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Carbonyl Emissions during Food Decay from Kimchi, Fish, and Salted Fish

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ABSTRACT

In this study, the emissions of carbonyl compounds as offensive odorants were measured using three food types (Kimchi, fresh fish, and salted fish) as a function of time. Odor samples for each food type, collected at 0, 1, 3, 7, and 14 days, were analyzed by high performance liquid chromatography (HPLC). Only three kinds of carbonyl compounds were quantified above their respective detection limits: formaldehyde, acetaldehyde, and acetone. The emission patterns of these compounds were distinguishable from each other. Formaldehyde tends to peak at the beginning and decrease through time with unique patterns. Conversely, acetaldehyde and acetone seem to increase gradually through time. The results showed that relative patterns of carbonyl emissions were more distinguishable by compound type rather than food type.

Key words: Carbonyl, Food decay, Kimchi, Fresh fish, Fish with salt

1. INTRODUCTION

An odor consists of volatile chemical compounds that humans or animals can perceive even at very low concentrations by the sense of olfaction. Odors, like noise, can be a nuisance or disturbance, as it can create uncomfortable feelings above certain levels. Malodor is thus defined as the signal of ill feeling through the sensory organ, and this experience is more mentally (or psychologically) damaging than physically damaging. Consequently, malodor issues are commonly treated as a delicate socio-environmental subject (Emerson and Rajagopal, 2004; Davoli *et al.*, 2003). However, as it is difficult to control odors in the environment, all the technical skills involved in the measurement and evaluation of odorants are in great demand.

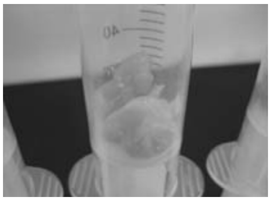
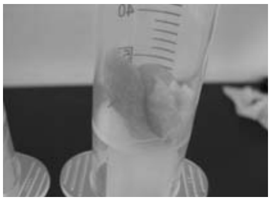
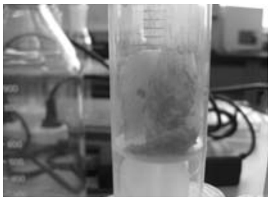
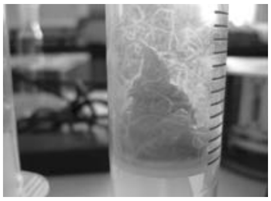
The chemical composition of a malodor can be assessed in relation to its diverse source characteristics (Whitehead and Cotta, 2004; Nahm, 2002). As some odorants are detectable at considerably small threshold concentrations, the mental and psychological impact caused by these compounds is more significant than others (Mackie *et al.*, 1998). This is because some of these compounds can be liable for their toxic effect on human beings when accumulated beyond a certain amount.

Decaying food is one of the most common sources of malodor in the environment. Odors are produced mainly by bacterial decomposition, volatilization and chemical reactions during the decaying process. The diversity and strength of odorant release from various food items may vary depending on several factors, such as the cooking process, quality and freshness of the food, temperature, etc. Among these odorants, carbonyl compounds have been designated as one of the most important chemical groups (Pang and Mu, 2006). Because of toxic and carcinogenic properties, the presence of carbonyls in the environment has been of great concern for public health and vegetation (CEPA, 1993). Some carbonyl compounds are well known for their odor characteristics and their roles in odor pollution in various respects (Kim *et al.*, 2008). In this study, the emission concentrations of carbonyl compounds were measured as a function of time during the food decaying process. All experiments were conducted at room temperature using three food types: Kimchi (KC), fresh fish (FF) and fish with salt treatment (FS).

2. MATERIALS AND METHODS

2. 1 Sample Collection

An equal amount (5 g) of fresh fish (FF), fish with salt treatment (FS), and Kimchi (KC) were sampled and placed inside a 100 mL (needless throwaway) syringe as shown in Fig. 1. Each syringe was then filled with air for a total volume of 60 mL, under the condition of not restricting air exchange and to allow for the collection of gas samples with Tedlar bags. For each food type, a total of five samples were prepared at the begin-

Experiment order	Elapsed time (No. of days)	KC[a]	FF[b]	FS[c]
1st	0			
2nd	1			
3rd	3			
4th	7			
5th	14			

Superscripts of a, b, and c denote Kimchi, Fresh fish, and Fish with salt, respectively

Fig. 1. A list of photographs showing the progress of the decay experiment at 0, 1, 3, 7, and 14 days.

Table 1. Basic information on the three major carbonyl compounds investigated during the study.

Order	Compounds	Cas No.	Acronym	Chemical formula	MW g mole^{-1}
1	Acetaldehyde	75-07-0	Acet-A	CH_3COH	44.05
2	Formaldehyde	50-00-0	Form-A	CH_2O	30.03
3	Acetone	67-64-1	Acetone	CH_3COCH_3	58.08

ning of the experiment to allow for measurements of the odorant concentrations at five different intervals (0, 1, 3, 7, and 14 days). For the analysis of each carbonyl, a 25 mL air sample was withdrawn from the syringe. It was then mixed with N_2 by injecting the sample into a 10 L Tedlar bag. Then, air samples from each Tedlar bag were passed through Lp DNPH cartridges (Supelco Inc., USA) at a normal set-up value of 10 min (at a fix-

Table 2. Concentration of carbonyl emissions from three food types: Kimchi (KC), fresh fish (FF) and fish with salt (FS).

(a) Raw data

Sample	Sample code	Number of days	Concentration (ppb)		
			Acet-A	Form-A	Acetone
Kimchi (KC)	A-1	0	7.77	33.8	14.7
	A-2	1	9.43	12.4	10.4
	A-3	3	9.63	7.59	9.62
	A-4	7	17.2	6.39	14.8
	A-5	14	29.0	2.70	10.9
Fresh fish (FF)	B-1	0	1.83[a]	450	14.5
	B-2	1	1.83	133	13.2
	B-3	3	1.83	43.1	19.8
	B-4	7	4.44	39.5	40.5
	B-5	14	1.06	8.59	34.2
Fish with salt (FS)	C-1	0	1.83	107	14.6
	C-2	1	0.712	61.3	45.0
	C-3	3	19.3	47.6	49.9
	C-4	7	49.9	39.5	42.1
	C-5	14	62.9	5.98	33.4

[a] The DL values for compounds with concentrations below the detection limit are underlined.

(b) Summary

Compound	Sample	Mean	SD	Median	Min.	Max.	N
Acet-A	KC	14.6	8.83	9.63	7.77	29.0	5
	FF	2.75	2.40	2.75	1.06	4.44	2
	FS	33.2	28.3	34.6	0.71	62.9	4
Form-A	KC	12.6	12.4	7.59	2.70	33.8	5
	FF	135	182	43.1	8.59	450	5
	FS	52.2	36.6	47.6	5.98	107	5
Acetone	KC	12.1	2.48	10.9	9.62	14.8	5
	FF	24.5	12.3	19.8	13.2	40.5	5
	FS	37.0	13.9	42.1	14.6	49.9	5

Concentrations in units of ppb

ed sampling flow rate, 0.8 L min^{-1}) via a Sep-Pak ozone scrubber (Waters, USA). After sampling, each cartridge was wrapped in aluminum foil and stored at 4°C before injection into the HPLC.

2.2 Carbonyl Analysis

Emissions of odorants are an important parameter used to assess the impact of chemical substances on air quality. The target analytes of this study are listed in Table 1. The analysis of the carbonyl compounds was performed using HPLC (Lab Alliance 500) equipped with a UV detector and dsCHROM software for peak integration. To initiate the analysis, the cartridges were eluted slowly with acetonitrile and filtered through 0.45 μm, mini spike, 13 mm, GHP Acrodisc filters (PALL, NY, USA) into 5 mL capacity borosilicate glass volumetric flasks. The eluate was manually injected into the HPLC system, equipped with a 20 μL sample loop. Carbonyl-hydrazones were separated on a Hichrom 250 × 4.6 mm ODS (octadecyl silane), 5 μm reverse phase C_{18} column using a mobile phase of acetonitrile+water (7 : 3 by volume) at a flow rate of 1.5 mL min^{-1} at a wavelength of 360 nm. Quantification of the carbonyls was performed against five point calibration curves drawn at 0.15, 0.3, 0.6, 1.2 and 4.8 ng μL^{-1} (at 20 μL injection volume). Liquid phase standards were prepared from the carbonyl-DNPH mix (Supelco, USA) at a wavelength of 360 nm.

The basic quality assurance for this research is provided in terms of detection limits (DL). The DL values for all of the carbonyl species were estimated by multiplying the standard deviation (SD) values of the least detectable quantities (in absolute mass or concentration unit) by a factor of 3. The DL values, if expressed in terms of mixing ratios (assuming a total sampling volume of 15 L), fell in the range of 1.46 (benzaldehyde) to 1.65 ppb (acrolein). The precision of analysis, if assessed in terms of the relative standard (RSE) value, tended to vary in the range of 1.06% (valeraldehyde) to 2.52% (isovaleradehyde).

3. RESULTS AND DISCUSSION

3. 1 General Pattern of Carbonyl Emission during Food Decay

In this study, the emission concentrations of carbonyl compounds were measured during the decaying process of three food types at room temperature: Kimchi (KC), fresh fish (FF), and fish with salt treatment (FS) (Table 2(a)). Our analysis of environmental samples based on the HPLC system allows us to quantify at least 13 carbonyl compounds. However, only three carbonyl compounds were measured above their DL from these decaying experiments: formaldehyde (Form-A), acetaldehyde (Acet-A) and acetone.

Acetaldehyde has a fruity smell and occurs naturally as an intermediate product in the respiration of higher plants. Acetaldehyde can be found in ripening fruit and vegetables, including apples, broccoli, coffee, grapefruit, grapes, lemons, mushrooms, onions, oranges, peaches, pears, pineapples, raspberries and strawberries (Acetaldehyde fact sheet), and it has been detected in the essential oils of alfalfa, rosemary, balm, daffodil, bitter orange, camphor, angelica, fennel, mustard and peppermint (Acetaldehyde fact sheet). Acetaldehyde also naturally occurs as a result of forest fires, volcanoes, animal waste and insects. The health impact of acetaldehyde is well known, as it is an irritant of the skin, eyes, mucous membranes, throat and respiratory tract (CEPA, 1993). Hence, exposure to acetaldehyde can cause such symptoms as nausea, vomiting, headache, dermatitis and pulmonary oedema (fluid in the lungs). As such, it is a substance which may reasonably be anticipated to be a carcinogen (Acetaldehyde fact sheet).

Formaldehyde is a flammable, colorless gas with a pungent, suffocating odor. It is released into the environment from both anthropogenic and natural sources. It occurs naturally in fruits and some foods, while it is formed endogenously in mammals, including humans, as a consequence of oxidative metabolism of many xenobiotics (IRIS, 2007). Combustion processes from automobile exhaust, power plants, incinerators, refineries, wood stoves, kerosene heaters and cigarettes account for the dominant fraction of its release into the environment (ATSDR, 1999). The primary routes of potential human exposure to formaldehyde are inhalation and dermal contact. If exposed to low levels of formaldehyde, irritation of the eyes, nose and throat can occur. Such exposure can also cause allergies by affecting the skin and lungs. At higher exposure levels, people can experience throat spasms and a build up of fluid in the lungs which can lead to death. Contact with formaldehyde can also cause permanent damage and severe eye and skin burns. It is also known as the cause of an asthma-like respiratory allergy. Hence, repeated exposure to formaldehyde may cause bronchitis, with coughing and shortness of breath (IRIS, 2007). In 2004, the National Occupational Health and Safety Commission classified formaldehyde as a potential carcinogen.

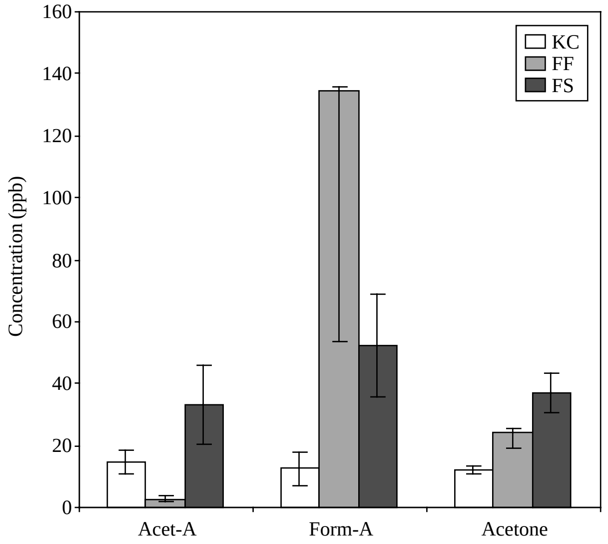


Fig. 2. Comparison of the mean emission concentrations of carbonyl compounds during the decaying process of Kimchi (KC), fresh fish (FF), and fish with salt (FS).

Acetone is a colorless compound with a distinct smell and taste. If skin is exposed to acetone, the compound can go into the blood supply and be carried into organs. However, the liver can break down small quantities of acetone into a less harmful form and utilize its energy for normal bodily functions. If a human breathes moderate- to-high levels of acetone for short periods of time, the following symptoms are expected to occur: nose, throat, lung and eye irritation, headaches, light-headedness, confusion, an increased pulse rate, effects on blood, nausea, vomiting, unconsciousness and shortening of the menstrual cycle in women (ACETONE, 1995).

If the emission patterns of the different food types are compared in terms of magnitude, the results of the KC appears to be the least variable, with the mean values of all compounds near 15 ppb (Fig. 2). However, if their differences are compared in absolute terms, their mean values differ by approximately two orders of magnitude. In the case of the FF sample (Table 2(b)), the emission patterns vary from 2.75 ppb (Acet-A) to

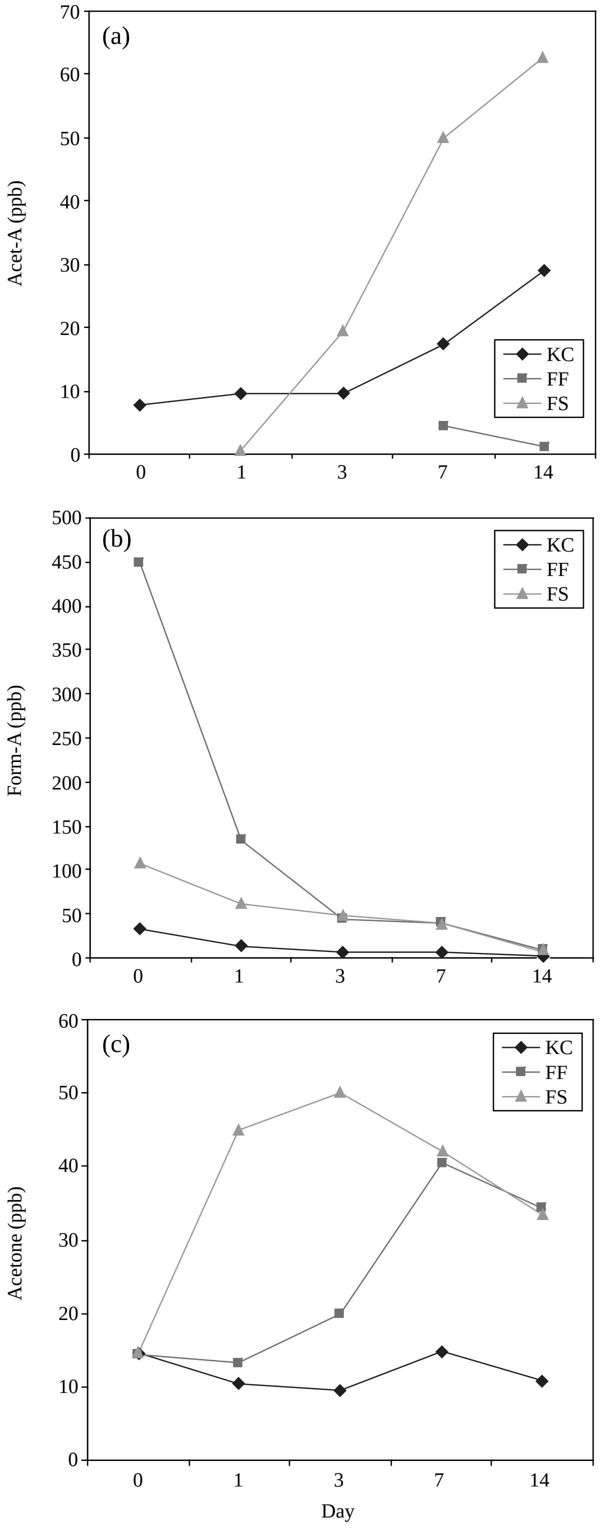


Fig. 3. Temporal changes in emission concentrations of carbonyl compounds during the decay process of Kimchi (KC), fresh fish (FF), and fish with salt (FS): the results are compared for each of the three compounds (a) Acet-A, (b) Form-A, and (c) Acetone.

135 ppb (Form-A). In the case of FS, the concentration differences are moderate between three compounds, in decreasing order of Form-A > Acetone > Acet-A.

3. 2 Temporal Variation of Food Decaying Process

The results derived using three food types showed that there are highly unique patterns for each compound in relative terms, but not between the different food types (Fig. 2). The concentrations (ppb) of formaldehyde formation decreased fairly consistently through time for all three types of food: from 33.8 (d=0) to 2.70 (d=14) in KC, 450 to 8.59 in FF and 107 to 5.98 in FS. In contrast, the concentrations of acetaldehyde increased in KC from 7.77 (d=0) to 29 ppb (d=7), and from 0.71 to 62.9 ppb in FS, as time advanced. However, in the case of the FF sample, the patterns of Acet-A emissions were moderately different from the others. More specifically, acetaldehyde initiated its emission after 7 days at concentration levels of 4.44 (d=7) and 1.06 (d=14) ppb. The emission concentrations of acetone also showed an upward trend, but the values tended to peak either by 1 day (FS) or 7 days (KC or FF).

As food begins to decay, the emission concentrations of an odor can vary as a function of time. Fig. 3 shows the emission patterns of these three carbonyl compunds for all three food types as a function of time. In all three cases, the values of Form-A were the highest at the beginning stage. In a number of previous studies, the highest concentrations of formaldehyde naturally occurring in foods are found in some fruits, up to 60 mg/kg (Tsuchiya *et al.*, 1975; Möhler and Denbsky, 1970), and some marine fishes (Tsuda *et al.*, 1988; Rehbein, 1986). Formaldehyde develops postmortem in marine fish and crustaceans through the enzymatic reduction of trimethylamine oxide to formaldehyde and dimethylamine (Sotelo *et al.*, 1995). Although formaldehyde can be formed during the aging and deterioration of fish flesh, it does not accumulate in fish tissue, due to subsequent conversion into other chemical compounds (Tsuda *et al.*, 1988). Formaldehyde formed in fish reacts with protein and can subsequently cause muscle toughness (Yasuhara and Shibamoto, 1995). It is thus suggested that fish containing the highest levels of formaldehyde (e.g., 10-20 mg/kg) may not be considered palatable as a human food source. It should also be noted that formaldehyde is often used as a preservative in some foods, such as some types of cheeses, dried foods and fish (Toxicological Profile for Formaldehyde, 1999).

As shown from our study, the emission of acetaldehyde is a significant process during food decay. Considering the environmental toxicity of acetaldehyde, its production pattern from decaying foods needs to be carefully evaluated. Acetaldehyde is used as a preservative for fruit and fish, as well as a flavoring agent. Hence, acetaldehyde emission can be expected from various food types. Our experimental results show that emission concentrations of acetaldehyde increased over time, especially from salted fish. Although acetaldehyde is produced by fish foods during decay, its harmful impact on live fish is also well known. Based on measured concentrations of acetaldehyde, the 96-hour LC_{50} (Lethal Concentration 50) was 30.8 mg-L^{-1} for fathead minnow (*Pimephales promelas*) (Brooke *et al.*, 1984). Other short-term LC_{50} values for fish, including the guppy (*Poecilia reticulata*), the pinfish (*Lagodon rhomboides*), and the bluegill (*Lepomis macrochirus*), range from 33 to 140 mg-L^{-1} (Von Burg and Stout, 1991; Geiger *et al.*, 1990; Deneer *et al.*, 1988; Grahl, 1983; Juhnke and Luedemann, 1978; Daugherty and Garrett, 1951). For microorganisms, the most sensitive effect of acetaldehyde is found with the protozoan *Chilomonas paramecium*, with a 48-hour EC_{50} (effective concentration) of 82 mg/L (Von Burg and Stout, 1991). Five-day LC_{50} values for the diatom *Nitzchia linearis* range from 237 to 249 mg/L (Patrick *et al.*, 1968). A 25-minute EC_{50} of 303 mg/L was reported for *Photobacterium phosphoreum* in a Microtox test (Chou and Que Hee, 1992).

Likewise, acetone concentration also increased as time advance during the experiment. Approximately 97% of the acetone released to the atmosphere comes from natural sources. It is a natural product of metabolism in the body (virtually every organ and tissue). Natural sources of acetone generally include forest fires, volcanoes, and the metabolism of vegetation, insects and animals (Acetone VCCEP Submission, 2003). Acetone also occurs naturally as a biodegradation product of sewage, solid waste, alcohols and as an oxidation product of humic substances. Acetone has been detected in a variety of plants and foods, including onions, grapes, cauliflower, tomatoes, morning glories, wild mustard, milk, beans, peas, cheese and chicken breast (Lovegren *et al.*, 1979; Grey and Shrimpton, 1967; Day and Anderson, 1965). The results of our study thus suggest that acetone may belong to a major carbonyl that is released during the food decay process.

4. CONCLUSIONS

In this study, the emission concentrations of carbonyl compounds were measured from three types of food samples during the decaying process over a 14-day period. The results of our analysis showed that concentration changes of carbonyls occurred fairly noticeably during the food decay process. The relative patterns of their emissions were characterized more distinctively by compound type rather than food type. This is because each compound tends to maintain relatively similar patterns of emission through time. For instance, although formaldehyde showed decreasing concentration through time, others tended to increase through time, regardless of food type.

Until recently, the number of data that quantified odor emissions from food waste gases was limited. To be successful in odor control, these data need to be obtained and evaluated carefully. The basic principles for controlling odors are the reduction of odors at the emission sources and/or the removal of odors from airstreams before discharge into the atmosphere. Source control can be affected by using low-emission processing and good housekeeping techniques. In order to develop environmentally sound, sustainable food waste operations, we need to integrate research areas including modern analytical techniques, the latest sensory technology for odor analysis, and a fundamental knowledge associated with the production of odor and pollutants.

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