



A GRAPHICAL METHOD FOR DETERMINING THE DRY-DEPOSITIONAL COMPONENT OF AEROSOL SAMPLES AND THEIR FIELD BLANKS

SUILOU HUANG,* KENNETH A. RAHN and RICHARD ARIMOTO†

Center for Atmospheric Chemistry Studies, Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882-1197, U.S.A.

(First received 29 October 1996 and in final form 3 March 1997. Published August 1997)

Abstract—During the Atmosphere/Ocean Chemistry Experiment (AEROCE), field blanks of certain elements in aerosol samples occasionally increased abruptly, always during periods of unusually high atmospheric concentrations. We hypothesized that the anomalous blanks were created by coarse aerosol entering the sampling shelters and depositing onto the blank filters. If so, samples taken nearby should have been similarly affected. To test this hypothesis, we developed a simple graphical method in which elemental masses in field blanks are plotted against elemental masses in pumped samples, and zones of proportionality between the two are sought. Data from Bermuda and Mace Head (coastal western Ireland) confirmed that depositional zones did indeed appear, but only for coarse-particle elements and only under certain conditions. Actual increases of crustal and pollution-derived elements agreed well with values predicted from settling velocities and sampling rates: blanks increased up to an order of magnitude or more but samples by less than 1%. Marine elements behaved like crustal elements in most samples but occasionally were much more enriched: blanks increased up to 30-fold and samples up to about 3%. It thus appears that when coarse-particle elements are present in high concentrations, their field blanks and samples may be measurably affected by dry deposition. Depending on the elements of interest, this dry deposition may have to be measured and the concentrations corrected. © 1997 Elsevier Science Ltd.

Key word index: Aerosol, dry deposition, blank, trace elements.

INTRODUCTION

Whenever atmospheric aerosol is sampled on filters, the proper blanks must be subtracted to obtain ambient concentrations. The two most common approaches are to use box blanks and field blanks. Box blanks are filters taken directly from the manufacturers. Field blanks are filters taken from boxes, handled exactly like samples, placed in identical samplers for the same times as samples (but without drawing air through them), and then analyzed like samples.

Field blanks are generally considered superior to box blanks because they can record regular contamination introduced during sampling, handling, or analysis (Berg *et al.*, 1993). Field blanks cannot detect irregular contamination reliably, however, because they are taken on different filters from the samples—random contamination of a blank does not necessarily imply simultaneous contamination of the

paired sample. Even when random contamination is detected, it is difficult to tell whether it resulted from sampling/analysis or from manufacturing. The practical effect of either type of random contamination is the same, however: samples so affected must be flagged in the data set. A third potential limitation of field blanks is that they can detect systematic contamination only when box blanks are regularly analyzed because systematic contamination is indistinguishable from increased box blanks. In studies where large numbers of field blanks are analyzed, box blanks are not always included. And fourth, field blanks are time consuming to collect and analyze.

Although field blanks have been used for many years to correct samples and detect contamination (e.g. Chen and Duce, 1983), the practical difference between field blanks and box blanks has never been studied systematically. The immediate stimulus for this study came during the Atmosphere/Ocean Chemistry Experiment (AEROCE), when we noticed that field blanks of some elements on Whatman No. 41 filters were occasionally much higher than the box blanks or means of the field blanks. Because most of these high field blanks appeared at the same times as high atmospheric concentrations of the elements, we felt that the simplest and most logical explanation for

*Author to whom correspondence should be addressed.

†Now at: Carlsbad Environmental Monitoring and Research Center, 1400 University Drive, New Mexico State University, Carlsbad, NM 88220-3575, U.S.A.

the high blanks was penetration of aerosol into the rain shelters and dry-deposition there rather than contamination of the field blanks. To test this idea, we developed a simple graphical technique to reveal the three components of actual field blanks, namely box blanks, contamination, and dry deposition. We then compared the apparent dry-deposition with predictions from calculations based on air flow through shelters, settling velocities for particles of various sizes, and atmospheric concentrations during sampling. Because observation agreed acceptably with prediction, we concluded that the majority of the high field blanks did indeed result from dry deposition. This article presents the graphical technique and shows how it was applied to field blanks and samples collected at two AEROCE stations in the North Atlantic Ocean: Bermuda and Mace Head, Ireland. For each site, we have tried to answer three practical questions: (1) whether elevated field blanks are really caused by dry deposition of aerosol inside shelters; (2) how much field blanks can routinely be elevated by dry deposition; and (3) how large the dry-depositional component of the sample is (i.e. how much the final elemental concentrations in samples would be affected if box blanks rather than field blanks were used). This last question is equivalent to asking whether field blanks are really necessary.

THE GRAPHICAL TECHNIQUE FOR SEPARATING COMPONENTS OF FIELD BLANKS

When a field-blank filter is placed into a sampler that faces upward and the geometry of the shelter allows air to flow through it at some fraction of the outside wind speed, some aerosol from the transiting air can dry-deposit onto the filter blank (Fig. 1a). The rate of this dry deposition depends on the particle-size distribution of the element or substance in question, or more accurately, on the settling velocity of particles of interest. The same thing should happen with samples: for shelters where more air can flow through

than is required for taking the sample, aerosol from the air above the main flow can dry-deposit into the air stream and onto the sample (Fig. 1b). The mass of this dry-depositional component (of blank or sample alike) should be proportional to the atmospheric concentration of the element, the settling velocity of its particles, and the exposure time of the filter, i.e. the time of sampling plus the time when the pump is not running. Since the net mass of the element in the sample (total mass less field blank) is also proportional to the element's atmospheric concentration (provided that the sampler operates continuously), the dry-deposition component of the field blank should be proportional to the net mass in the corresponding sample. Thus the total mass of an element in a field blank should be the sum of a quasi-constant box-blank component and a dry-depositional component proportional to the net mass of the element in the paired sample. A plot of field blank vs net sample should then be a straight line with slope equal to the ratio of settling velocity to face velocity through the filter, and intercept equal to the box blank. Detailed versions of these relations are derived in Appendix A.

Two assumptions of this picture should be noted. The first is that the settling velocities of elements at a given site are effectively constant, i.e. that the elements' particle sizes do not change enough with concentration to vary their average deposition velocities noticeably from sample to sample. While this seems true for most elements at the sites considered here, we have evidence that marine aerosol generated locally may sometimes be coarse enough to have substantially increased depositional velocities (see below). Second, as noted above, the linear dependence of the "depositional blank" on net mass in the sample assumes that sample and blank are exposed to the same air. But if the sample pump shuts off part of the time, for example, when winds leave the desired sampling sector, the ratio of depositional blank to net sample will increase. The magnitude of this artifact and the procedure for correcting it are discussed in the next section.

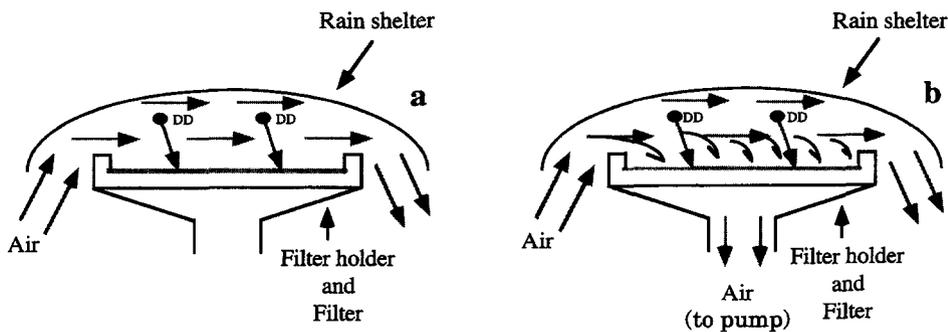


Fig. 1. Diagrams of aerosol samplers: (a) for field blank; (b) for sample.

Because atmospheric concentrations of elements are distributed log-normally, plots of masses in field blanks vs net samples should always use logarithmic axes. On such "field-blank plots," the box-blank component should appear as a horizontal zone (independent of net mass in sample), and the dry-deposition component as a 45° zone at the right-hand end of the plot (Appendix A). The "position" of this 45° zone (a constant ratio of the value on the vertical axis to the value on the horizontal axis), i.e. the ratio of field blank to net sample when box blank is negligible, is shown in Appendix A to equal the ratio of dry-deposition velocity to face velocity. Outliers due to random contamination during manufacturing, handling, or analysis are easily discerned as isolated points above either zone; analytical errors can occasionally produce a point outside the zones. Random contamination is not considered further here.

(Log-log plots cannot show the occasional cases where field blanks are higher than samples, i.e. where net masses are negative. Although this effect may stretch the plots slightly to the left, so few samples have negative net masses that the problem is unimportant in practice.)

Depending on the relative magnitudes of an element's box blanks, dry-depositional velocities, and samples, its field-blank plot can in theory have (a) a box-blank zone and a dry-depositional zone, (b) only a box-blank zone, or (c) only a dry-depositional zone. High blanks, low depositional velocities, and low samples tend to mask dry-depositional zones, whereas low box blanks, high depositional velocities, and high samples tend to reveal them (Fig. 2). (We have not yet seen any plots where dry deposition masks box blanks.)

Box blanks are determined by the nature of the filter material and how it is manufactured. For example, the major impurities in cellulose filters, Cl and Na, result from cooking the wood with NaOH liquor and bleaching the resulting cellulose fibers, respectively. In contrast, the Zn and Cr impurities largely result from handling the cellulose with metallic rollers. The dry-depositional zones are positioned by their ratios of dry deposition to net sample. Since this ratio equals the ratio of settling velocity to face velocity of sampling, it is possible to estimate where each element's line will fall. From settling velocities for particles of various sizes and typical flow rates for our

samples, we have estimated these ratios to range from <0.0003% to 2% (Table 1). Thus even for most coarse-particle elements under most conditions, deposition should be less than about 1% of net sample. For fine-particle elements, deposition should be less than 0.1% of net sample. If these estimates are correct, dry deposition to samples can generally be ignored and field blanks will be unnecessary. A possible exception would be for aerosol generated locally by high winds, such as in a dust storm over a desert or in a gusty rainstorm over the ocean, when particle sizes could temporarily be much larger than normal. For example, if particles reached 100 μm in size, they would have settling velocities of 30–35 cm s^{-1} and would be deposited as fast as aerosol was being sampled. Net masses of elements in samples are determined by flow rates of samples, integrated times of samples, and atmospheric concentrations. Atmospheric concentrations are determined by proximity to source, intensity of transport, and extent of deposition.

The point where the lines of box blank and dry deposition cross may be called the "critical mass" of the sample (Appendix B), i.e. the minimum mass necessary for a 45° depositional zone to appear on the field-blank plot. This mass is a function of the box blank and dry-deposition velocity of the element. If the mass of an element exceeds its critical mass, its field-blank plot will show both the box-blank and the field-blank components; otherwise, only the box-blank component will appear.

TWO CASE STUDIES

Sampling

For illustrating typical relations between field blanks, box blanks, and samples, we have selected data from Bermuda and Mace Head, two of the four AEROCE sampling sites. Bermuda is in the semitropical western North Atlantic, Mace Head in the temperate eastern North Atlantic. At both sites, aerosol was sampled daily with Whatman No. 41 cellulose filters ($8 \times 10 \text{ in} = 20 \times 25 \text{ cm}$) and custom-made samplers on 20-m towers located at coastal sites. Computer-controlled systems helped avoid local contamination (Arimoto *et al.*, 1992, 1995). Flow rates were about $45 \text{ m}^3 \text{ h}^{-1}$, corresponding to an average face velocity of 31 cm s^{-1} .

Table 1. Predicted ratios of settling velocity to sampling velocity for aerosol particle of various sizes

Diameter (μm)	Settling velocity, V_{dd} (cm s^{-1})	Sampling velocity, V_{s} (cm s^{-1})	$V_{\text{dd}}/V_{\text{s}}$ (%)
0.1	< 0.0001	31	< 0.0003
0.3	0.0005	31	0.003
1	0.005	31	0.02
3	0.05	31	0.2
10	0.5	31	2

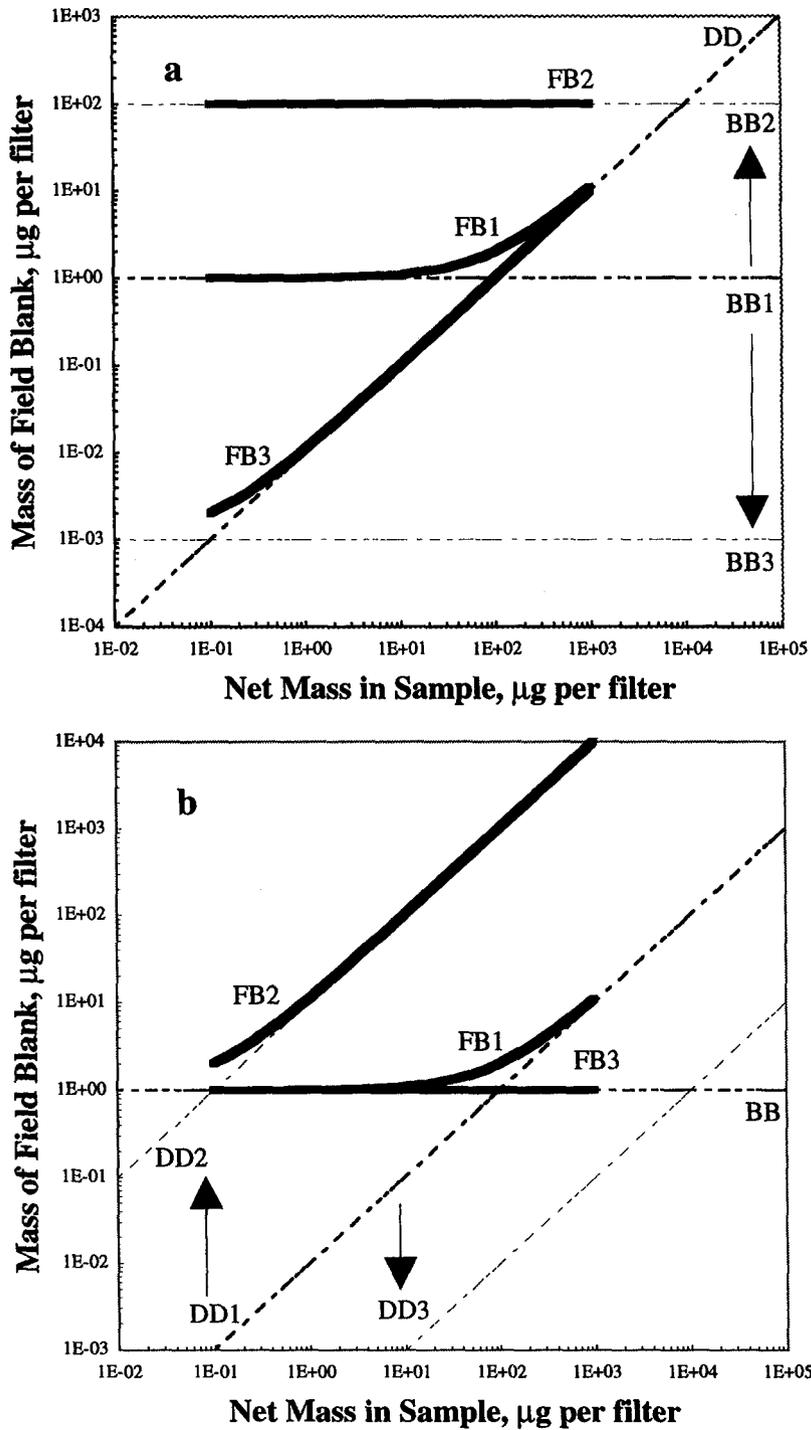


Fig. 2. Schematic log-log plots of field blank vs sample: (a) box-blank lines BB1, BB2, and BB3 vary relative to dry-deposition line DD; (b) dry-deposition lines DD1, DD2, and DD3 vary relative to box-blank line BB. Correspondingly, the field blank lines FB1, FB2, and FB3 vary with BBs and DDs.

Actual sampling times sometimes differed from 24 h because the wind came from outside the sampling sector and/or bad weather prevented the operators from changing the filters on schedule. At Bermuda, the mean exposure time was 26 h (with a range of 12 h

to 97 h) but the mean sampling time was 14 h (with a range of 2 h to 45 h). Thus in constructing our plots, the net mass of samples had to be scaled upward by a factor whose mean was 2.8. (This linear scaling assumes that mean ambient concentrations with the

pump off were the same as with it on.) At Mace Head, the mean exposure time was 57 h and the mean sampling time 24 h (ranges of 16–192 h and 2–112 h, respectively); hence the mean correction for net mass was a factor of 4.9.

At both sites, field blanks were taken regularly. Elemental concentrations were measured with instrumental neutron-activation analysis by R. Arimoto and colleagues. At each of the stations, we selected about 80 pairs of field blanks and samples collected between 1991 and 1994. We examined the crustal elements Al and Sc, the pollution-derived Cr, Zn, and Sb, the crustal/pollution V, Fe, and Co, the marine-derived Na, Mg, Cl, Br, and I, and the crustal/marine Ca. Because concentrations of Se, Mn, Mg, and the rare-earth elements were below detection limits in most blanks, we could not use the graphical technique for them.

Results from Bermuda

At 32.24°N, 64.87°W in the North Atlantic Ocean, Bermuda is regularly exposed to air masses from North America and Africa. Its aerosol varies strongly with the season: in July and August, the Bermuda/Azores high-pressure system controls the circulation and brings African air and Saharan dust; during other seasons the high-pressure system retreats and allows the westerlies to bring pollution from North America

(e.g. Chen and Duce, 1983; Arimoto *et al.*, 1992, 1995; Huang *et al.*, 1996). Therefore, at Bermuda we can study field blanks of marine, crustal, and pollution elements.

At the left-hand side (low net masses) of field-blank plots for all elements at Bermuda, the points formed a horizontal zone that almost certainly represents box blanks. Since we measured few box blanks, however, we cannot eliminate the unlikely possibility that this horizontal zone also represents systematic contamination. Lacking direct evidence for systematic contamination, we treat the horizontal zones as box blanks. The values of box blanks read from these plots are given in Table 2; the field-blank plots of the major classes of elements are discussed below.

Crustal elements. Field-blank plots for several crustal and crustal/pollution elements at Bermuda are shown in Fig. 3. Plots for the crustal elements Al and Sc, which are associated with coarse particles from soil or coal flyash, contain flat box-blank zones that are three decades long but only factors of two to three thick. Their right-hand ends grade smoothly into 45° depositional zones that rise by an order of magnitude over box blanks but contain at most 20% of the samples. As predicted from the ratio of settling velocity to sampling velocity (Table 1), deposition in these latter zones accounts for only 0.1% to 1% of net sample. Field-blank plots for the crustal/pollution

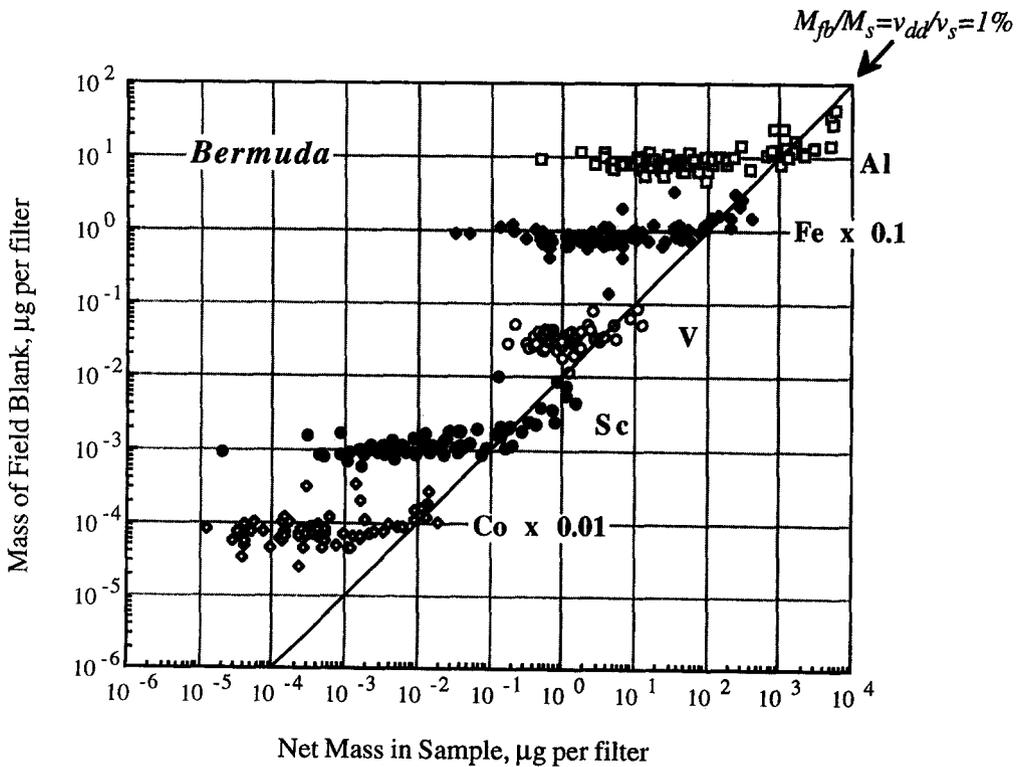


Fig. 3. Field-blank plots for Al, Fe, V, Co, and Sc at Bermuda.

Table 2. Box blanks for various elements in Whatman No. 41 filters, derived from field-blank plots shown in this paper

Element	Box blank, $\mu\text{g filter}^{-1}$
Na	100
Al	8
Cl	350
Ca	50
Sc	0.001
V	0.03
Cr	0.6
Fe	8
Co	0.008
Zn	0.3
Br	2
Sb	0.007
I	0.2

elements Fe and Co also have long box-blank zones and clear depositional zones, although the depositional zones are less pronounced than those of Al and Sc are (fewer points and field blanks increasing by factors of only three to four). The reason for Fe and Co's weaker depositional zones may be related to their increased fine-particle pollution compared to Al and Sc (e.g. Chen and Duce, 1983; Arimoto *et al.*, 1992, 1995), their relatively higher box blanks, or both. The plot for V, which has the greatest pollution component of these five elements, shows the smallest depositional zone (where field blanks increase by barely a factor of two).

For years it has been known that Bermuda receives multiple pulses of Saharan dust each summer and that these pulses produce the highest concentrations of crustal elements of the entire year (Duce *et al.*, 1976; Chen and Duce, 1983; Arimoto *et al.*, 1995). In our samples, too, the highest Al, Sc, etc. come from Saharan dust—14 of the 16 samples in Al's depositional zone were reported to be colored: nine yellow, three off-white, one gray, and only one uncolored. Thus 86% of the depositional samples (12 of 14) had the yellowish-brown color typical of Saharan dust. This means that depositional blanks for crustal elements at Bermuda are actually particles of Saharan dust that penetrate into the shelters and deposit on the blank filters.

The depositional-mean particle size of the Saharan dust (with respect to sampling shelters) can even be derived from our data. Knowing that for each point on the 45° line the ratio of *Y*-axis to *X*-axis (depositional blank to net sample) is just the (constant) ratio of settling velocity to sampling velocity (Appendix A), one can easily read this ratio for a Saharan element from its field-blank plot, insert our sampling velocity of 31 cm s^{-1} , and solve for the effective deposition velocity. For Al, this calculation gives a mass-weighted deposition velocity of 0.22 cm s^{-1} , which corresponds to a "depositional mean" diameter of about $6 \mu\text{m}$ for the Saharan particles. This size agrees, perhaps fortuitously, with the peak of the mass-size function of Saharan dust (also about $6 \mu\text{m}$) calculated

by Schütz (1980) for Saharan dust transported 5000 km from the Sahara toward the Caribbean. Our approximate deposition velocity also agrees well with estimates of Arimoto *et al.* (1996) based on cascade-impactor samples.

It is important to note how small the depositional effect on the samples is compared with the blanks. Whereas deposition increases the field blanks by up to an order of magnitude, it increases the samples by less than 1%. In other words, the difference between using box blanks and field blanks to correct for crustal elements at Bermuda is insignificant.

Pollution elements. The field-blank plots of pollution-derived elements at Bermuda also have well-defined shapes. Good examples include the fine-particle elements Cr, Zn, and Sb, whose 45° depositional zones are thus expected to lie up to an order of magnitude below those of the coarse-particle crustal elements and have dry deposition contributing only 0.1% or less to the net samples. It therefore comes as no surprise that field-blank plots of these pollution-derived elements show no hint of depositional zones (Fig. 4). Field blanks are not needed for pollution elements at Bermuda.

Unfortunately, the lack of a depositional zone for the pollution elements prevents us from verifying that their ratios of deposition to sample are as low as predicted. The most that can be said from Fig. 4 is that these ratios cannot be higher than about 1%.

Marine elements. The field-blank plots of the marine elements, shown in Fig. 5 for Na, Cl, Br, I, and Ca, are generally more irregular than those for the crustal and pollution elements. The plot for Ca is the simplest, with a well-defined box-blank zone extending over nearly two decades. No dry-depositional zone is seen, perhaps because Ca's box blanks are high enough to move its points away from the 1% depositional line. The other elements have more-complex plots. For example, Na and Cl have two-part plots, with a narrow box-blank zone similar to Ca's but with a cluster of higher points extending upward from the middle of the box-blank zone. These points represent enhanced dry deposition (which occasionally can reach 10% to 30% of the net sample) that is not linked linearly with sample mass. We speculate that the higher deposition is caused by unusually large particles of sea salt generated locally by high winds. Support for this idea comes from wind records at the site, which show that speeds during ten days with high field blanks were $8.2 \pm 1.8 \text{ m s}^{-1}$, as opposed to $3.6 \pm 2.2 \text{ m s}^{-1}$ for 14 d with low field blanks.

Note that no dry-depositional zone is seen at the right-hand end of Na and Cl's plots—the box-blank zones of Na and Cl extend nearly horizontally past the 1% line. This means that the dry-depositional effect of the normal, or undisturbed, marine aerosol at Bermuda accounts for less than 1% of the sample mass, just like the results for the crustal elements.

Of these marine elements, Br has the broadest zone of elevated box blanks—more than two orders of

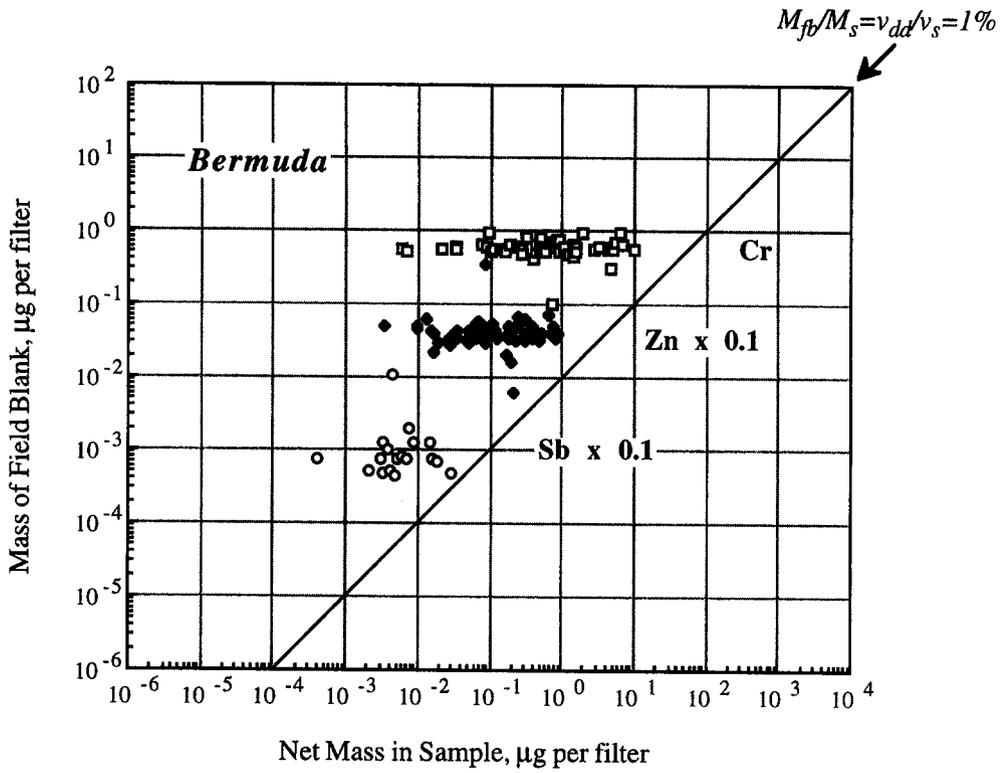


Fig. 4. Field-blank plots for Cr, Zn, and Sb at Bermuda.

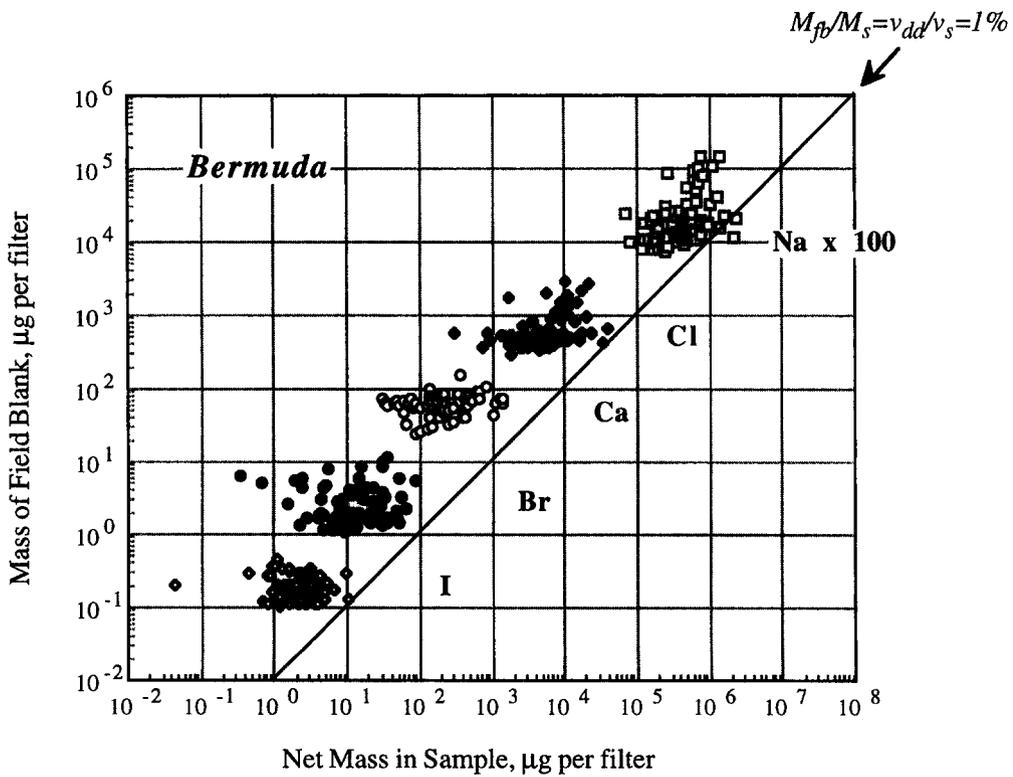


Fig. 5. Field-blank plots for Na, Cl, Ca, Br, and I at Bermuda.

magnitude. No dry-deposition component is observed. The plot for I is confined to approximately one decade in width. Because marine I is found mostly in fine particles, we were surprised to find that it also had a zone of elevated field blanks. Perhaps this is a consequence of gaseous I's being taken up very quickly by fresh primary marine particles, even very coarse ones, and becoming enriched in sea salt by factors of 100 to 200 over sea water (Seto and Duce, 1972). Mg is not plotted here because it has so very few blanks above its detection limits that no clear trend can be seen in the scattered data.

In summary, field blanks for marine elements at Bermuda are necessary if concentrations in individual samples, including those collected under high wind conditions, are to be determined to better than 10% to 30%.

Results from Mace Head

The AEROCE station at Mace Head is located at 53.43°N, 9.73°W, along the Atlantic coast of south-western Ireland. During most of the year, air comes to Mace Head from the west, with long trajectories over the North Atlantic Ocean. During October through December, however, transport from the east, i.e. from Ireland, Great Britain, and western Europe, becomes an important contributor to the aerosol (Merrill, 1994).

At Mace Head, only the field-blank plots for pollution elements have the same form as at Bermuda. The plots for crustal and marine elements differ considerably from those at Bermuda.

Crustal elements. Plots for Al, Fe, V, Co, and Sc at Mace Head (Fig. 6) are essentially flat; none show clear dry-depositional zones. Although the mean box blanks of these elements and their minimum masses in net samples were about the same as at Bermuda, their maximum masses were lower by an order of magnitude or more. This absence of a true high end accounts for the missing depositional zone. The lack of high crustal concentrations at Mace Head is probably because it does not receive strong pulses of desert dust in the way that Bermuda receives them from the Sahara (Arimoto *et al.*, 1995). The patterns for V and Co are more irregular than for the other elements, possibly because of difficulties in detecting these elements in the presence of the higher concentrations of sea salt at Mace Head than at Bermuda (see section on marine elements).

Pollution elements. The field-blank plots for Cr, Zn, and Sb at Mace Head are almost identical to those at Bermuda: box-blank values are the same, and the dry-deposition component is undetectable (Fig. 7). This result suggests that even though Mace Head is influenced by European pollution, dry deposition of fine-particle pollution elements remains unimportant, as it must if particle size remains its controlling factor.

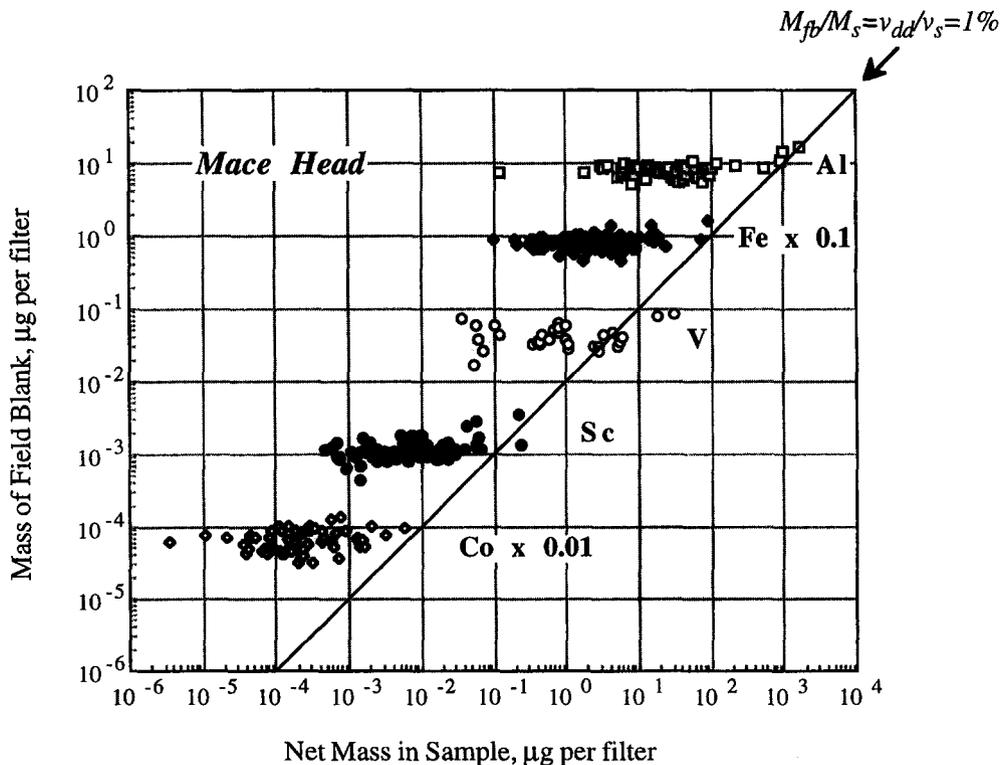


Fig. 6. Field blank plots for Al, Fe, V, Co, and Sc at Mace Head.

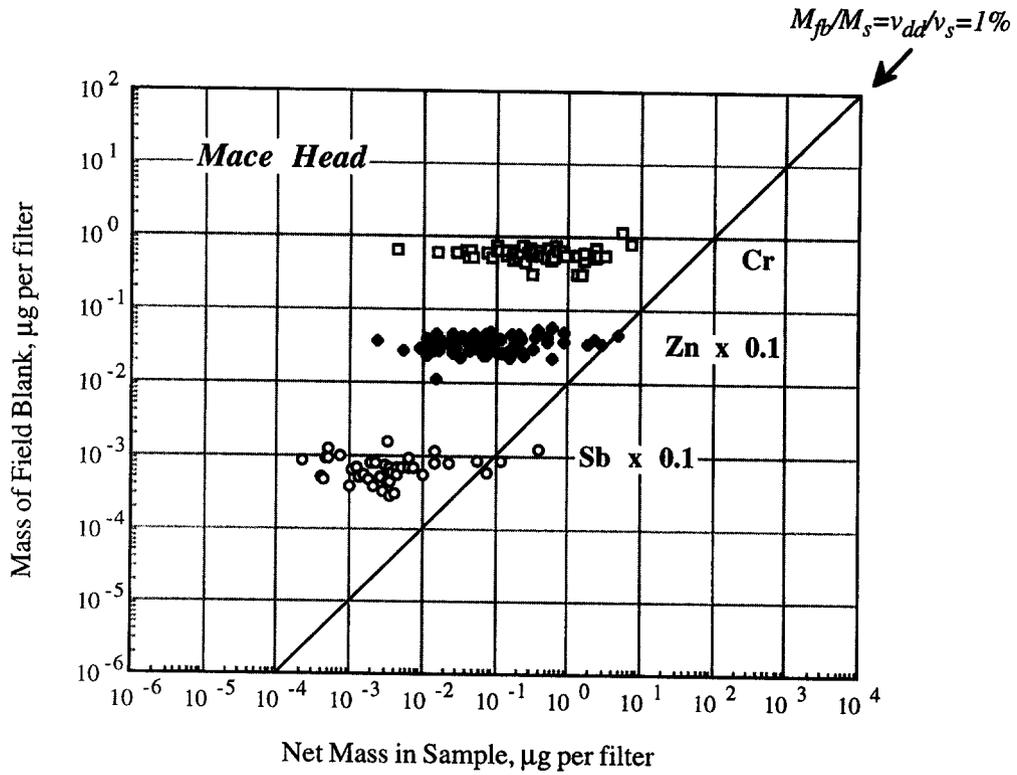


Fig. 7. Field-blank plots for Cr, Zn, and Sb at Mace Head.

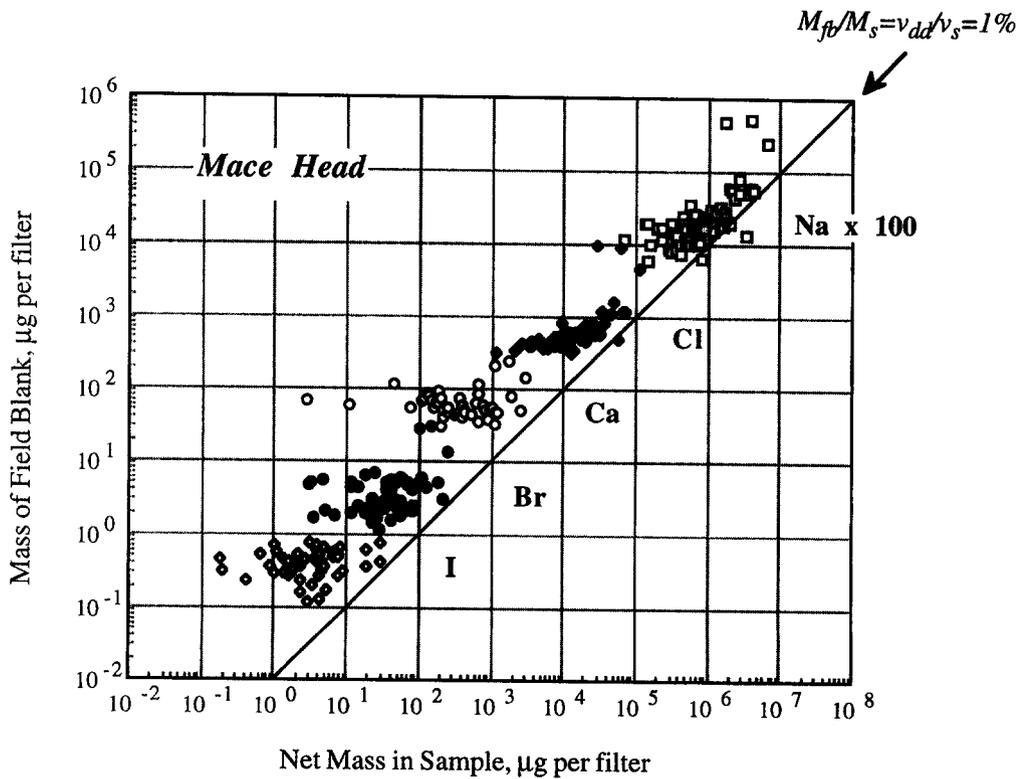


Fig. 8. Field-blank plots for Na, Cl, Ca, Br, and I at Mace Head.

Marine elements. Compared with Bermuda, the field-blank plots for marine elements at Mace Head are more regular and agree better with the expected shape (Fig. 8). Those elements with significant primary-marine (coarse-particle) components, Na, Cl, and Br, extend up to half an order of magnitude farther to the right (have up to threefold higher concentrations). Of these, Na and Cl both show clear 45° depositional zones of the type that was absent at Bermuda. Interestingly, however, the ratio of deposition to net sample in this zone, 2% to 3%, is several times greater than the crustal depositional zone at Bermuda but a few times lower than values for marine aerosol at Bermuda.

What accounts for the higher concentrations of marine aerosol at Mace Head? Assuming higher wind speeds to be the simplest possibility, we checked the sampling records and confirmed that this was correct: speeds of 15–20 m s⁻¹ were frequent there but rare in Bermuda, where the effective maximum speed during our samples was about 10 m s⁻¹. Thus at Mace Head, high winds are frequent enough to produce a regular 45° zone for its primary marine elements.

The mixed marine/pollution element Br has two horizontal zones at Mace Head, broadly similar to its pattern at Bermuda but less pronounced. Although the most likely explanation is two characteristic box blanks (probably from two batches of filters), we have no direct evidence to support it. As at Bermuda, Br shows no indication of a depositional zone. The secondary marine element I has an irregular field-blank plot that roughly resembles Br's but extends farther to the left of the 1% line. The marine/crustal Ca shows only a box-blank zone, as it did at Bermuda.

One interesting feature shown by Na, Cl, Ca, and Br is the presence of three very high field blanks at the extreme right-hand end, up to an order of magnitude above all other blanks. The reason for these high values is not yet known—it is not just high wind speeds because they were no higher than for the other samples with depositional blanks. It is also unrelated to total time on the tower, for times of these samples did not differ significantly from those of other samples. It did rain during the collection of these samples, however.

SUMMARY, CONCLUSIONS, AND SUGGESTIONS FOR FUTURE WORK

This work shows that both field blanks and aerosol samples can contain a detectable dry-depositional component of coarse-particle elements when samples are sufficiently affected by strong sources of coarse aerosol. Qualifying sources found at these two AEROCE sites include deserts and the sea. Coal flyash near uncontrolled sources might also produce dry deposition of the type seen here. We also observed that even after being transported several thousand

kilometers from its source, desert dust remains coarse enough to produce dry-depositional effects, provided only that concentrations at the receptor are high enough. Because the two sites studied so far sampled the marine atmosphere, we do not know how far from the ocean marine aerosol can be transported and still produce dry-depositional effects. It appears both theoretically and in practice that fine-particle aerosol will not produce detectable dry-depositional effects on samples or field blanks taken under normal sampling conditions. Such effects cannot be excluded when atmospheric concentrations are very high or sampling times are very long, however.

We suggest that when study sites are well removed from sources, atmospheric concentrations of elements are not high, and giant particles have been removed by transport and aging, field blanks may not be necessary. Nearer strong sources, however, field blanks should be considered.

We close this paper with two general remarks. (1) Although we have focused on trace elements, our general approach to understanding field blanks and dry deposition to filters should apply to any other particulate substance, including the common ions and organics. (2) Perhaps the most important finding is the most qualitative one, namely that every sample and field blank where excess air flows above it will contain a dry-depositional component of aerosol. The only question is whether the deposition can be detected relative to the conventional pumped component of aerosol.

Acknowledgements—We wish to thank Barbara J. Ray and Ursula Tomza of URI/CACS for many analyses and enlightening discussions. It was they who first proposed the idea of dry deposition to field blanks. Subsequent study has proven them correct.

Samples were taken by A. Grasspool (Bermuda) and G. Spain, D. Brown, and M. O'Dowd (Mace Head), and were analyzed at the two-megawatt research reactor of the Rhode Island Nuclear Science Center, Narragansett. This work was supported by NSF grant ATM-90-13062.

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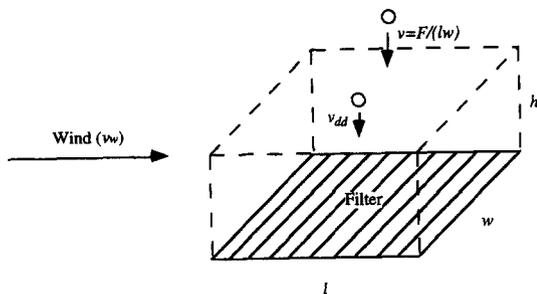
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APPENDIX A. DERIVATION OF THE EQUATION FOR FIELD BLANK VS NET AEROSOL SAMPLE

Consider two filter-sampling setups of the type shown in Fig. 1, where air from outside can enter and move horizontally over the filter whether the pump is on or off. One setup is for field blanks, the other for sampling aerosol with a pump. Variables of interest include length and width of the filter (l and w), wind speed through the shelter is (v_w), atmospheric concentration of element X as mass per unit volume (C), dry-deposition velocity is



(v_{dd}), flow rate provided by the pump as volume per unit time (F), face velocity through the filter is ($v = F/lw$), and sampling time is (T).

The box blank of element X is M_{bb} . We assume that its value remains constant during sampling. The dry-deposition component of the field blank (and the sample) increases monotonically during the sampling, however, in response to the atmospheric concentration C of element X. Here we assume for simplicity that C remains constant during the sampling period, even though it can vary significantly and usually does. Since variable ambient concentrations affect sample and field blank equally, the average concentration forms an acceptable substitute for the integral of concentration over sampling time.

Aerosol in air just above the filter will settle downward and dry-deposit onto it with an effective deposition velocity v_{dd} that is independent of the wind speed. Assuming that the air moves rapidly enough over the filter so as to fully replenish the deposited aerosol, the rate of dry deposition to the filter will be independent of wind speed. This can also be seen from the speed of air moving across the filter. For example, in a sampling time T , the number of times N that air can

move across the filter (parallel to side l) is just T divided by the time t per pass:

$$N = \frac{T}{t} = \frac{T}{\left(\frac{l}{v_w}\right)} = \frac{v_w T}{l} \tag{A1}$$

But the effective height h of the deposition layer per pass over the filter is the product of deposition velocity and time per pass:

$$h = v_{dd} t = v_{dd} l / v_w \tag{A2}$$

The total height of air from which aerosol is dry-deposited in time T is thus Nh :

$$Nh = \left(\frac{v_w T}{l}\right) \left(\frac{v_{dd} l}{v_w}\right) = v_{dd} T \tag{A3}$$

which is independent of wind speed and dimensions of the filter.

The mass of aerosol dry-deposited to the filter in time T (the “dry-deposition blank”) will then be that contained in the box of height $v_{dd} T$ and base lw :

$$M_{dd} = C v_{dd} T l w \tag{A4}$$

The field blank M_{fb} is then the box blank M_{bb} plus the dry-deposition blank:

$$M_{fb} = M_{bb} + M_{dd} = M_{bb} + C v_{dd} T l w \tag{A5}$$

The net mass of aerosol sampled in time T (i.e. the total mass collected on the filter minus its field blank, or the mass of truly suspended aerosol collected by the filter) will be the mass contained in the air pulled through the filter, which equals the atmospheric concentration multiplied by the volume of air sampled:

$$M_s = C V_{air} = C F T = C v_s l w T \tag{A6}$$

The total mass in the sample is the net mass plus the field blank:

$$M_t = M_s + M_{fb} = C v_s l w T + M_{bb} + C v_{dd} T l w \tag{A7}$$

Now, if the atmospheric concentration C drives both the dry-depositional blank and the net aerosol sample, these two latter quantities should be related linearly, and the field blank (already a function of the dry-deposition blank) should also be a simple function of the net aerosol sample (assuming that the particle size of element X does not change with C). This second consequence is of course just the initial observation that spurred this entire paper. (We stress that this conclusion implies nothing about the magnitude of the field blank compared with the aerosol sample, just that they are related linearly.)

The predicted relation between the field blank and the (net) aerosol sample can be derived in four simple steps. Noting that the equations for the field blank (A5) and the net aerosol sample (A6) have $C l w T$ in common, equation (A5) may be rewritten:

$$M_{fb} = M_{bb} + C v_s l w T \left(\frac{v_{dd}}{v_s}\right) = M_{bb} + M_s \left(\frac{v_{dd}}{v_s}\right) \tag{A8}$$

In other words, the plot of the field blank M_{fb} vs the net sample M_s is a straight line of the form $y = a + bx$, where the y -intercept a is the box blank M_{bb} and the slope b is the ratio of the deposition velocity to the sampling velocity, or v_{dd}/v_s . As M_s decreases to very small values, M_{fb} approaches M_{bb} , i.e. the dry-deposition component becomes negligible and

the field blank approaches the constant box blank. As M_s increases to very high values, the constant box blank becomes negligible relative to the increasing depositional blank, and the field blank M_{fb} approaches the deposition blank $M_s(v_{dd}/v_s)$.

Because atmospheric data are distributed nearly log-normally rather than normally, log-log plots are appropriate. With log-log axes, the left side of the plot, where the mass of the net sample decreases to very low values, appears as an extended horizontal tail with the field blank approaching the box blank asymptotically. The right side of the plot, where the depositional blank far exceeds the box blank, appears as a 45° tail with the field blank approaching the depositional blank asymptotically. Near the center of the plot, where neither component greatly exceeds the other, the line curves smoothly from one regime to the other (Fig. 2).

APPENDIX B: DERIVATION OF THE "CRITICAL VALUE" OF NET MASS IN AEROSOL SAMPLES

The box-blank line and the dry-deposition line cross at the point where they equal one another. The "critical value" of M_s for this point can be derived by equating these two components of the blank:

$$M_{dd} = M_{bb} \quad (\text{B1})$$

$$C v_{dd} T l w = M_{bb} \quad (\text{B2})$$

$$C v_s T l w \left(\frac{v_{dd}}{v_s} \right) = M_{bb} \quad (\text{B3})$$

$$M_s \left(\frac{v_{dd}}{v_s} \right) = M_{bb} \quad (\text{B4})$$

$$M_s = M_{bb} / (v_{dd}/v_s). \quad (\text{B5})$$