

Appendix A

Odor Characterization, Assessment and Sampling

Odor Characteristics

Odors are characterized and measured psycho-sensory, social, and somatic well as by their physical-chemical



by their impacts as properties.

Sensory Characterization

Sensory evaluation of odors involves description of the odor character as well as measurement of odor intensity, pervasiveness, and quantity. **Character** of an odor is a word description of what it smells like, e.g., rotten cabbage, rose, cinnamon. The character of an odor and its desirability (good, bad, or neutral) influences its acceptability when perceived.

Intensity is a measure of the perceived strength of an odor. This is determined by comparing the odorous sample with a “standard” odor, often various concentrations of n-butanol in odor-free air. Intensity is expressed in terms of micrograms per liter of butanol ($\mu\text{g}/\text{l}$) in liquid, milligram per cu. meter ($\text{mg}/\text{cu. m}$) in air, or ppm butanol. Intensity is also used to calculate pervasiveness.

Pervasiveness (persistence) describes how noticeable or detectable an odorant is as it's concentration changes. A pervasive odor is one that can be perceived by people even though the odor has been diluted many times. Pervasiveness of an odor is determined by serially diluting the odorant-containing sample and measuring the intensity at each dilution. When the results are plotted on log-log paper, an intensity slope is established. A flat slope (e.g., 0.2) would reflect a very pervasive odor because the odor can still be detected after millions of dilutions. Conversely, a steeper slope (e.g., 0.5) would reflect a much less pervasive odor, or one that would not be detectable

after only a few hundred dilutions. Organic sulfur-containing compounds, e.g., dimethyl disulfide, can often be described as pervasive because the odor may be detected off-site where it is present at very low concentration. The fact that it is not smelled on-site even though it is present at higher concentrations than it is off-site, can be explained by the masking effects of ammonia. The latter typically would have such an intense odor close to the source, that other co-occurring odorants would not be perceived.

Quantity of odor, as measured on a sensory response scale (i.e., based on odor detection), is expressed in terms of how many dilutions it takes before it is no longer detectable, although the exact character of the odor may not be discernible. This is often expressed as dilutions to threshold or odor units.

If the quantity is expressed in parts per million (ppm) or billion (ppb) or in moles or micrograms per cubic meter of specific chemical compound, then the determination is no longer sensory, rather, the value represents the physical, chemical amount of an odorant (explained in greater detail in this appendix).

Odor Assessment

Effective management of odorous emissions requires a systematic method for odor assessment and sampling. This can involve a perceptual response method, an analytical instrument approach, or a process that uses elements of both approaches. Regardless of how specific odorants are determined (chemically or perceptually), managing odorous emissions and alleviating odor nuisance remains the desired end result of odor evaluations and assessments.

Field Practice Options

Several approaches available for field assessments of odor include:

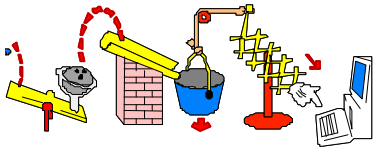
1. pro-active use of on-site and community odor surveys by site or facility operator and staff (see the Springfield odor survey forms at the end of this appendix)
2. use of portable sensory instruments by trained odor inspectors (see the St. Croix sensory example performance standard procedure at the end of this appendix)
3. application of public nuisance criteria
4. evaluation of odor samples by an odor panel
5. use of an annoyance survey coupled with quantitative chemical analysis of odorous air samples in a potentially impacted community

6. establishment of quantitative standards for known odorous compounds coupled with regular air sampling and chemical analysis

Although several of these approaches (1,2,4) use measurement and evaluation, they may fail to provide accurate assessments for several reasons. First, the concentration of the offending compound(s) may be below current standards. Second, there may not be standards for them, or, third, in the case of the odor panel, responses may not correspond to the evaluations of people in the affected community. For these reasons, odor or annoyance surveys (approach 5) may assist operators, communities, and regulators in fairly determining and evaluating odor problems and effectiveness of abatement actions.

The use of odor or annoyance surveys, especially in combination with air sampling (approach 6), can help objectively determine the presence or absence of nuisance odors in a community. This approach differs significantly from the three typical approaches used by regulatory agencies to deal with odor problems. In addition to collection of air samples for odorous compounds in an affected community (such as described below), an odor or annoyance assessment might include a scientifically designed public opinion survey, which draws opinions from randomly selected individuals in the community. To keep the odor component of a community survey unbiased relative to other community annoyances and environmental impacts, the survey may also include questions about other environmental factors such as noise, traffic, stray or wild animals, and other community characteristics.

Physical-Chemical



Both organic and inorganic compounds have been identified as odorous constituents of wastewater, solids, and biosolids. Compounds typically of concern can be formed during aerobic or anaerobic decomposition of proteins and carbohydrates that are abundant in wastewater and biosolids. Table A-2 lists common odorous compounds associated with biosolids. Many of these compounds are intense (see discussion below) and have odor thresholds in the parts per billion (ppb) concentration ranges. Odor threshold is the minimum concentration required for an individual to perceive the odorant. The main odorants emitted from biosolids include:

Ammonia. Ammonia is most often found in emissions from freshly alkaline stabilized materials and during early phase composting. Table A-1 shows the considerably greater odor threshold for ammonia than for reduced sulfur compounds. At least 100 to 1000 times more ammonia than reduced sulfur compound is needed per unit volume of air for an average person to detect it, even with the variation in reported odor thresholds.

Ammonia also has an important special characteristic that field site operators need to recognize. At high concentrations, it is so intense that it strongly masks odors from other compounds, such as those containing reduced sulfur groups. Thus, a misleading assessment report indicating no potential for off-site odor, could result if only ammonia were detected directly at the field

storage site. In fact, reduced sulfur compounds also might be present, but not detectable, because of ammonia masking. However, as the air 'parcel' containing both types of compounds moves downwind, beyond the storage/application site perimeter, ammonia could be diluted below its detection threshold. In contrast, the reduced sulfur compounds, although also diluted below their on-site concentrations, may still be concentrated enough to remain above their detection thresholds. For this reason, odor assessments at field storage sites should include some monitoring for off-site reduced sulfur or amine odors.

Ammonia that is emitted comes from anaerobic bacterial digestion of proteins found in the stored materials. As the pH of the materials increases above 8.0, more ammonia is released. Ammonia is often accompanied by release of amines, and if chlorine is used, chloramines may be released as well.

Inorganic sulfur compounds such as hydrogen sulfide. Hydrogen sulfide (H₂S) often gets the most attention because of the familiar rotten egg odor associated with it. However, it is rarely detected in field stockpiles. Often other compounds or combinations of compounds listed in Table A-2 are the primary cause of odor in biosolids. When pH is less than 9.0, hydrogen sulfide can be generated from wastewater solids under anaerobic conditions. Increasing the pH to 9.0 or higher, as happens when biosolids are lime stabilized, can eliminate H₂S emissions.

Organic sulfur compounds. Dimethyl disulfide (DMDS) and dimethyl sulfide have been associated with odorous emissions from biosolids composting operations. Also, it has been measured at wastewater solids and dewatering facilities, pelletizing facilities, and digester gas. In general, DMDS is a by-product of chemical or microbial degradation (anaerobic) of proteins.

Mercaptans or thiols are a generic class of straight-chained organic compounds that contain a single sulfur molecule. Methyl mercaptan is the most common thiol measured in biosolids emissions. Table A-2 shows methyl mercaptan has a low odor detection threshold, i.e., quite small amounts are easily detectable. Thus, its presence can lead to odor complaints. Two methyl mercaptan molecules combine to form one DMDS molecule. Active ingredients of garlic (allyl sulfide) and onions (propanethiol) have precursors that are similar to mercaptans; spoiled broccoli also produces mercaptans and DMDS. The boiling point of methyl mercaptan is 6°C, which makes it a gas at room temperature. Therefore, measurement techniques that use tedlar bags are acceptable.

Volatile fatty acids (VFAs). These short chain (< C₈) fatty acids have the general formula C_nH_{2n} + COOH and are typically generated during anaerobic decomposition of vegetable materials, such as hay, straw, grass, leaves, silage, etc. VFAs include: formic, acetic, propionic and lactic, butyric and iso-butyric, valeric, and iso-valeric, caproic and iso-caproic, and heptanoic acids. VFAs are volatile and are subject to rapid microbial decomposition under aerobic conditions. Production of phytotoxic quantities of VFAs during composting (prior to compost maturation) are known to occur. The VFAs are

APPENDIX A – ODOR CHARACTERIZATION, ASSESSMENT AND SAMPLING

most likely to be involved in odorous emissions when vegetative matter is present, such as occurs in the first stages of a composting operation when grass and green matter are delivered and sorted. They are unlikely to occur with biosolids alone.

Amines. These compounds can be produced in easily detectable quantities during high temperature processes. In composting, amines result from microbial decomposition that involves decarboxylation of amino acids. The amines that are produced are easily volatilized when temperatures are elevated above about 27°C. In biosolids produced with polymeric flocculating agents, high ambient temperatures can accentuate volatilization of amines that may be microbially split off from the core backbone of the polymer. Amines include: methylamine, ethylamine, trimethylamine, and diethylamine. Amines often accompany ammonia emissions, and if chlorine is used chloramines may be released.

Table A-1. Range of Odor Thresholds for Selected Sulfur Compounds, Ammonia, and Trimethylamine as reported in the literature †

COMPOUND	ODOR CHARACTER	A µg/l	B µg/l	C µg/l	D µg/l	E µg/l	F µg/l	G µg/l
Hydrogen Sulfide	Rotten eggs	0.47	0.47	4.70	0.5 - 10.0	4.8	0.50	8.1
Dimethyl Sulfide	Decayed cabbage	0.10	1.00	3.00	2.5 - 50.8	1.00	1.00	--
Dimethyl Disulfide	Vegetable sulfide	--	1.00	--	0.1 - 346.5	--	--	--
Methyl mercaptan	Sulfidy	1.10	1.10	0.50	4.0 X 10 ⁵ -82	2.10	0.50	1.6
Ammonia	Pungent, irritating	--	37.0	470	26.6 -39,600	46,800	17,000	5,200
Trimethylamine	Fishy, pungent	--	--	--	0.8	0.21	--	0.2

† Letters correspond to the references cited as follows: A = Bowker et al. 1989; B=Versucheren, 1996; C=National Research Council, 1979; D=Ruth, 1986; E=Leonardos et al., 1969; F=Buonicore and Davis, 1992; G= Amoore and Hautala, 1983.

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TableA-2. Selected odorous compounds observed in association with manure, compost, sewage sludge and biosolids as reported in the literature with corresponding ranges of odor threshold values †‡

Compound	Odor Character	Odor Threshold	
		$\mu\text{l/l}$	($\mu\text{g/l}$)
<i>Nitrogenous compounds</i>			
Ammonia	Sharp pungent	5.2 ‡	(150)
Butylamine	Sour, ammonia-like	1.8 ‡	(6200)
Dibutylamine	Fishy		(0.016)†
Diisopropylamine	Fishy	1.8 ‡	(1300)
Dimethylamine	Putrid, fishy		0.13 (470)
Ethylamine	Ammonical	0.95 ‡	(4300)
Methylamine	Putrid, fish	3.2 ‡	(2400)
Triethylamine	Ammonical, fishy	0.48‡	(0.42)
Trimethylamine	Ammonical, fishy		0.00044 ‡
<i>Nitrogenous Heterocyclics</i>			
Indole	Fecal, nauseating	(0.00012 - 0.0015)†	
Skatole	Fecal, nauseating	(0.00035 - 0.0012)†	
Pyridine	Disagreeable, burnt pungent	0.17‡	(0.95)
<i>Sulfur-containing compounds</i>			
Dimethyl sulfide	Decayed vegetables	(0.0003 - 0.016) †	
Diphenyl sulfide	Unpleasant	(0.0026) †	
Dimethyl disulfide	Vegetable sulfide	(1.00)†	
Hydrogen sulfide	Rotten eggs	8.1‡	(0.000029)
Sulfur dioxide	Pungent, irritating	1.1‡	(0.11)
Amyl mercaptan	Unpleasant, putrid	(0.0003)†	
Allyl mercaptan	Strong garlic, coffee	(0.000005)†	
Benzyl mercaptan	Unpleasant, strong	(0.013)†	
Crotyl mercaptan	Skunk-like	(0.00000043)†	
Ethyl mercaptan	Decayed cabbage	0.00076‡	(0.0000075)
Methyl mercaptan	Decayed cabbage, sulfidy	0.0016 ‡	(0.000024)
Propyl mercaptan	Unpleasant	0.0000025 - 0.000075	
n-butyl mercaptan	Skunk, unpleasant	0.00097	(0.000012)
Thiocresol	Skunk, rancid	(0.0001)†	
Thiophenol	Putrid, garlic-like	(0.00014)†	
<i>Other chemicals or compounds</i>			
m-Cresol	Tar-like, pungent	0.000049-0.0079	(37)
n-butyl alcohol	Alcohol		0.84‡
Chlorine	Pungent, suffocating	0.31‡	(0.0020)
Acetaldehyde	Pungent fruity	0.050 ‡	(0.034)

† O'Neill and Phillips, 1992; Vesilind et al., 1986; converted from weight by volume concentration (mg/m^3) to $\mu\text{g/l}$

‡ Amore and Hautala, 1983; $\mu\text{l/l}$ is the odor threshold for dilutions in odor-free air, and $\mu\text{g/l}$ is the odor threshold; both units are equivalent to parts per million.

Odor Determination

Odor Sample Collection

The need for odor sample collection is most likely to occur in the case of a longer term, constructed storage facility that has been unable to resolve odor emissions. In such a case, the facility operators may seek a more analytical approach upon which to base a remediation program. The proper collection of an air sample containing odorous compounds is essential for accurate analysis of the source of the odor. This is true for both qualitative and quantitative methods of odor analysis. The composition of an odor can range from a single chemical compound to a complex mixture of compounds. The components of the odor will often dictate the method of sampling. Therefore, insight as to which compounds or type of compounds may be contributing to the odor is desirable. Without this, a sampling method that can handle a broad range of compounds would be necessary. After identifying the type or group of odorants present, an appropriate sampling method can be used.

Several aspects should be considered when choosing an appropriate sampling method. The physical and chemical properties of the odorant will often determine which sampling method is desirable. Some of these properties are the polarity, volatility, and stability of the chemical compounds associated with the odor. To analyze the sample accurately, the composition of the odorant(s) must remain intact during sample collection. Condensation, adsorption, or permeation of the odorous compounds through the walls of the collection system can cause errors. For example, the boiling point of DMDS is 109°C, which means it is a liquid at ambient temperature. This physical property greatly influences DMDS emissions and measurement: elevated temperatures will dramatically increase DMDS emissions. When measuring DMDS and other compounds with high boiling points, it is important not to use sampling techniques that allow the sample to cool before it enters the analytical detector. Otherwise, these compounds will condense on the interior of the sample container, such as Tedlar bags, and results will be negatively biased.

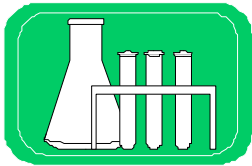
There are two main types of sources that are the focus of air sampling, area sources (such as from a pile) and point sources (such as from a stack); point sources can be more reliably sampled than area sources. At a biosolids storage site and its surrounding neighborhoods, ambient (outdoor) air would typically be the source for sample collection. The odors may still be intense (strong) even though the odorants are less concentrated at increasing distances from the facility. If scrubbers are used, stack emission samples are collected in the stack after scrubbers.

Odor samples can be collected in canisters, Tedlar bags, flux chambers, and adsorbent tubes. Adsorption tubes filled with Tenax packing and/or activated carbon are the most common types of traps used for ambient air sampling. Industrial hygienists often utilize specific adsorbent tubes for on-site analysis of specific individual compounds like ammonia, hydrogen sulfide, etc.

Sample Analysis

The ability to detect, identify, and quantify odorants in biosolids and other stored materials is an essential tool in the study of odors and in the development of prevention and mitigation treatments. If there is some correlation between the concentration of odorants found by an analytical method and the odor itself, then this tool is most useful. Since some odorants have low odor thresholds, the detection limit of an analytical method must be low or the odorants must be concentrated prior to analysis. The odorants and their concentrations in a sample will influence the choice of a method of analysis. The sampling approaches described below cover the range of simple, rapid, field methods for easy practical use through to the very complex instrumentally dependent methods, requiring laboratory analysis.

Sensory Odor Analysis



Characterizing the sensation experienced by inhaling an odorous sample is the object of a sensory odor measurement program. The human body experiences sensations, processes them, and then reacts. The olfactory system senses odor. Sensory analysis is most effective for samples containing complex mixtures of odorants or odorants at concentration levels below detection of an instrumental technique. It also produces simple, useful results that are meaningful to all concerned. Standardized testing protocols are now available for measuring odor intensity (ASTM E 544-75-88) and odor to threshold ratio (ASTM E679-91).

Odor Character Descriptors - In addition to the intensity of an odor, what an odor smells like is a big factor in determining whether it is objectionable. What an odor smells like is called the odor character and can be described through the use of various descriptors--words or phrases that most accurately represent the quality of the particular odor of concern. Each panelist is asked to describe the odor that was sensed. The problem with odor descriptors like "sweet," "musty," "sour," "putrid," "rotten," etc. is that different individuals may use a variety of words or phrases to describe the same odor. Even using what is called a "Hedonic Scale," which provides the panelist with a numbered scale or one with odor descriptors already provided, does not eliminate the human factor and the subjective nature of odor relative to its effect on different individuals.

Trained Odor Investigators - An extension of the use of simple odor descriptors is the odor patrol which utilizes trained odor investigators--people who have been trained to detect odor intensities. These people have "calibrated" their noses to certain odor intensities. They are trained to go "on site" and rate the odor intensity on a numeric scale. (see Chapter 2 for examples). Some examples of the types of written reports used for record keeping on-site and for citizen odor complaints appear at the end of this Appendix.

Scentometer - For direct field measurement of dilution-to-threshold, this hand-held device is sometimes used. Varying proportions of ambient (odorous)

air, drawn through a activated carbon filter, are introduced to an individual's nose. The ratio of ambient air to filtered air at which the individual detects an odor becomes the dilution-to-threshold. Odor inspectors using this method require training and experience so they can develop confidence in its application. This device has been used successfully by some inspectors in a few states.

Olfactometry - An olfactometer with an odor panel is another way to conduct a sensory analysis of odorous air samples. An olfactometer is an apparatus that presents an air sample containing the odorous component to an individual at varying dilutions with odor-free air. The object is to determine what level of dilution is necessary for each panelist to begin to detect an odor. From a series of these exposures, results for the odor panel can be calculated. These results can be expressed in the form of an odor to threshold ratio, or dilution level required for a percentage of the panel to detect the odor.

The Butanol Wheel - The intensity of an odor is also an important parameter when measuring odors. However, since the characteristic odors of various compounds are so different, it is difficult for individuals to compare the relative strengths or intensities of different odors. This can be overcome by using a reference compound to which the odor strengths can be compared. In this way, odors can be analyzed so that individuals not subjected to the actual odors can understand the results. The reference compound that is most widely used is n-butanol. A Butanol Wheel (2 - Procedure A) is used to measure the intensity (strength) of an odor by this comparative method.

The Butanol Wheel is similar to the olfactometer because it delivers the odorous compound and dilution air into ports to make different dilutions. The odorous compound in this case is the butanol vapor. The intensity of an odorous sample is measured by determining at what dilution level of the Butanol Wheel the sample matches the strength of the butanol vapor. An odor panel (group of people, each one exposed to the odor sample and butanol reference independently) is used to make the comparisons. By calculating the dilution of n-butanol vapor to which the odorous sample is equivalent, it is possible to express the intensity of the unknown odor in terms of a known intensity.

One of the principal differences between the forced-choice ascending concentration and the butanol wheel methods is that in the latter the odorous sample is tested at full strength against a series of diluted standards, whereas in the olfactometer method, the odorous sample itself is diluted as it is being evaluated. This difference results in assessment of odor intensity as well as dilution threshold ratio, two different sensory characteristics of the odor. This makes these two sensory test methods complementary to each other.

Chemical Analyzers and Instruments

There are many instruments and methods that can accurately measure odorous compound concentrations. One that combines sampling and analysis

is a hand-held reactive absorbent tube, which is available for ammonia, hydrogen sulfide, and several other compounds of concern to industrial hygienists. There are single compound analyzers, such as a hydrogen sulfide (H₂S) meter, that measures one analyte. Multiple compound analyzers, like a gas chromatograph (GC), can measure more than one analyte. There are specific detectors for a GC that are sensitive to certain types of compounds. If these types of compounds are unknown or their mixture is complicated, then a mass spectrometer detector and an electronic library of compounds is necessary. The latter is an expensive and sophisticated analytical approach and one that is usually reserved for a research setting, not typically routine monitoring.

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SPRINGFIELD, MA ODOR NOTIFICATION FORM

The purpose of this form is to identify odors than can potentially migrate off Bondi Island, where the Springfield WWTP is located and to communicate those observations to the respective island facilities. Such a form could be applied to a large field storage site.

NOTIFIER/PHONE _____ / _____
 Odor Date/Time _____ Strength: weak, moderate, strong
 Location of Odor _____
 Temperature: _____ Wind speed/direction _____

Source	Odor Type Detected			
	Primary Treatment	Secondary Treatment	Biosolids	Other
WWTP	Primary Treatment	Secondary Treatment	Biosolids	Other
Incinerator	Smoke	Ash	Hopper Juice	Other
Cover Tech	Leaf/Earthy	Yard Waste	Raw Paper Sludge	Other
Landfill Gas	Natural Gas	Other		
RCI Landfill	Sludge	Other		
RCCI Compost	Compost	Other		
Waste Stream	Sludge	Ammonia		
Street BioFilter	Chemical	Sewage		

Odor Descriptors: (check all that apply) sewer putrid foul decayed
 chemical fecal (like manure) garbage truck rotten eggs burnt smoky
 musty earthy

Source contacted _____; Source copied _____

Message left _____; Senior Operator _____

Odor confirmed by Sr. Operator? Yes No

Comments:

RESIDENT ODOR COMPLAINT FORM
Courtesy of Springfield Regional WWT Facility

Date / Time of Odor _____ AM PM

Wind Direction / Speed _____

Air Temperature / Relative Humidity _____

Weather Conditions _____

Senior Operator _____

RESIDENT INFORMATION

Name _____

Address _____

City _____

Zip Code _____ Telephone No. _____

Odor Description (circle all applicable) sewer putrid foul decayed chemical
fecal (like manure) garbage truck rotten eggs burnt smoky musty earthy

Duration / Frequency of Odor

Intensity of Odor Weak / Moderate / Strong

Senior Operation Information (Detailed)

EXAMPLE OF PERFORMANCE STANDARDS FOR ODOROUS EMISSIONS FROM A PERMANENT CONSTRUCTED FACILITY

Example adapted from a Compost Site Conditional Use Permit, courtesy of St. Croix Sensory, Inc.

Odor Testing

1. This odor testing practice references the odor intensity of the ambient air to an “Odor Intensity Referencing Scale (OIRS)”.
2. The odor of the ambient air is matched (ignoring differences in odor quality) against the OIRS (see Section B in the following section) by trained inspectors. The inspector reports that point, or in between points, on the reference scale which, in her(his) opinion, matches the odor intensity of the ambient air.
3. The procedure followed for field odor testing is in accordance with Procedure B - Static-Scale Method of ASTM E-544, except for the following adaptations:
 - a. The geometric progression scale ratio = 3.
 - b. Use screw-cap containers for reference concentrations of butanol in water.
 - c. Inspectors may memorize the OIRS.
 - d. Inspectors may use a charcoal filter, breathing mask to avoid olfactory adaption (fatigue) in the ambient air.
 - e. Inspectors sniff ambient air and match its intensity to the reference scale.
 - f. Inspectors breathe charcoal filtered air for three minutes in between sniffings of ambient air.
 - g. Odorous air sampling shall be performed upon the complainant’s property. The inspector shall not be accompanied by the complainant and results shall be released after a written report is filed. The inspector shall not conduct the odorous air sampling if the complainant is present.
 - h. The inspector shall also sample the ambient air immediately upwind from the compost site to determine the presence and level of any odors entering the site from other sources. These records and observations shall be a part of the written report
 - i. The Odor Intensity Referencing Scale (OIRS) will use numbers and descriptions corresponding to butanol concentrations as indicated below:

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<u>No.</u>	<u>Category Description</u>	<u>N-Butanol (ppm)</u> <i>In air/ in water</i>
0	No Odor	0/ 0
1	Very Faint	25/ 250
2	Faint	75/ 750
3	Distinct, Noticeable	225/ 2250
4	Strong	675/ 6750
5	Very Strong	2025/ 20250

Reasonable operating conditions will allow for X (a designated number) or fewer recorded sniffings by an inspector of the ambient air over a period of Y minutes with a geometric average OIRS value of:

- a) 3.0 or greater if there is a permanent residence upon the property, or,
- b) 4.0 or greater if the property does not contain a permanent residence.