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Application of Field Blanks in Odour Emission Research

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In the Netherlands field blanks are mandatory when sampling odour emission. Field blanks are matrices that have negligible or unmeasurable amounts of the substance of interest. They are used to document possible contamination during sampling, transport and storage of samples. Although field blanks are well established in odour emission research, interpreting the results needs further attention. This can be attributed to the fact that published information on the topic is rare if not absent. In the present study, general statistical measures of field blanks used in odour measurement research, are reported. The objective of the study was to provide insight in the distribution of field blank values.
During 2013 and 2014, field blanks were analysed as part of regular investigations into odour emissions. Point sources were most frequently observed (87%), as well as the use of diluting stack samplers (72%). It was found that average odour concentration and standard deviation of the dataset were 1.39 and 0.379 $\log(ou_E/m^3)$ respectively, both expressed on a logarithmic scale (base 10). Median values of odour concentration of field blanks taken with stack sampler methods, differed significantly from lung sample methods, being a factor two higher. Since the implementation of stack sampler methods requires more processing aids than the lung method, the chances are that that traces of odour are carried over from one sampling sessions to another. This stresses the need for effective cleaning of sampling equipment between sampling sessions.

1. Introduction

In the Netherlands, atmospheric odour pollution is a well-known phenomenon. Data compiled by Statistics Netherlands (CBS), show that in 1990 approx. 20% of the Dutch population was affected. In 1993 a goal was set by the Ministry of Public Health, Physical Planning and Environment to have the percentage of residents complaining about odour pollution, reduced to 12% in 2000 (VROM, 1993). In order to achieve this objective, over the years, more and more emissions became subject to regulations. Presently, all major odour emissions in the Netherlands, emanating from industrial and agricultural sources, are regulated by local government (VROM, 2007).
Monitoring odour emissions, which are bound to regulatory limits, is executed by eight institutions. Four of these are in a position to ascertain the concentration and hedonic tone of given samples. As required by the Dutch Activities Decree (VROM, 2007), institutions monitoring odour emissions shall be accredited to standards laid down in either ISO/IEC 17025 (ISO, 2005) or in ISO/IEC 17020 (ISO, 2012). Compliance is tested by the Dutch Accreditation Council (RvA).
Presently, assessment by RvA of procedures for sampling of point sources is combined with TS 15675 (CEN, 2005). This technical specification supplements ISO/IEC 17025 (ISO, 2005) by providing clarification and additional information. One of the topics included concerns the application of field blanks. With regard to odour emissions, this item was taken on by RvA in 2011/2012. As a result, field blanks are now firmly embedded in odour emission research executed in the Netherlands.
Although taking field blanks is well established in odour emission research, interpreting the results needs further attention. The main reason being a lack of knowledge on the distribution of values of field blanks, can be attributed to the fact that published information on the topic is rare if not absent. In order to provide insight in the distribution of field blank values, this paper reports on an exploratory study that was undertaken. Although the study is not yet completed, preliminary results are reported.

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2. Materials and methods

2.1 Field blanks

Field blanks are part of a quality control system that is well known in environmental research. It comprises instrument blanks, methods blanks, trip blanks, field blanks, and equipment blanks. In case of odour measurements, only method blanks, trip blanks, and field blanks are relevant. The purpose of blanks is to trace sources of artificially introduced contamination. For instance, a method blank can only be contaminated in the laboratory while a field blank can be contaminated by faulty sampling equipment or by sources present during transport to the laboratory or storage in the laboratory. In order to decide whether a specific analytical result is contaminated a baseline of known measure and free of contamination is required.

Field blanks are defined as matrices that have negligible or unmeasurable amounts of the substance of interest (Strub, 2005). They are handled identically to genuine samples and prepared by exposing the sampling media to the environment at the sampling site except that no genuine sample is taken. Instead, odourless gasses such as high grade nitrogen or synthetic air are used as source in case of odour measurements. As such, field blanks are equally exposed to all sources of artificially introduced contamination as genuine samples. Therefore, field blanks are useful in documenting contamination of the analyte arising from sample collection, sample handling or from general conditions during sampling.

Since field blanks are part of a quality control system, the frequency of application may be subject to regulations. In the USA, the Environmental Protection Agency, EPA region 3, recommends one blank per day per matrix or one blank per twenty samples per matrix, whichever is more frequent (EPA, 2015). In Canada one field blank per sample set is recommended (Strub, 2005), and in the Netherlands one field blank per sample set per source (NEN, 2012).

Being a part of quality control system, field blanks should not be applied without proper control limits. They can be expressed as: (1) a fixed value, (2) a value relative to the test result of the genuine sample, and (3) a combination of (1) and) (2). Fixed values are usually calculated as the average of a given set of field blanks expanded to the upper side of the 95% confidence interval of a single observation. Although the size of dataset used may be debatable, the rationale underlying the method is correct, justified, and easily understood. In the second method, permissible values of field blanks are expressed as a percentage of the test result of the genuine sample. Usually the percentages chosen are such that they are much smaller than the expected measurement error. This approach has an arbitrary element in deciding what amount of contamination can be neglected against the measurement error. The combined method usually applies a fixed value to the lower end of the measuring range and a relative value to the remaining part. In general, the dividing line between a fixed value and relative values is not sufficiently well explained. Therefore the method lacks scientific backing.

When exceeding the control limit, appropriate measures should be taken. Field blanks values concerned should be checked to determine the source of contamination, and to determine the impact upon the sample (Strub, 2005). As a result, the field blank value may be rejected. A more radical approach involves a priori rejection of field blank value exceeding the limit value followed by root cause analysis of the problem encountered. It should be noted that by retracting suspected field blanks values the results of the corresponding genuine samples are equally suspected. Therefore, these should be retracted too.

Information regarding field blanks should be reported along with the genuine results. Artefacts in sampling procedures, as deduced from information generated by field blanks and other blanks, should be investigated and remediated. Likely effects upon the data collected should be discussed in the final report. Correction of data by subtraction of field blank values, also called ‘blank correction’, is permissible when specifically part of a method procedure. In all other cases, blank correction is <u>not</u> appropriate.

2.2 Sources

Values of field blanks included in the present study were made available by institutions involved in monitoring sources of odour emission in the Netherlands which are bound to regulatory limits. They were taken during 2013 and 2014 as part of regular investigations into emissions emanating from the production of pet food, vegetable oil, coatings, asphalt, granulated manure, holding ponds for industrial waste water, tank farms for storage bulk fluids, e.g. crude oil and edible oil, as well as from treatment of sewage and many other sources. All field blanks included in the present study were taken as single sample preceding regular sampling of a single source. The analytical results were used for assessment of contamination occurring during sampling, transport, and storage of genuine samples.

Field blanks in the Netherlands are taken by eight different institutions, and analysed by four independently operating laboratories. In this study, institutions involved in sampling of odour emissions are designated by ‘Institution 1’ to ‘Institution 8’, and odour laboratories by ‘Laboratory 1’ to Laboratory 4’. Since sampling institutions vary in volume of trade, as do odour laboratories, their contribution to the present study is unequal.

The input of the various institutions and laboratories to the present study is summarized in Table 1. The listed numbers concern data prior to outlier detection.

Table 1 Distribution of observed number of field blanks over sampling institutions and odour laboratories

	Samples	%		Analyses	%
Institution 1	104	14	Laboratory 1	126	16
Institution 2	46	6	Laboratory 2	362	47
Institution 3	350	46	Laboratory 3	107	14
Institution 4	39	5	Laboratory 4	170	22
Institution 5	17	2			
Institution 6	107	14			
Institution 7	20	3			
Institution 8	82	11			
Total	765		Total	765	

As odour sources polluting the atmosphere come in a variety of configurations e.g. point sources, area sources, complex sources and diffuse sources, an array of dedicated sampling methods exists e.g. lung sampling method, diluting stack sampling method (DSS), wind tunnel sampling method, and the upwind-downwind sampling method. Standard combinations of sources and sampling methods are summarized in Table 2.

Table 2 Combinations of source configuration and odour sampling method

Source configuration	Sampling method
Point source (e.g. smoke stack, air scrubber)	Lung method, DSS-method
Aerated area source (e.g. biofilter)	Temporary hood combined with the lung method
Non-aerated area source (e.g. settling pond)	Wind tunnel combined with the lung method
Complex source (e.g. waste tip, landfill site)	Upwind-downwind sampling using the lung method
Diffuse source (e.g. naturally ventilated building)	Lung method

2.3 Analyses

Analysis of odour concentration of field blanks was according to EN 13725 (CEN, 2003). Since field blanks are supposed to have negligible or unmeasurable amounts of the substance of interest, analyses are around the lower limit of detection (LOD) of the laboratory performing the analyses. As a result, the required number of eight individual threshold estimates (ITE's) per analysis was not always achieved. In those cases, personal thresholds of part of the panel members sample were beyond the lowest available dilution of the olfactometer used. The results concerned were reported with a less than sign (<). Because the LOD of odour laboratories is attributable in no small part to technical limitations e.g. the lowest attainable dilution to be presented to assessors, the quality of the diluent, etc., it can be argued that without these limitations assessors may have been able to produce a valid ITE. Therefore, data with a less than sign are accepted in the present case while ignoring the sign.

2.4 Statistics

Prior to calculation, all data were converted by logarithmic (base 10) transformation. Normality of data was tested using the Anderson-Darling test method. No deviation from normality was observed ($p<0.005$). Subsequently, data were scrutinized for upper bound outliers using 3s as cutoff criterion. Effectively, this makes the chances for data to be identified as an outlier 1:10000. One outlier was detected and subsequently removed. As a result, 764 odour concentrations of field blanks were available for statistical analyses.

Statistical analysis of the present dataset was intended to quantify general measures of the log transformed distributions of the sampling methods, i.e. average, standard deviation and standard error of field blanks. Furthermore, differences between sampling methods with respect to their mean and variance were evaluated. F-tests were used under the null hypothesis that variances of the compared methods were from the same distribution, and two sided t-test statistics were used under the null hypothesis that means of the compared methods were the same. Because number of observations and variances were not equal among sampling methods, we applied t-tests with unequal sample size and variance. In both the F-tests and t-tests, null hypotheses were rejected ($p<0.05$).

3. Results

Field blanks were taken at various source configurations, each requiring dedicated sampling methods. As some sources are more common than others, the input of various sampling methods to the present dataset varies. Table 3 summarizes the distribution over sources and sampling methods. This listed numbers concern data after outlier detection.

Table 3 Distribution of the observed number of field blanks values over source configurations and sampling methods.

Sampling method	Source configurations				
	Point source	Aerated area source	Non-aerated area source	Complex source	Diffuse source
DSS method	546	0	0	0	0
Lung method	116	0	0	0	0
Lung method	0	0	0	0	23
Wind tunnel method	0	0	41	0	0
Upwind-downwind method	0	0	0	38	0
Total	662	0	41	38	23

Statistical analyses of the present dataset were intended to quantify general statistical measures for the available combinations of sampling methods and source configurations. The results are summarized in Table 4.

Table 4 General statistical measures for methods of odour sampling: minimum (min), maximum (max), mean ($\bar{x}$), standard deviation (s) and standard error of mean (s.e.) of field blanks values, and identification of statistical significant differences between means and variances where sampling methods with different letters within the same column differ from each other ($p<0.05$)

Sampling method	Parameter				
	min $\log(ou_E/m^3)$	max $\log(ou_E/m^3)$	$\bar{x}$ $\log(ou_E/m^3)$	s $\log(ou_E/m^3)$	s.e. $\log(ou_E/m^3)$
DSS method	0.60	2.39	1.46 a	0.337 a	0.014
Lung method (point sources)	0.48	2.51	1.12 b	0.448 b,c	0.042
Lung method (diffuse sources)	0.85	1.85	1.22 b	0.271 a	0.058
Wind tunnel method	0.60	2.11	1.43 a	0.373 a,c	0.059
Upwind-downwind method	0.48	1.94	1.23 b	0.358 a,c	0.059
Overall	0.48	2.51	1.39	0.379	0.014

4. Discussion

Point sources are most frequently observed in the present study (87%). This can be attributed to the fact that the majority of waste odours commonly found in practice are traceable to the production of commodities. Since most production takes place in confined spaces, process odours are ducted to a smokestack, and released into the atmosphere from there.

As ambient conditions in smokestacks (temperature and humidity) frequently favour condensation of samples, in-line predilution, using the DSS sampling method, is often applied. When applied properly, this prevents condensation of air flows directed to the sample container as well as condensation of the sample itself during sampling, transport, and storage. Together with the predominance of point sources in the present study, this explains the high frequency of the DSS method observed in the present study (71%).

Average and standard deviation vary between sampling methods. Expressed on a metric scale, logarithmic averages are represented by the median value of the distribution concerned. Median values of odour concentration of field blanks of the DSS sampling method, the lung sampling method (point sources), the lung sampling method (diffuse sources), the wind tunnel sampling method, and the upwind-downwind sampling method amounted to 29, 13, 17, 27, and 17 ou_E/m^3 respectively. The median value over all sampling methods was 25 ou_E/m^3. Furthermore, it was found that the mean values (log 10 base) of odour concentration of field blanks taken with DSS method and with the wind tunnel method were not significantly different ($p>0.10$). The same applies to the lung method applied to point sources and diffuse sources, and the upwind-downwind sampling method ($p>0.10$). On the other hand, mean values of odour concentration of the DSS method on one

side, and both lung methods on the other, were significantly different ($p<0.01$), except for the difference between long method applied to diffuse sources versus the wind tunnel method, $p<0.05$). Expressed on a metric scale, the highest median value belonging to the DSS-distribution is 29 ou_E/m^3, whereas the lowest median value presented by the lung method applied to point sources is more than a factor 2 lower. It should be realized that field blank values cannot be lower than the LOD of the laboratory, as defined by the lowest dilution level of the olfactometers involved.

The difference observed in median values between the lung methods on one hand and the DSS and wind tunnel methods on the other may be explained by the fact that the lung method is a simple and straight forward sampling method in need of very few attributes. Only a few metres of tubing are needed to bridge the gap between source and the sample container. The lack of complicated sampling equipment greatly reduces the chance that traces of odour from previous sampling sessions are carried over to the current one, thus keeping contamination of field blanks at a the lowest possible level. Our results show that generally some field contamination does occur in case of DSS and wind tunnel methods. Considering the increase in their median values compared to the lung methods, in most cases this presents a negligible amount far below the variance that is normally observed between replicates of source samples (Klarenbeek et al., 2014).

The variability between sampling methods was highest for the lung method applied to point sources, and here significantly differed from the variability in the DSS method and the lung method applied on diffuse sources. The overall standard deviation of field blanks in the present study was 0.379. Since sampling and analyses took place over an extended period of time, and various sampling institutions and analytical laboratories were involved, the present standard deviation can be compared to the standard deviation of reproducibility (s_R). Earlier, Klarenbeek et al. (2014) reported a standard deviation of 0.282 (log base 10) that was calculated using an integrated analysis of a number of proficiency tests (PT). The PT's concerned were focussed on waste odours commonly found in practice, and included the same laboratories as in the present study. The difference between the standard deviation of reproducibility, as calculated by Klarenbeek et al. (2014), and the standard deviation in the present study can be interpreted as a measure for variation related to uncontrolled contamination occurring when sampling odour emissions. As there is no evidence that this phenomenon is exclusively linked to sampling of field blanks, it may be manifest in all sampling of odour sources. However, as the odour concentration of regular sources is higher than those of field blanks, this may effectively suppress variation arising from uncontrolled contamination during sampling.

As to contamination of odour samples arising from sample collection and sample handling, sampling institutions and their respective samplers go into great detail to prevent contamination of genuine samples. In the Netherlands, all sampling institutions are in possession of one or more standard operating procedures (SOP's) addressing the matter. In case of mechanical equipment used for sampling, e.g. a DSS, most SOP's prescribe thorough cleaning after use as well as replacing contaminated parts by clean ones when changing sources at the sampling site. Furthermore, batch control on residual odours of one-way sampling materials, e.g. sample containers, is also prescribed. However, despite all SOP's applied and all other efforts made to prevent contamination of the genuine sample, uncontrolled contamination is always lurking. In case of field blanks, uncontrolled contamination can be ascertained by comparing the analytical result of the field blanks to those of the corresponding trip blank and to the method blanks. In cases of a significant difference between the values of the field blank and the trip blank, suspected contamination can be attributed to the sampling equipment used. On the other hand, a significant difference between the value of a trip blank and the method blanks may point in the direction of contamination arising from sample handling or from conditions during sample transport and/or storage. Since analytical results of trip blanks and method blanks in odour emission research are lacking, the present data cannot be further refined.

When establishing a control limit for field blanks, the fixed value approach is the preferred method. As pointed out, this method is correct and justified. Based on the present dataset, the median value expanded to the upper side of the 95% confidence interval, $10^{1.39} * 10^{(0.381*1.96)} = 24 * 5.58 = 136$ ou_E/m^3, can be designated as limit value for field blanks. It should be noted that this value is a general value leaving the differences between sampling methods, see Table 4, untouched.

5. Conclusions

When sampling odour emissions, clean sampling equipment is a prerequisite. In order to verify the status of the equipment used, field blanks are taken prior to sampling. Since information on general statistical measures of field blanks is scarce, interpreting the analytical results can be a problem. To clarify the situation, a study was undertaken reviewing 764 odour concentrations of field blanks. It was found that the majority of the investigated emissions (87%) took place via a smokestack. Furthermore, a diluting stack sampler was most frequently used as sampling device (72%). The latter is explained by the fact that ambient conditions in stacks often require predilution during sampling.

The median value over all sampling methods of odour concentration of field blanks was 24 ou_E/m^3. Median values of field blanks taken with the DSS method and the lung method differed significantly by a factor two. Since the implementation of the DSS method requires more processing aids than the lung method does, the chances are that that traces of odour are carried over from one sampling sessions to another. This stresses the need for effective cleaning of sampling equipment between sampling sessions.

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