Dealing with ultra-low spray deposits in experiments

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Summary

In spray drift experiments, measuring spray deposits far downwind may yield deposits values that approach or go below the level of detection. Particularly, when deposits are corrected for background concentrations of whatever origin, in principle values at or even below zero may result. A conventional way to deal with those data is to adjust them to zero or a 'very low but positive' value. Alternatively, zero and negative deposits are simply removed from the data set. In either way, such adjustments may affect the results in a way the researcher may not have foreseen or intended. In this study different common methods of dealing with ultra-low deposition values are compared. It is discussed how these methods may affect the results and their interpretation. An alternative method is introduced and discussed which may reduce the negative implications of the common methods. The study is supported by various computational examples.

Key words: Spray drift, level of detection, experiments, probability

Introduction

In experiments involving downwind deposits of spray drift, these deposits can be very low and near the level of detection. In repeated trials, both low and high deposits may vary caused by external factors. For instance, wind speed and wind direction are likely to vary slightly between repetitions. Typically, if a large enough number of repetitions is available, deposits will follow a certain probability distribution. Usually, measured deposits must be corrected for a background signal, which can originate from different sources. For instance, the sample materials or the solvent used for washing the samples may contribute to the background signal. The background signal may vary and will follow its own probability distribution. While correcting the deposits for background signals, one has to be aware of these distributions as well. As the background signal has the unit of deposits, it can be interpreted as an 'equivalent' background deposit, although it is not a spray deposit in physical sense.

Real spray deposits are limited to non-negative values, therefore a normal probability distribution may be not be fully adequate. However, if variation is relatively low the deposits may well be normally distributed. Mathematically, each repeated sampling can be considered as an instance drawn from its corresponding probability distribution.

Real spray deposits are measured deposits corrected for background deposits. For ultra-low deposits, one has to deal with subtracting low values from other low values, both following their own probability distribution. This may lead to negative spray deposits, which clearly is physically unrealistic but statistically possible. Different ways to deal with non-positive deposits is the subject of this study.

Materials & Methods

Background levels interpreted as deposits

In practice, when analysing samples for spray deposits, background levels of fluorescence occur for clean sample material and clean demineralised (demi) water to wash the collectors. Obviously, background values are not due to spray deposits in a physical sense, yet in the computational procedure these will show up as values with units of deposits. Therefore, the background values are treated as 'equivalent deposits'. Often, these background values follow a normal distribution closely.

Since clean samples must be treated the same way as collectors exposed to spray drift, the background values of clean samples may differ when the laboratory method changes. For example, not only the size of the collector is important, but also the volume of water to flush the samples. Examples in the Results section will illustrate this.

Statistics of measuring low values

In a first approach, all probability distributions are considered to be normal distributions, determined by a mean μ and standard deviation σ. Using normal distributions has the advantage that means and variances can be simply added in mixed distributions provided the mixing quantities are unrelated.

Assume the measured deposits are normally distributed with mean μ_m and standard deviation σ_m. If mean and standard deviation of the background are μ_b and σ_b, respectively, the corrected deposits are described by:

$$\begin{aligned} \mu_c &= \mu_m - \mu_b \\ {\sigma_c}^2 &= {\sigma_m}^2 - {\sigma_b}^2 \end{aligned} \qquad (1)$$

Since measured deposits are the sum of corrected deposits and background signal, the above equation must result in positive values of corrected mean and variance. If spray deposits are very low, $\mu_m \approx \mu_b$. and the corrected distribution stretches to negative deposits. Clearly this is a physical impossibility, yet a result from statistical interpretation of variance in quantities.

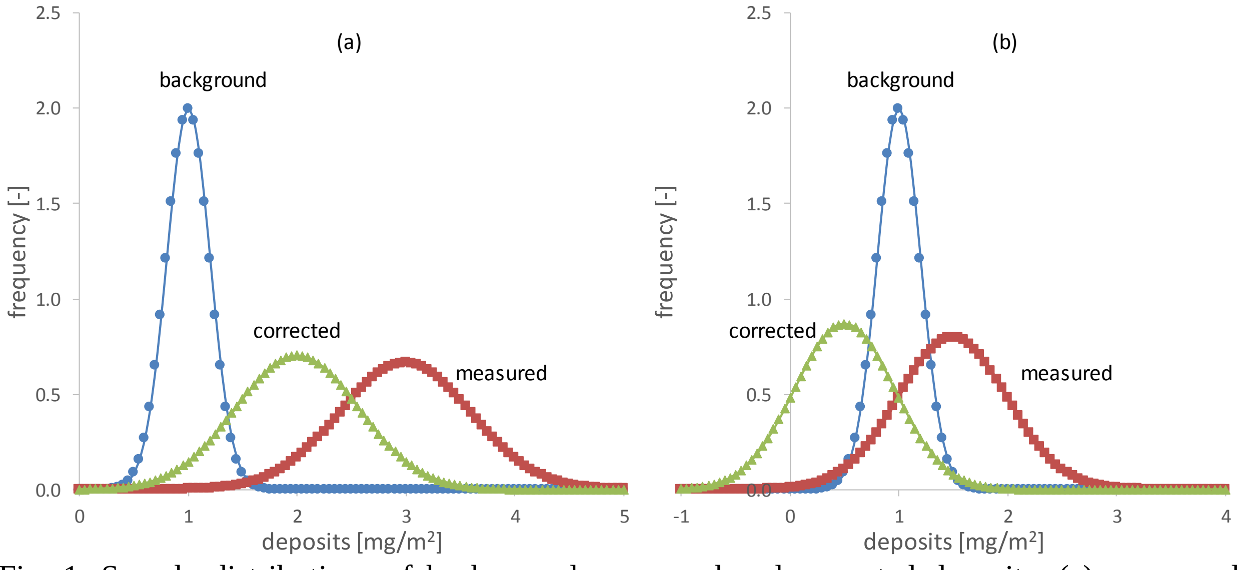

Fig. 1. Sample distributions of background, measured and corrected deposits. (a): measured deposits significantly larger than background values; (b): measured and background values show significant overlap; corrected distribution has significant part below zero.

Assume y_m is a single measured deposit. Usually the corrected deposit y_c is computed by subtracting the average background:

$$y_c = y_m - \mu_b \qquad (2)$$

This has two consequences that one should be aware of. First, the variance of corrected samples equals that of the measured samples, which is a slight overestimation that may be insignificant since often $\sigma_m^2 >> \sigma_b^2$. Secondly, if spray deposits are very low, that is $\mu_m \approx \mu_b$, for some samples the measured deposit may be less than the average background, $y_m < \mu_b$, which results in a negative deposit $y_c < 0$. This is a common problem when dealing with low values close to background values.
Several procedures have been applied to overcome this unphysical result. First, since negative values cannot be true deposits, these values probably indicate zero deposits, so a negative y_c is adjusted to zero. Secondly, considering a small positive detection level y_0 below which deposits cannot be ascertained, it is well possible that all deposits below the detection level are actually exactly at this level (which is a 'worst case' approach). So all values $y_c < y_0$ can be adjusted to y_0 itself. The practical consequences of these two procedures are discussed in the following sections. A new approach is introduced as a third option, in which the distribution of the background values is accounted for, while preventing the occurrence of negative deposits.

Procedure A: negative deposits adjusted to zero

Fig. 2a shows how the distribution of corrected deposits changes by pushing negative values to zero. Clearly the distribution is distorted unrealistically. This causes the mean value to increase. The height of the peak at zero deposits relates to the integral of negative deposits. For sufficiently narrow distributions, that is if $\mu_c >> \sigma_c$, hardly any negative values will occur. The ratio μ_c/σ_c appears to be an important parameter. Fig. 2b indicates how the relative mean m/σ changes as a function of μ/σ, depending on whether zero values are included (Z) or excluded (NZ) from the evaluation. For $\mu_c = 0$, the mean m_c of the distorted distribution has increased to about 0.4 σ_c (Z) or 0.8 σ_c (NZ). Particularly, if deposits are processed after taking the logarithm first, all zero values will be lost since log(0) does not exist.

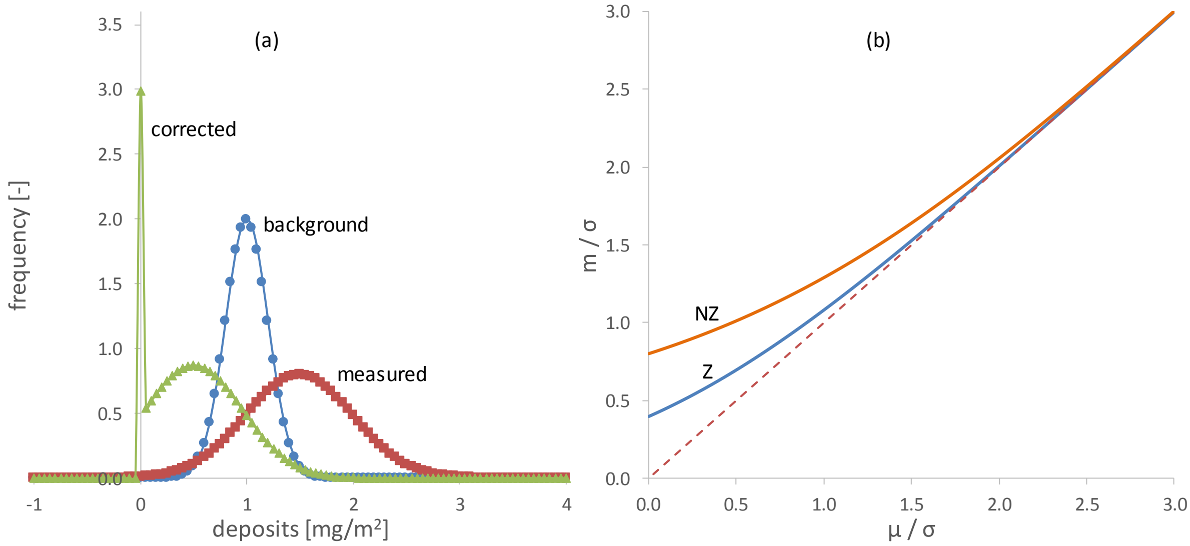

Fig. 2. (a) Distributions of Fig. 1b; negative corrected deposits clustered at zero deposits, resulting in a distorted distribution. (b) Relative mean (m/σ) of distorted distribution as function of μ/σ with (Z) and without (NZ) taking account of zero deposits.

Procedure B: negative deposits adjusted to small positive

Pushing zero and negative values to a small positive value will lead to a distorted probability distribution similar to Fig. 2a. Again, mean values will increase. However, no values will be lost when transferred to log values. Still, such values show up in a unrealistic way.

Procedure C: alternative approach

Measuring a spray deposit is essentially equivalent to drawing an sample from the corresponding probability distribution. Occasionally, such a deposit can be on the lower end of the distribution and may be less than the average background when the distributions for background and measured values overlap considerably, as in Fig. 1b. Each measured deposit y_m equals the sum of background and corrected deposit, both of which are equivalent to drawing a sample value from their respective probability distributions. Clearly, the drawn background value cannot be larger than the measured deposit, as the corrected deposit always is non-negative. This means that the drawn background can only take values between 0 and y_m. The expected (most likely) background value equals the mean over the range 0 through y_m:

$$m_b = \int_0^{y_m} f_b\, x\, dx \Big/ \int_0^{y_m} f_b\, dx \qquad (3)$$

Where f_b is the probability distribution of background values. It can be shown that $m_b \leq y_m$ and $m_b \leq \mu_b$ in all cases. Using this value m_b of background deposit, the most likely corrected deposit corresponding to y_m equals

$$y_c = y_m - m_b \qquad (4)$$

which resembles Eq.(2), but will always produce corrected values $y_c \geq 0$. For large enough measured values, say $y_m > \mu_b + 3\sigma_b$, Eq.(3) yields $m_b \approx \mu_b$, and Eq.(4) approaches Eq.(2).
In scaling the deposits relative to the mean background value μ_b, the relation between y_m and y_c can be studied with σ_b as a parameter. Fig. 3a shows y_c as a function of y_m for various values of σ_b. For small σ_b, m_b is close to μ_b, as long as $y_m > \mu_b$. When $y_m < \mu_b$, the mean m_b is close to y_m itself and $y_c \approx 0$. For increasing σ_b the mean m_b decreases more smoothly when y_m decreases, resulting in a smooth decay of y_c as well. The dashed line indicated the values of y_c when Eq.(2) is applied; clearly for $y_m < \mu_b$, the corrected deposit y_c becomes negative. Fig. 3b shows an example of a measured deposit y_m inside the range of possible background values. Mean m_b is the average over the range 0 through y_m (indicated by the solid red line). Corrected deposits y_{c0} and y_{c1} correspond with the results of Eq.(2) and Eq.(4), respectively.

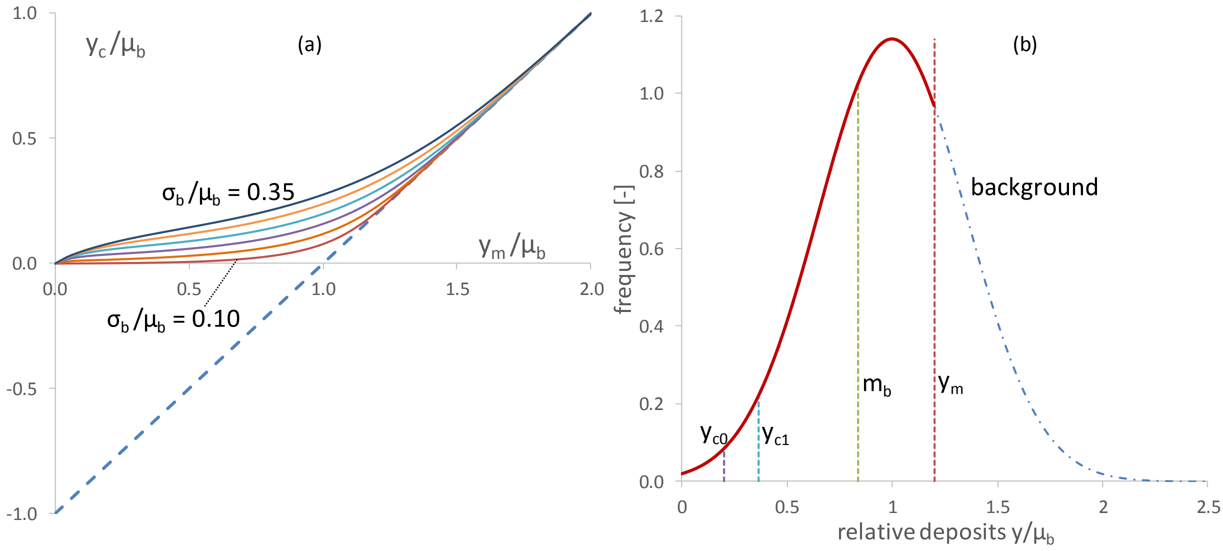

Fig. 3. (a) Corrected deposit, relative to average background μ_b, as function of measured relative deposit, for different ratios σ_b/μ_b (0.10, 0.15, .., 0.35). Dashed line: corrected deposit when Eq.(2) is applied. (b) Example of a small measured deposit y_m within the range of possible background values (σ_b/μ_b = 0.35); showing most likely mean m_b, basic corrected deposit y_{c0} (Eq.(2)) and alternative deposit y_{c1} (Eq.(4)).

From measured signal to deposit

As an example, a fluorescent technique is assumed for measuring deposits of sprays and spray drift. A fluorescent dye is dissolved in the sprayer tank and each spray drop contains a known concentration of the dye. The amount of dye ending up on a collector is a measure of the level of deposits on that collector. The collector of surface areas S is washed using a fixed volume V of water. The effluent is sampled by a fluorimeter. The sensitivity of the fluorimeter is given by the factor φ, relating the concentration in the effluent [μg L^{-1}]and the fluorimeter units [U]. In principle φ is a constant depending on the fluorimeter, its settings and the type of dye used. Let f be the fluorimeter reading, then the deposit y on the collector is given by:

$$y_c = \frac{(f - f_b)\,\varphi\, V}{S} \tag{5}$$

Where f_b is the fluorimeter reading of the background (obtained from washing a set of clean collectors). Note that y_c is the corrected deposit, since the background has been subtracted in the equation. Similarly, the equivalent background deposit is given by

$$y_b = \frac{f_b\,\varphi\, V}{S} \tag{6}$$

This equation expresses that the background deposit can be minimized by minimizing V and maximizing S, assuming this does not affect f_b. For a selected collector, S is fixed and only the volume V can be minimized. However, f_b is the sum of a contribution f_w of the solvent (water) and of the collector material f_{col}. Clearly, f_w cannot be changed by washing with water that is itself responsible for f_w. On the other hand, f_{col} may depend on V or S. Thus, the background deposit y_b is not a constant but depends on the collector type and size and the analysing procedure. It also depends on the fluorescent dye through the factor φ, even though the collectors in the background are untreated and receive no dye at all.

Results

Background levels of deposits

Untreated filter strips (Technofil TF-290, 0.50x0.10 m^2) were washed in 1.0 L of demi water. Spherical collector (Siebauer nylon-wired cleaning pads, diameter 0.09 m) were washed in 0.050 L of demi water. Fig. 4a shows the cumulative distribution of the equivalent deposits of 21 untreated filter strips and the fitted normal distribution. The deposits include the contribution of the water solvent. The equivalent deposits have mean 22.4 μg·m^{-2} and standard deviation 2.0 μg·m^{-2}. The equivalent deposits of 19 untreated spherical collectors are shown in Fig. 4b; their mean and standard deviation are 17.2 and 4.8 μg·m^{-2}, respectively. Although the mean deposits for these two collector types appear similar, this is a coincidence.

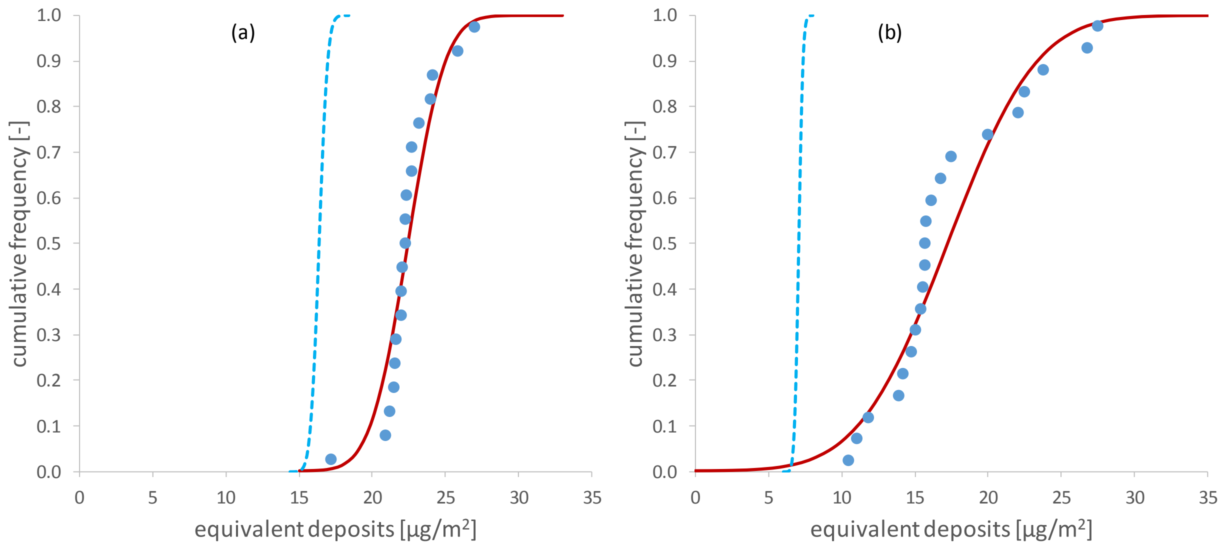

Fig. 4. Measured equivalent background deposits on clean collector materials (dots) and fitted normal distribution (solid red line) including water solvent contribution; dashed line indicates equivalent deposits for water; (a) filter strip collectors 0.50x0.10 m^2; (b) nylon wired spherical collectors 0.09 m diameter.

The dashed curves indicate significantly different values of the equivalent deposits for the demi water used to wash the samples. This reflects the differences in water volume and collector size for these two cases. The variance for the spherical collectors is higher than that for the filter strips. This may be due to the relatively large variance in size and shape of the spherical collectors.

Spray drift vs distance downwind

Usually, spray drift deposits are expressed as a function of downwind distance. In many cases an exponential function of distance fits the average deposits of repeated trials sufficiently well. The measured deposits of individual trials at a certain distance can be considered as stochastically drawn samples from an appropriate distribution function. The mean of this distribution function must correspond to the value given by the exponential function at that distance. The variance of the deposits can have many origins that will not be discussed here.

The detection threshold reflects the uncertainty in the measured deposits due to variance of the method. For very low deposits this uncertainty equals the uncertainty of background deposits. The detection threshold in the examples is assumed to equal $2\sigma_b$. Corrected deposits less than this threshold cannot be distinguished from zero deposits. As stated above, background deposits may depend on sample size S and volume V to wash the samples. Consequently, the detection threshold for 500 cm^2 strip collectors may differ from that for 1000 cm^2 strip collectors or spherical collectors.

An example of measured deposits of spray drift is shown in Fig. 5a, showing deposits before and after correction for background deposits. Down to 10 m filter strip collectors of 500 cm^2 were used; further downwind 1000 cm^2 collectors were used, showing different background and threshold values. Many corrected deposits for $x \geq 15$ m are less than 0. In Fig. 5b the same corrected deposits are shown, against a logarithmic y axis. The red dots indicate deposits that are limited to a small positive value (equal to the threshold, in this case), effectively deviating from corrected deposits only for $x \geq 15$ m. Green squares indicate deposits computed following the alternative weighted approach. The solid lines represent fitted power-law functions. The curves for corrected and alternative deposits are relatively close, but the curve for deposits limited to the threshold values is clearly different and leading to higher deposits for $x>10$ m. The 'small-pos' curve crosses the threshold line only at about $x=30$ m. However, both corrected and alternative deposits are below the threshold level for $x \geq 15$ m, so differences can be hardly considered significant.

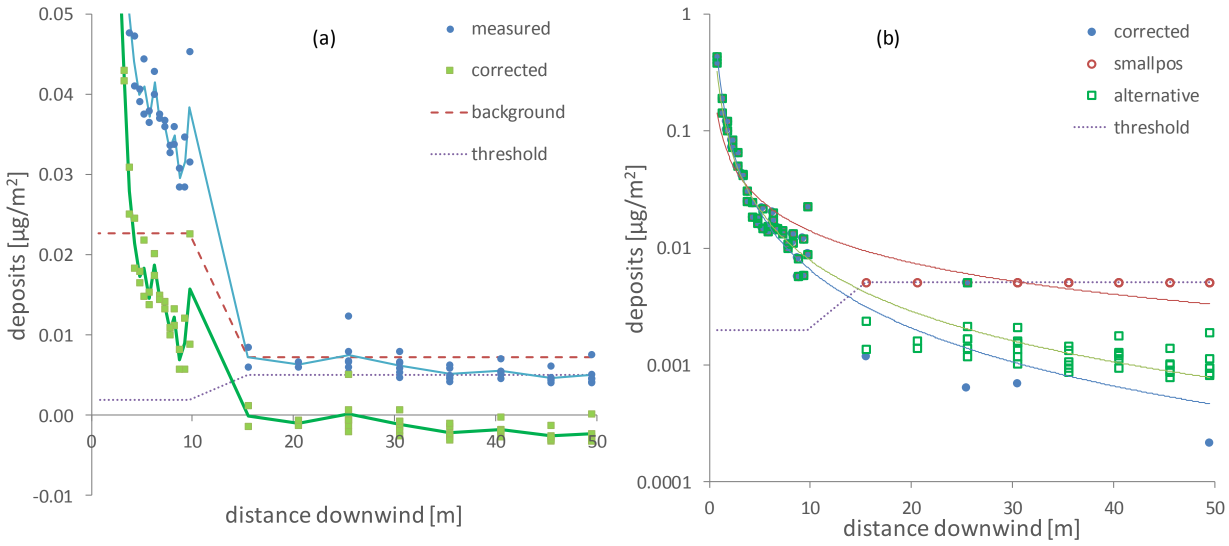

Fig. 5. (a) example of measured deposits as a function of distance; in the corrected deposits background is subtracted; (b) same example showing corrected deposits, deposits limited to threshold values, and deposits computed according to alternative approach; power-law functions are fitted.

The green squares in Fig. 5b are relatively close and all well below the threshold, for x≥15 m. This seems to indicate that standard deviation in deposits for the alternative method is significantly lower than the threshold (which equals twice the standard deviation of the background). This may be due to the flattening effect of the alternative method (see left part of Fig. 3a). However, a comparison of the standard deviation of the original corrected deposits, deposits according to the alternative method, and background deposits (Fig. 6) shows indeed that standard deviation of the alternative method is lowest. However, surprisingly, in many cases the standard deviation of the original corrected deposits is less than that of the background as well, for ultra-low deposits (x≥15 m).

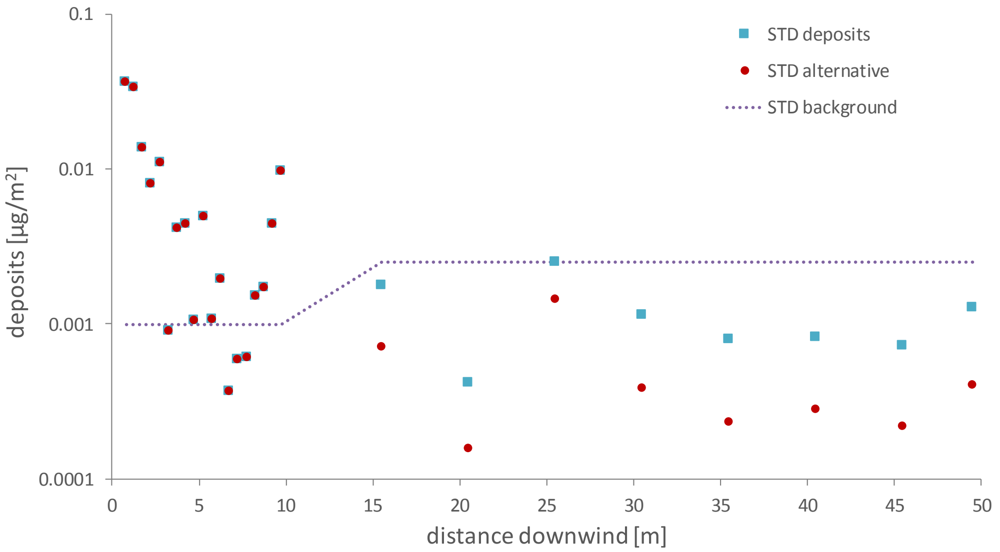

Fig. 6. Standard deviation of corrected deposits (blue squares) and alternative deposits (red dots) compared to standard deviation of background (dashed line), as a function of downwind distance.

Discussion

Mathematically, it can be shown that the way ultra-low deposits are dealt with, may affect the final results. This is particularly true when the variance of measured deposits is relatively large. The presence of background deposits is not a problem per se. However, the variance in background deposits determines the threshold level. Keeping this variance as low as possible is an important issue, although the researcher cannot control all factors. Examples of factors he can control, are minimizing variance in collector sizes and washing volumes, and so on. For instance, the relatively large variance in background deposits for spherical collectors is likely due to the variance in size of such collectors.
It may seem strange that computations for untreated collectors are subjected to a sensitivity factor φ related to the fluorescent dye used, as no dye is used at all in those cases. Even stranger is the dependence on washing volume V and collector size S when assessing equivalent background deposits of demi water. Yet, such computations do not stand on their own but are related to actual deposits on treated collectors. As a consequence, background deposits computed this way depend on the procedure to analyse the deposits. Therefore background deposits may change when the procedure changes.
So far, the origin of variance in actual spray deposits has not been discussed. Implicitly, however, variance was introduced as originating from a physical source (e.g. changes in environmental conditions, variance in collector size or shape). The accuracy of the measuring device (e.g. fluorimeter) may not have been accounted for. Particularly in procedure C, the statement that background deposits must be limited to the range 0 through y_m, implicitly assumes that readings of the measuring device are completely accurate and exact. Although essentially this cannot be

true, variance of the readings of the fluorimeter itself is probably very low. A possible bias in readings will affect all readings, both the (uncorrected) measured and the background values. As a consequence, such bias is not expected to cause problems.

The examples use a normal distribution of measured deposits. Clearly, deposits cannot be negative, so a normal distribution may not fit too well on the lower end of the measured distribution. A lognormal or gamma distribution may be more appropriate. However, the normal distribution was used for simplicity and serves the purpose of this paper well enough. The examples used in this study indicate that normal distributions could be used without problems, although there may be situations a non-negative distribution is required.

The various methods to deal with ultra-low deposits clearly show that different results can be expected. However, the examples also indicate that such differences may be at or below the detection level. This means that observed differences may not be significant at all. In the example of downwind spray deposits, corrected deposits were clearly below the threshold. When corrected deposits are close to the threshold level (that is, not too far above or below), effects are more likely to be significant.

The alternative method using weighted corrections for background deposits leads to deposition values below the threshold, but the values seem to be accurate. That is, variance is relatively low and indeed much lower than that of the background deposits. The weighting method, however, suppresses variation by forcing potential negative deposits to a positive level. Remarkably, Fig. 6 seems to indicate that standard deviation of the original deposits is lower than that of the background as well. Although the number of repetitions in this example is relatively low (N=6 for each distance beyond 15 m), but the observed result is remarkable and unexplainable, so far.

Acknowledgement

The author thanks the Dutch Ministry of Economic Affairs (project number BO-20-002-003) for funding this research.