

Odor Emissions from Refinery Sites

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Abstract—an approach for the evaluation of potential odor sources of refineries and storage tank farms is presented. The method comprises three steps: initial expert examination, estimation of odor emission rates, and dispersion calculations to predict odor perception frequencies in the neighborhood of the site under investigation. The aim is to quantify the effect of suspected odor emission sources, thus rating their relevancy in order to channel investment in the most effective way. Calculation methods and selected results of olfactory measurements are presented. The facts are illustrated by three actual case studies.

Keywords—refinery; refinery emissions; tank farm; tank emissions; odor emissions; odor propagation; odor dispersion; olfactory measurement; olfactometer; olfactometry; crude oil; mineral oil; crude oil storage; mineral oil storage.

I. INTRODUCTION

If refinery sites are situated near housing compounds, frequently local residents complain about annoyances caused by mineral oil related odors. So refinery operators get under pressure to act – and want to act, for improvement of the situation. But where to begin? Abatement measures such as, for example, mounting of tertiary seals to floating roof tanks, cost lots of money; money that might be wasted, if it turns out, that the odor problem still persist afterwards, apparently caused by other emission sources.

Driven by the motivation to identify and classify odor emission sources in order to optimize investment, Müller-BBM has carried out several studies, beginning in 2003, covering several refinery and tank storage sites. The methodology used for this purpose combines expert analysis, API-manual emission factors and calculation procedures, self-developed calculation methods, olfactory measurements, and atmospheric dispersion modelling. A special feature of the method is the combination of emission and meteorological time series, each with hourly resolution, thus considering in detail local meteorological conditions.

The following will give an extract of the calculation and estimation methods, will discuss selected measurement details and present three case studies of the assessment of potential and presumed odor emission sources from refineries and tank storage sites.

II. METHODOLOGY

A. General

The general methodology follows a stepwise approach:

- Step 1, expert examination: This comprises the selection of presumably relevant odor emission sources for further investigation, followed by the technical analysis of the selected processes, the recording of operating parameters, apparatuses, and potentially odorous products. In this phase, expert interviews with the operational staff on site are an important source of information.
- Step 2, estimation of emission rates: Based on the results of step 1, odor emission rates are estimated. This involves the application of approved calculation procedures, e.g. methods described in API-manuals (API: American Petroleum Institute). For special purposes, also modifications or completely specific methods must be elaborated. Another point is the gathering of substance-specific physical-chemical data, such as density, vapor pressure and molecular weight of substances involved in the processes. As established methods for the calculation of emissions do not cover odor emissions, olfactory measurement of field and laboratory samples is essential.
- Step 3, processing of dispersion calculations. With odor emission rates established in the previous steps, dispersion calculations are carried out in order to predict odor ground level concentrations (GLC) and odor perception frequencies in the surrounding neighborhood of the site under investigation. For this, we use a Lagrangian particle propagation model. An important feature of this model is the use of meteorological time series (wind direction, wind velocity, and dispersion class). This means, that realistic emission scenarios such as punctual or periodic incidents, fluctuating emissions, seasonal variations, and even wind-induced emissions can be incorporated in the model.

B. Olfactory measurements

It is obvious, that the gathering of olfactory data is crucial. Samples can be taken directly on site, e.g. exhaust gas of a

fixed-roof tank retention valve, or can be prepared in the laboratory, e.g. from the headspace of a liquid mineral oil sample. The technique of olfactory measurement is based on the human sense of smell. The odorous gas, usually prepared or sampled in an odor neutral cellophane bag is presented to a panel of testers. Firstly, it is infinitely diluted with odorless air. Step by step, the dilution is decreased, up to the point, where the testers begin to perceive scent, i.e. up to the odor threshold limit. This by definition equates the concentration of one odor unit (OU) per cubic meter. The testing procedure can be understood from Fig. 1. The apparatus for diluting and presenting the sample to the testers is called olfactometer.

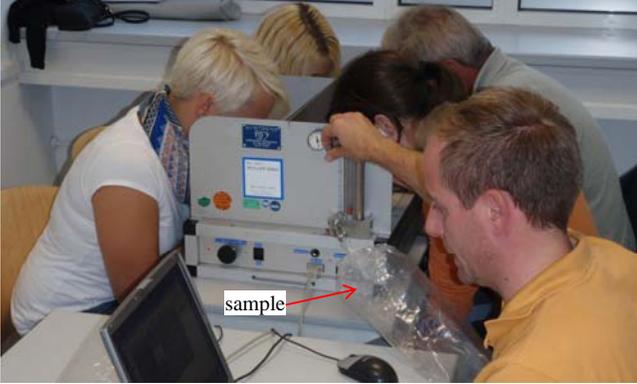


Fig. 1. Laboratory testing of an olfactory sample.

III. CASE STUDIES

A. Kerosene tank farm

1) Situation

The operator of a tank farm for storage and turnover of kerosene was planning to increase the yearly turnover about 50%. In the past, already occasional complaints from the neighborhood about mineral oil related odor nuisances had occurred. The special situation of the site is characterized by the fact that an office building is located in a distance of only about 30 meters opposite to the site. Moreover, the pressure retention valves of the tanks are faced to the upper floor windows of the building at more or less identical height.

Müller-BBM was asked to deliver an expert opinion to predict prospective odor perception frequencies in the neighborhood of the tank farm. The study should deliver basic information to decide, if, and if so, to which extent, emission abatement measures should be taken.

2) Estimation of an odor emission time series

Emissions from fixed roof tanks arise if gas is displaced during the filling process and from breathing of the gas phase, i.e. from pressure alterations caused by temperature alterations. The former is easily calculated from the tank geometry and the tank filling level, usually available as measured data in at least hourly resolution. The breathing exhaust can be calculated using the ideal gas law and the vapor pressure function of the stored liquid on basis of also available measured data of the liquid phase temperature. Additional information is needed about the night-day temperature pattern of the gas phase which is caused by the absorption of solar radiation during the day

and cooling of the gas phase by night. For this purpose, data from technical guidelines, such as API- or VDI-manuals (VDI: Verein Deutscher Ingenieure; German association of engineers), experimental data or other plausible assumptions may be considered. Finally, the response pressure of the pressure retention valves of the tank must be taken into account.

The resulting equations for the calculation of the exhausted (or, as the case may be, inhaled) volume V (referring to atmospheric pressure P_{atm} and ambient temperature T_{amb}), emerging from the transition from state 1 to state 2 are as following:

$$V = \frac{P^* - P_2}{P_{\text{atm}}} \cdot V_2^f \cdot \frac{T_{\text{amb}}}{T_2^g} \quad (1)$$

$$P_2 = \begin{cases} P^* & \text{if } P_+ > P^* > P_- \\ P_- & \text{if } P^* < P_- \\ P_+ & \text{if } P^* > P_+ \end{cases} \quad (2)$$

P_- : P_{atm} + lower response pressure of the retention valves

P_+ : P_{atm} + upper response pressure of the retention valves

$$P^* = (P_1 - P(T_1)) \cdot \frac{V_1^f}{V_2^f} \cdot \frac{T_2^g}{T_1^g} + P(T_2) \quad (3)$$

$$T_1, T_2 = \min \begin{cases} T_1^{\text{liq}}, T_2^{\text{liq}} \\ T_1^{\text{g}}, T_2^{\text{g}} \end{cases} \quad (4)$$

$$T^{\text{g}} = T^{\text{liq}} - \Delta T_{\text{Night}} + \Delta T_{\text{Max}} \cdot \cos^2 \left\{ \frac{h-12}{24} \cdot \pi \right\} \quad (5)$$

P_1 : Pressure before the transition (state 1)

$T_1^{\text{liq}}, T_2^{\text{liq}}$: Temperature of the liquid phase in state 1 and 2 resp.

$T_1^{\text{g}}, T_2^{\text{g}}$: Temperature of the gas phase in state 1 and 2 resp.

V_1^f, V_2^f : Free gas space volume in the tank in state 1 and 2 resp.

ΔT_{Night} : Maximum difference between liquid and gas phase temperature at night (the gas phase temperature drops below the liquid phase temperature).

ΔT_{Max} : Maximum difference of gas phase temperature between day and (following or proceeding) night.

h : Hour of the day

$P(T)$: Vapor pressure of the liquid at temperature T (usually expressed as Auguste- or Antoine-equation, e. g. $\log(P) = A - B/T$ with A, B = material specific constants).

Equations (1)-(5) can be used to calculate the hourly exhaust volume. For the specification of emission rates, additional information about the odor concentration is needed. For this, field samples from the tank gas space as well as laboratory head space samples of the stored product (i.e. kerosene) were analyzed. The results are shown in Fig. 2. There seems to be a divergence between laboratory and field samples, which might indicate, that the tank vapor space was not saturated with the odorous substances according to the liquid temperature. However, it is plausible to assume a temperature-dependent odor concentration according to the red line shown in the picture, at least in terms of a conservative approach.

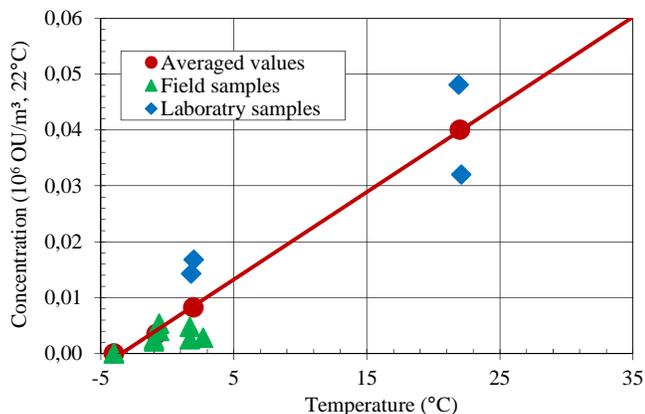


Fig. 2. Measured odor concentrations of kerosene vapor laboratory and field samples (OU: odor units).

Fig. 3 shows the resulting hourly time series for a kerosene tank, based on actual filling level- and storage temperature-data (already with respect to the planned increase of turnover). The emissions caused by loading campaigns and breathing are clearly distinguishable.

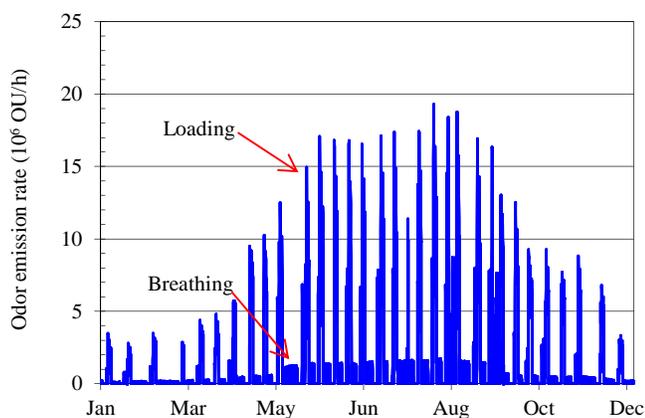


Fig. 3. Odor emission rate time series for a kerosene tank (OU: odor units).

3) Results of the dispersion calculations

On the basis of emission rate time series calculated as described above, dispersion calculations using a Lagrangian particle propagation model were carried out. Results are presented in the following: Fig. 4 presents the spatial distribution of calculated annual odor perception frequencies in the atmospheric layer 18-21 meters above ground level, i.e. in

height of the upper floor windows of the office building opposite to the tanks. The underlying emission scenario comprises four fixed roof tanks for storage and turnover of kerosene with an overall turnover rate of approximately 1.1 Million tons per year and no specific abatement measures. The maximum of the predicted perception frequency in front of the upper floor windows of the office building is 13.8 % or 1,210 hours per year which is not acceptable according to the applicable national regulations.

Fig. 5 shows the effect of emission abatement on the maximum predicted odor perception frequency. It can be seen, that an emission reduction >90 % is required to reduce the perception frequency below an acceptable level of 2 %. A potential abatement measure might be the installation of internal floating roofs to the tanks. In such case, a design that is capable of an abatement of this extent must be chosen or additional measures, such as the application of a paint coat with a higher radiance factor must be taken into account.

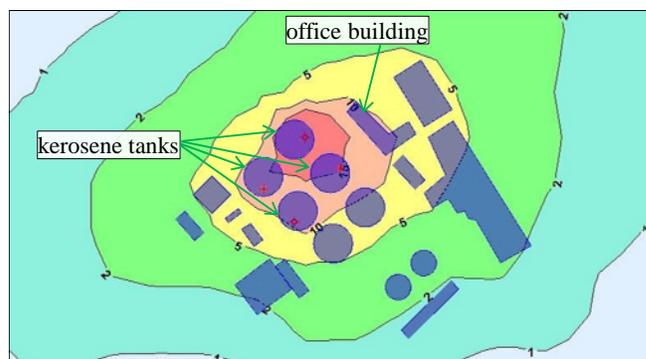


Fig. 4. Calculated annual odor perception frequencies 18-21 meters above ground level based on the emissions of four kerosene tanks of a tank farm without further abatement measures. Green: >2 %, yellow: >5 %, light red: >10 % (>175, 438, 876 hours/year).

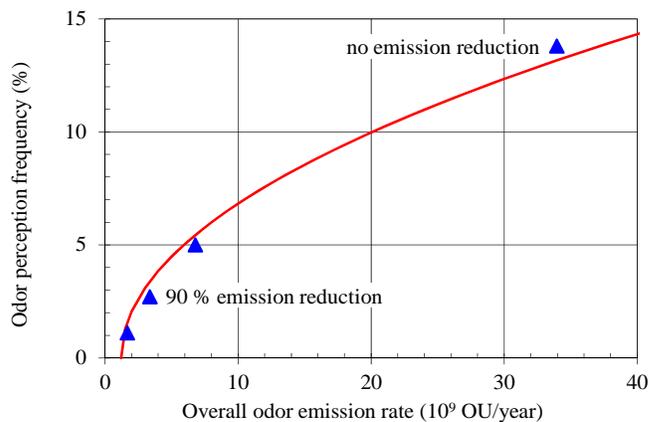


Fig. 5. Effect of emission abatement on the maximum predicted odor perception frequency (OU: odor units).

B. Intermediate storage space for slightly contaminated sewage water

1) Situation

A refinery used an otherwise not employed retention area, primarily intended as utility space for a storage tank, as an intermediate storage for slightly contaminated sewage water.

As the nearest housing compound is situated in about 350 meters distance, it was discussed, if this could cause unacceptable odor perceptions in the neighborhood. Müller-BBM was asked to deliver an expert opinion to predict odor perception frequencies.

2) Estimation of an odor emission time series

Emission rates from contaminated water surfaces can be measured using sampling equipment as shown in Fig. 6: Filtered air is drawn through a defined space at a defined flow rate. From this gas stream a sample bag for olfactory measurement is filled using a vacuum cylinder.

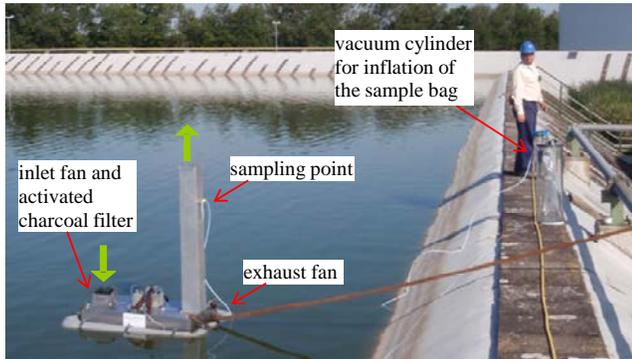


Fig. 6. Olfactory measurement of the emission rate from a contaminated water surface.

Sampling actually was performed on a warm summer day. It turned out, that samples taken in the early morning, at lower temperatures, showed significant lower odor concentration than samples taken in the midday heat. Therefore, it seemed to be appropriate, to consider temperature dependent odor emission rates. The influence of temperature on the emission rates could be derived from the experimental results. As maximum and minimum daily ambient temperatures for the site can be drawn from publicly available meteorological data, an emission time series could be constructed, considering as well daily and seasonal temperature alterations. The result is shown in Fig. 7.

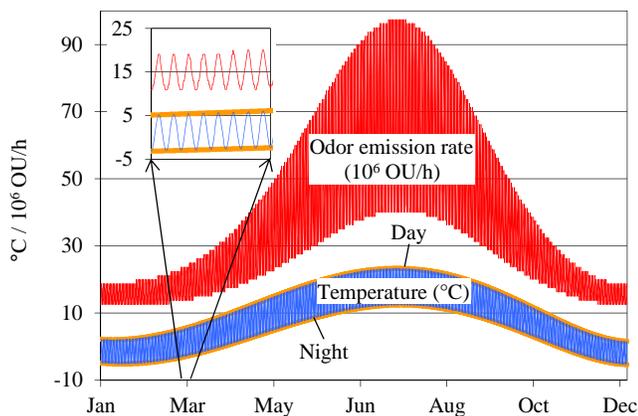


Fig. 7. Odor emission rate time series of a slightly oil contaminated water surface considering daily and seasonal temperature alterations (OU: odor units).

3) Results of the dispersion calculations

Results of the dispersion calculation based on the emission rate time series displayed in Fig. 7 are shown in Fig. 8. It can

be seen that annual odor perception frequencies up to 10 % must be anticipated in the neighborhood. Therefore, with respect to potential odor nuisances, the retention area should not be used permanently as an intermediate storage for contaminated sewages.

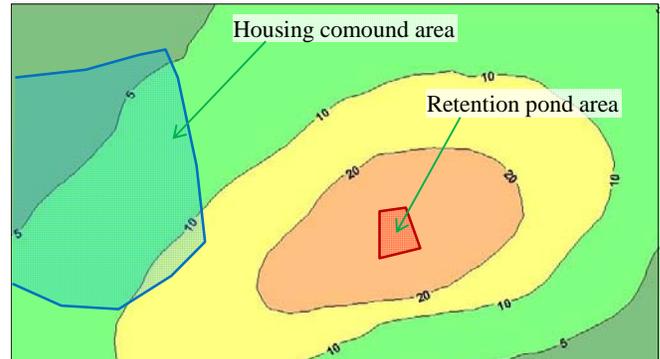


Fig. 8. Annual odor perception frequencies caused by a slightly oil contaminated water surface (5 % = 438 hours per year, 10 % = 876 hours per year etc).

C. Odor perceptions during a refinery turnaround

1) Situation

During the shutdown and inspection of a refinery, it occurred, that strong odors, characteristically related to mineral oil products, were observed in the region. The incident lasted for about 6-8 hours and covered an area, more or less around a straight line, up to about 25 kilometers distance to the refinery site. Despite the large distance between the refinery site and the places of the odor perception incidents, it was suspected, that some activity related to the refinery shutdown could be responsible. Müller-BBM was asked to deliver an expert opinion that should work out possible causes for the incident.

2) Searching for emission sources and estimation of emission rates

It turned out, that definitely no activity with potential emissions took place, despite the final cleaning of apparatuses with hot steam. The waste steam was disposed via the flaring system. Of course, the permanent emissions from storage tanks also had to be taken into account.

a) Flaring

Only little information about the operating parameters was available. There was an estimate of the steam flow rate and the general statement, that supporting gas was used. The amount of supporting gas could not be specified. On this base, only a more or less plausible assumption of potential emissions could be made. An odor emission rate of 10^9 odor units per hour seems possible. It would mean that 30 tons per hour of steam, contaminated with 1 % oil components that have a medium odor threshold limit of 0.3 milligrams per odor unit, are released. This emission rate was assumed in order to verify, if generally odor perceptions at great distances can be caused by flaring.

b) Background emissions: crude oil storage

It was known from former investigations that crude oil storage is the dominant source of background odor emissions

for the site under consideration. The emissions of the crude oil tanks of the refinery and a nearby crude oil tank farm were estimated as follows. All crude oil tanks under consideration are floating roof tanks. Initially the loss of hydrocarbons was calculated on basis of the method described in the API manual 19-2. The total losses (L_T) consist of static losses (L_S) and working losses (L_W).

$$L_T = L_S + L_W \quad (6)$$

The static losses are a function of the vapor pressure of the stored liquid and comprise all losses caused by sealing systems and fittings, where the stored liquid is directly exposed to the ambient air. The most important causal factors for static losses are the rim sealing and insufficiently sealed guidance poles. The API manual 19-2 provides a detailed catalog of emission factors. An interesting feature is that most of them depend on the wind velocity. This means, as meteorological data usually are available in form of hourly time series, that emission rate time series can be calculated with respect to this as well as accounting for the dependency of the vapor pressure on the storage temperature.

The working losses arise from the movement of the floating roof during charging and discharging of the tank as can be seen from Fig. 9. Typically working losses are secondary to the static losses.

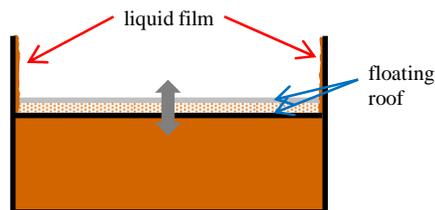


Fig. 9. Working losses of a floating roof tank.

To estimate odor emissions from hydrocarbon losses, additional information about the olfactory properties of the crude oil is needed. Table I summarizes olfactory measurement results. Obviously, the olfactory properties of different types of crude oil vary within a wide range. Typically Arabic and Russian sorts are strongly odorous, whilst oil sorts from the North Sea do not produce strong odor. In the refinery and tank farm under investigation mainly Arabic and Russian sorts are stored and processed. In terms of a conservative approach, the data of sample 4 was used. It can be also seen from Table I that the correlation between hydrocarbon and odor concentration depends on the liquid temperature which is not surprising as differently odorous substances may have different vapor pressure functions.

TABLE I. OLFACTORY PROPERTIES OF CRUDE OIL VAPORS.

	°C	odor (10 ⁶ OU/m ³)	hydrocarbons (kg/m ³)	correlation 10 ⁶ OU/kg
sample 1	20	2	0,4	4
	28	30	0,9	40
sample 2	20	1	0,4	3
	28	20	0,8	20
sample 3	20	0,1	0,1	1
	28	0,2	0,4	1
sample 4	20	40	0,4	100
	26	90	0,5	180
sample 5	20	0,04	0,5	0,1
	26	0,02	0,6	0,03

OU: odor unit)

3) Results of the dispersion calculations

On the basis of nearby measured meteorological data of a period of 48 hours around the incident, an odor emission time series was generated and dispersion calculations were carried out. Additionally a constant emission rate from flaring was assumed as described above. The results were evaluated in form of hourly odor GLC maps. One of these exemplarily is shown in Fig. 10. This is no proof for a causal connection and generally, the results do only rudimentarily coincide with the actual observation of odor incidents. But it can be seen from the picture that basically and under particular meteorological conditions, odor emission sources as those under investigation are able to cause odor perceptions even at a long distance.

Another interesting fact can be seen from Fig. 10: the odor propagation splits into two directions. This is because of the rotational shift of the wind direction in higher atmospheric layers due to the Coriolis Effect. The emission from the storage tanks takes place near ground level and without any thermal plume rise. In contrast, the emission height of the flare is about 70 meters plus the thermal plume rise due to the heat content of the emitted steam.

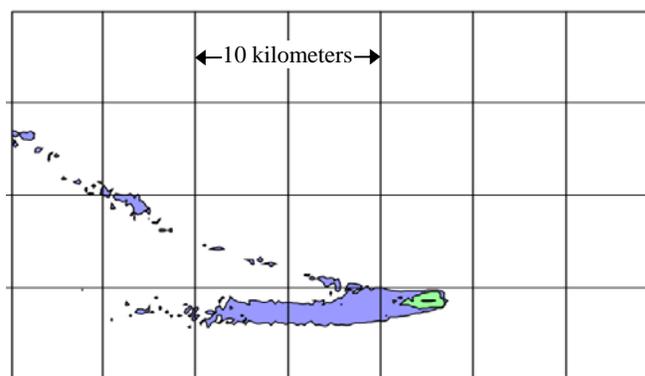


Fig. 10. Odor GLC, 1-hour average, exemplarily shown for one hour of the 48-hour period of investigation. Green: 1 odor unit per cubic meter, blue: 0.25 odor units per cubic meter. Conventionally, is assumed, that an hour is considered as an hour with odor perceptions, if the average odor concentration is greater or equal to 0.25 odor units per cubic meter.

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