 30 ppm after 1 week and 1000 ppm after 2 weeks, after which it remained almost unchanged; for putrid potato and rice the levels reached were much lower at 4 and 1 ppm, respectively, after 2 weeks, then decreased gradually; for putrid apple the concentration of sulphur compounds remained below 0.01 ppm.

The concentration of methyl mercaptan (and sulphur compounds in general) increased similarly in the order apple < rice < potato < cabbage < fish. For putrid fish the methyl mercaptan concentration increased continuously for 9 weeks and reached 1000 ppm. The dimethyl sulphide concentrations of all the putrid foods were lower than those of the other sulphur compounds and there was little difference among the putrid foods except for apple.

The highest concentrations of sulphur compounds were measured in the headspace gas of putrid fish and cabbage at about 1000 ppm. There was a considerable increase in the concentrations of all sulphur compounds in all putrid foods for first 2 weeks, and little variation thereafter.

The intensities of the offensive odour estimated by sensory tests increased in the order apple < rice < cabbage < potato < fish. Dimethyl trisulphide was detected in the headspace gas from putrid fish and potato by GC–MS. Fig. 3 shows the mass spectrum of the sample compared with that of the standard substance. This substance was detected in poultry manure and paper mill effluent by Hoshika[10] and in effluent from a sludge treatment plant by Zeman and Koch[11].

Fatty acids

Figs. 4–6 show the variation in the fatty acid concentrations in the leachate from each putrid food. The unit (ppm) used for fatty acid concentrations represent mg/l.

About 1000 ppm of fatty acids was determined in the leachate from putrid fish after storage for 1 week, as shown in Fig. 4. During the first week all fatty acid concentrations increased rapidly, and more slowly thereafter. After 4 weeks, all fatty acid concentrations except that of *n*-hexanoic acid were above 1000 ppm. After 10

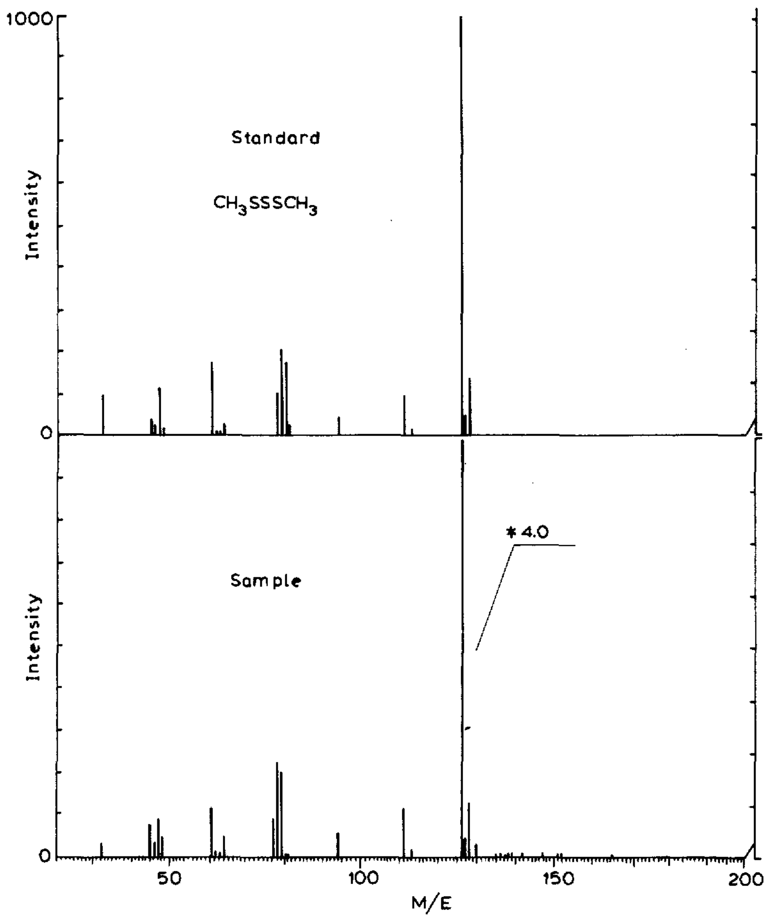

Fig. 3. Mass spectrum of methyl trisulphide.

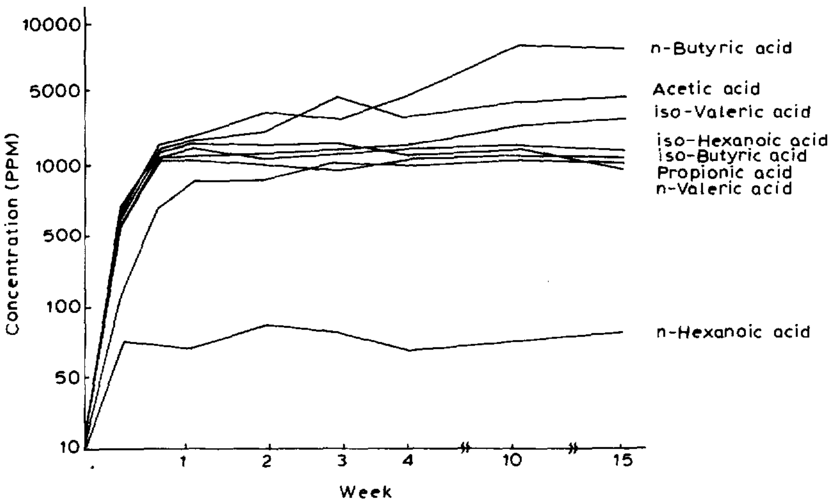

Fig. 4. Variation of fatty acid concentration in the leachate produced from putrid fish.

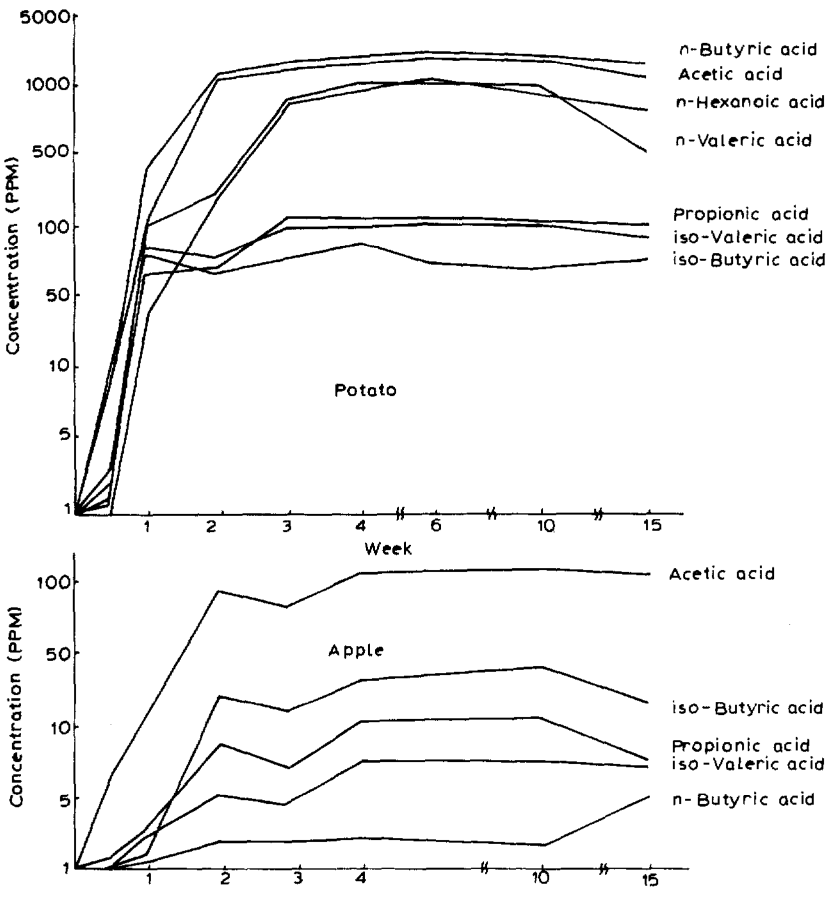

Fig. 5. Variation of fatty acid concentration in the leachate produced from putrid potato and apple.

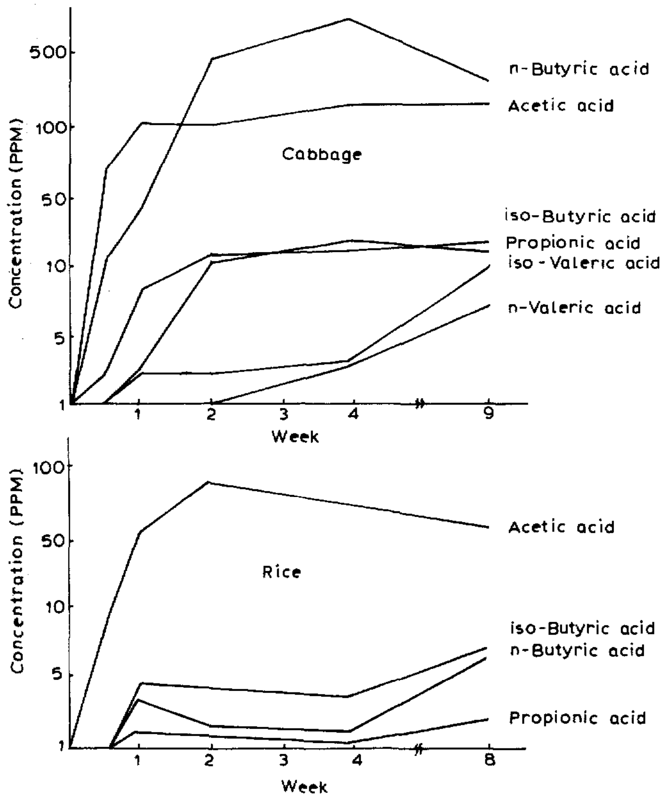

Fig. 6. Variation of fatty acid concentration in the leachate produced from putrid cabage and rice.

weeks the *n*-butyric acid concentration reached 8700 ppm. The concentrations of fatty acids above heptanoic acid were below 10 ppm.

The fatty acid concentrations in putrid potato were similar to those in fish, the acetic and *n*-butyric acid levels being heigher. The pH fell with increase in fatty acid concentration.

The fatty acid concentrations in cabbage were one order of magnitude lower than those in potato. The acetic and *n*-butyric acid concentrations in cabbage were in the range 200–700 ppm and those of other fatty acids were far lower. The acetic acid concentration in putrid apple was about 100 ppm after 2 weeks, and those of other fatty acids were far lower. The fatty acid concentrations in putrid rice were lower than those in the other foods and only a few fatty acids could be found in its leachate.

In general, fatty acid concentrations showed a tendency to increase in the order rice < apple < cabbage < potato < fish. The acetic and *n*-butyric acid concentrations in all foods were higher than those of other fatty acids. The fatty acid concentrations in all foods increased rapidly for the first 2 weeks and showed little variation thereafter, similarly to sulphur compounds. These results agreed with those for poultry manure reported by Burnett[1].

TABLE I

VARIATION OF ODOUR CONCENTRATION AND ACCEPTABILITY OF THE HEADSPACE GAS FROM PUTRID FOODS

Food	*Parameter*	*Week*						
		1	*2*	*3*	*4*	*6*	*9*	*15*
Fish	Odour concentration	200	1000	1500	2600	1600	2000	2000
	Acceptability*	−2	−3	−4	−4	−3	−3	−3
Potato	Odor concentration	64	2000	1000	800	1600	3200	1600
	Acceptability*	−2	−3	−3	−3	−2	−2	−2
Cabbage	Odor concentration	32	400	800	400		160	200
	Acceptability*	−1	−2	−3	−2	−2	−1	−1
Rice	Odor concentration	8	40	40	40		120	120
	Acceptability*	−1	−2	−2	−2	−1	−2	−2
Apple	Odor concentration	320	400	200	640	400	1000	1000
	Acceptability*	+1	−1	−1	−2	−2	−2	−2

* Scale for acceptability: +1, pleasant; 0, not clear; −1, slightly unpleasant; −2, unpleasant; −3, very unpleasant; −4, extremely unpleasant.

Amines

The trimethylamine concentration found in the headspace gas from putrid fish was 0.02 ppm after 3 days, 0.3 ppm after 1 week, 0.63 ppm after 2 weeks and 0.70 ppm after 3 weeks. The methylamine and ethylamine concentrations were below 0.1 ppm. The amine concentrations in the other foods were below the detection limit (0.01 ppm). Hence the amine concentrations were far lower than the fatty acid and sulphur compounds levels.

Sensory test

The results of the sensory tests on the odour concentration and acceptability of the headspace gas from all putrid foods are given in Table I.

The odours of the headspace gas from putrid fish and potato were very unpleasant or extremely unpleasant. The unpleasantness increased in the order apple $<$ rice $<$ cabbage $<$ potato $<$ fish. The odour concentration was proportional to unpleasantless except for the odour of putrid apple, which was not unpleasant, although it had a high odour concentration. The odour concentration of all putrid foods increased rapidly for first 2 weeks and subsequently showed little variation.

DISCUSSION

Many fatty acids and sulphur compounds generated by anerobic decomposition have been detected in all putrid foods except apple, but the concentrations of the individual component differed among the foods. There was a tendency for concentrations to increase for the first 2 weeks of storage and then to level off. The more fatty acids and sulphur compounds are produced by putrefaction, the more intense is the offensive odour.

Alkaline components, including amines and ammonia, were present in only small amounts and were not an important factor in odour production. It has been confirmed that fatty acids and sulphur compounds play an important role with regard to the offensive odours of solid waste, in agreement with results reported for a series of odours[1–4]. Yasuhara[3] performed chemical analyses and sensory tests on swine manure and reported that fatty acids and sulphur compounds were the main components, cresols increased the odour intensity and skatole changed the odour quality. It was concluded that although the main substances are fatty acids and sulphur compounds in pig slurry, poultry slurry, sewage treatment plant effluent and solid waste, each difference in odour is due to small amounts of other substances.

The concentrations of sulphur compounds are proportional to the protein content in food. The more protein is present in the food the higher is the concentration of sulphur compounds after putrefaction. Protein contents are 50% in fish, 18% in cabbage, 10% in potato, 8% in rice and 1.5% in apple (dry weight). Sulphur compounds are mostly produced from amino acids, which are mainly anaerobic decomposition products of proteins. Hydrogen sulphide is produced from cystine and cysteine, and methionine is a precurser of methyl mercaptan and methyl sulphide[12]. Fatty acids are produced by fermentation of saccharides and hydrolysis of proteins and fats.

These studies indicate that different foods produce the same volatile compounds, but in different concentrations.

Work in these laboratories on the analysis of alcohols, ketones, esters and compounds in the headspace gas from putrid foods has been reported recently[7]. These substances are qualitatively similar to fatty acids and sulphur compounds, but the concentrations of the individual components differed among the foods. There was little correlation between concentration and sensory tests for these substances.

CONCLUSION

The gases generated by decomposition of foods increase rapidly for first 2 weeks, then level off. Fatty acids and sulphur compounds are the main substances responsible for the offensive odours of solid waste and amine compounds do not play an important role. The odour intensity of putrid food depends on the concentration of fatty acids and sulphur compounds. The concentrations of fatty acids and sulphur compounds generally increase as the content of protein in the food increases. Different foods produce the same volatile compounds, but their concentrations differ among the food varieties. These results are consistent with those reported for other odour sources.

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