THE WDCPC NON-SEA SALT SULPHATE CORRECTION ALGORITHM

H.1   OVERVIEW

Precipitation samples collected at stations influenced by oceanic air masses can contain sulphur from both marine and non-marine sources. Keene, et al. (1986) and Hawley et al. (1988) suggest that long term oceanic salinity is stable enough to estimate the sea salt sulphate (SS) and non-sea salt sulphate (NSS) based on the mass concentrations of the reference species sodium, and magnesium in seawater[1]. An algorithm consistent with the use of sea salt tracers has been implemented by the WDCPC to estimate the SS and NSS sulphate contributions to wet precipitation samples.

The algorithm employs a series of cascading range tests that compares the sample's ion ratios to those in seawater. Depending on which of the three ions, sodium, magnesium, or chloride, is selected as the best correcting method, one of these formulas is used:

$[NSS\_ SO_4] = [SO_4] - (0.25 \times [Na])$ or

$[NSS\_ SO_4] = [SO_4] - (2.09 \times [Mg])$ or

$[NSS\_ SO_4] = [SO_4] - (0.14 \times [Cl])$

Note: Usually the sodium tracer is used. Because it is non-conservative, the chlorine tracer is used only when the sodium and magnesium sample concentrations are unavailable. The constants are derived from the seawater ratios of sulphate to the tracer species (Keene et al., 1986).

The measured sulphate concentration value is not altered by the algorithm. Instead, the algorithm creates and stores three generated values in the WDCPC database along with the measured total sulphate sulphur concentration, SO4_S:

- Calculated NSS sulphur component (Variable XSO4_S)
- NSS estimation method code (Variable XSO4MET)
- Calculated Below Detection Limit flag for NSS sulphur component (Variable XSO4_SB).

To obtain the SS sulphur from the measured sulphur concentrations in the original sample, data users are required to subtract the NSS amount from total measured SO4_S from the original sample.

Before the algorithm completes execution, it checks for negative values of $[NSS\_SO_4]$. Negative values indicate that the methodology is not sufficiently precise to indicate presence of non-sea salt sulphate. If a negative $[NSS\_SO_4]$ value is found, then it is replaced by +0.00**.**

H.2   DEFINITIONS

All concentrations are in mgL^{-1}.

NSS estimation method codes (xso4met)
:
    1: Calculation based upon [na]
    2: Calculation based upon [mg]
    3: Calculation based upon [cl]
    4: $[NSS\_ SO_4]$ is set to [so4], because [so4] is BDL

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[1] Both sets of authors make two important assumptions about the sea salt component in precipitation: 1) fractionation does not occur during either air mass formation or deposition, and 2) the conservative reference species found in the sample are comprised solely from sea salt. Because of both assumptions, sodium and magnesium are strongly preferred over chlorine as tracers of sea salt.

5: [NSS_ SO$_4$] is set to missing, because all the tracer ions are missing[2]
6: [NSS_ SO$_4$] is set to missing, because [so4] is missing
7: [NSS_ SO$_4$] is set to [so4], because all the tracer ions are BDL
8: [NSS_ SO$_4$] is set to [so4], because of unusual or non-standard conditions
9: [NSS_ SO$_4$] is set to [so4], because the station is not within 100km of the ocean.

NSS below detection limit (BDL) flag (xso4_sb):

0: [NSS_ SO$_4$] is above the detection limit
1: [NSS_ SO$_4$] is BDL, but is a positive value
2: [NSS_ SO$_4$] has been set to +0.00, after initially calculating a negative concentration.

H.3   DETAILED PSEUDO CODE

Convert sulphate as sulphur [so4_s] to sulphate [so4] /* the database stores sulphate as sulphur, not sulphate */
Assume that [NSS_ SO$_4$] is not BDL. (xso4b = 0)

The following constants were determined from the seawater concentrations of sulphate and its potential tracers (in mg L^{-1}):
so4_sw = 2700   -- the seawater sulphate concentration
mg_sw = 1290   -- the seawater magnesium concentration
na_sw = 10800   -- the seawater sodium concentration
cl_sw = 19374   -- the seawater chloride concentration.

na_corr = so4_sw/na_sw;   -- the sodium correction factor for seawater sulphate = 0.25
mg_corr = so4_sw/mg_sw;   -- the magnesium correction factor for seawater sulphate = 2.09
cl_corr = so4_sw/cl_sw;   -- the chloride correction factor for seawater sulphate = 0.14

IF the station IS NOT within 100km of the ocean THEN DO
        do not calculate Sea salt fraction, however set xso4 = so4
        set xso4met = 9   /* Station is not within 100km */
        END If
ELSE IF (NOT Oceanic derived salt) OR (Severe Weather Occurred) THEN DO
        do not calculate Sea salt fraction, however set xso4 = so4
        set xso4met = 8   /* Non-standard conditions */
        END Else If
ELSE DO   /* Process the stations that are within 100km under standard conditions */
        CASE when the sulphate concentration is missing DO
                set xso4met = 6 /* Sulphate is missing */
                set xso4 = to the 'missing' value
                END Case
        CASE when the sulphate concentration is BDL DO
                set xso4met = 4 /* Sulphate is BDL */
                set xso4b = 1   /* The NSS is BDL */
                set xso4 = [so4]   /* assume that all the sulphate is NSS */
                END Case
        CASE when [cl] is NOT (missing or BDL) AND
                    [mg] is NOT (missing or BDL) AND
                    [na] is NOT (missing or BDL) DO
                Compute the ratio of the tracer ions in the sample to the ratios of the tracer ions found
                in seawater. When the ratio of mg to na (ratio A) is close to one, the na correction

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[2] Also, xso4net is set to 5 and [NSS_SO$_4$] is set to missing, when at least one tracer is missing while the remaining tracers are all BDL.

factor is selected. When A is not close to one, then the absolute value comparison in the next case has the effect of selecting the ratio of na to cl (ratio B) or the ratio of mg to cl (ratio C) that is closer to one.

$$A = ([mg]/[na]) / (mg\_sw/na\_sw)$$
$$B = ([na]/[cl]) / (na\_sw/cl\_sw)$$
$$C = ([mg]/[cl]) /(mg\_sw/cl\_sw)$$

CASE when (0.75 <= A <= 1.25) DO
    set xso4 = [so4] – na_corr[na]
    set xso4met = 1
    END Case
CASE when (ABS(B-1) < ABS(C-1)) DO
    set xso4 = [so4] – na_corr[na]
    set xso4met = 1
    END Case
OTHERWISE DO
    set xso4 = [so4] – mg_corr[mg]
    set xso4met = 2
    END Otherwise
END Case

If we have reached these CASE statements, then at least one of the tracer ions, na, mg or cl is missing or is below the detection limit. Examine each tracer in the order na, mg and cl and choose the first one with a non-missing value above the detection limit.
CASE when [na] is NOT (missing or BDL) DO
    set xso4 = [so4] – na_corr[na]
    set xso4met = 1
    END Case
CASE when [mg] is NOT (missing or BDL) DO
    set xso4 = [so4] – mg_corr[mg]
    set xso4met = 2
    END Case
CASE when [cl] is NOT (missing or BDL) DO
    set xso4 = [so4] – cl_corr[cl]
    set xso4met = 3
    END Case
OTHERWISE DO   /* [na], [mg], and [cl] are all missing or BDL */
    IF [na], [mg], and [cl] are all BDL THEN DO
    /* Treat the SS fraction as negligible */
        set xso4met = 7
        set xso4 = [so4]   /* assume that all the sulphate is NSS */
        END If
    ELSE DO /* at least one of the tracers is missing while the others are BDL */
        set xso4met = 5
        set xso4 = to the 'missing' value /* NSS cannot be determined */
        END Else
    END Otherwise
END Else
Check if the formulas have produced a negative NSS value. If so then set it to 0.01.
(After conversion of sulphate back to sulphur and rounding off, the NSS value, xso4_s, becomes 0.00).
IF xso4met < 4 THEN   /* Was one of the NSS estimation formulas selected? */
    IF xso4 <= 0 THEN DO
        xso4 = 0.01
        xso4b = 2
        END IF
Convert xso4 to xso4_s /* convert sulphate to sulphate as sulphur */
Round xso4_s to the hundredths place

set xso4_sb = xso4b

/* End of Algorithm */

NOTE: At the WDCPC, this algorithm is implemented in the SAS Data language. SAS sequentially steps through the CASE structure, and executes the first CASE statement whose test is satisfied. Any remaining CASE statements in the same selection structure are ignored regardless if their tests would be satisfied or not.

H.4   References

Keene, W. C., Pszenny, A. A. P., Galloway, J. N. and Hawley, M. E. (1986) Sea-salt corrections and interpretation of constitutent ratios in marine precipitation. *J. Geophys. Res.* **91**(D6), 6647-6658.

Hawley, M.E., Galloway, J. N. and Keene, W. C. (1988) Standard error calculations for non-sea salt constituents in marine precipitation. *Water, Air, and Soil Pollution* **42**, 87-102.