Illinois State Water Survey
Health and Environmental Application Laboratory

Standard Operating Procedure
For
IPD/CPD Calculations for Atmospheric Deposition Samples

SOP Number: DA.HEAL.0.IPD.4.1

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Revision History

Starting Revision Number	Ending Revision Number	Revision Date	Revisions Made
3.2	4.0	9/1/23	Added limits for ion and conductivity percentage difference acceptability. Updated Table 3.
4.0	4.1	10/8/24	Updated table 3.

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1.0 Purpose

The purpose of this SOP is to have a permanent reference location for calculating the Ion Percent Difference (IPD) and the Conductivity Percent Difference (CPD) used by the HEAL to determine samples needed for reanalysis.

2.0 Scope & Applicability

This SOP is to be used when modifying the data programs used to calculate the IPD and CPD.

3.0 Summary of Procedure

Whenever the IPD or CPD calculations are updated, it is necessary to search for the tables with the original values. This method keeps all the pertinent information needed as well as the references on where to find the information in one place, simplifying all calculations.

4.0 Definitions

CPD	Conductivity Percent Difference
IPD	Ion Percent Difference
ppm	part per million

5.0 Personnel Qualifications

The person updating the IPD and CPD should be familiar with the chemistry and mathematics involved in the calculations. Although this SOP explains the use of the tables, some previous chemistry knowledge is required.

6.0 Procedure

The IPD and CPD are used to determine what precipitation samples are needed for reanalysis. The calculations needed for the IPD can be found in Table 1. Concentrations are converted from mg/L to µeq/L using the conversion factors in Table 2. All values are measured with the exception of bicarbonate ion (HCO_3^-). The HEAL uses the 2017 annual mean value of the atmospheric concentration of carbon dioxide found at Mauna Loa Observatory, Hawaii as found in Table 3. The calculations needed for the CPD can be found in Table 4 using the disassociation constants found in Table 5.

Table 1 Ion Percent Difference (IPD)

$$IPD = \frac{(Anions - Cations) \times 100}{Anions + Cations}$$

where:
Cations = $(Ca^{2+}) + (Mg^{2+}) + (K^{+}) + (Na^{+}) + (NH_4^{+}) + [H_3O^{+}\ (\mu eq\ /L) = 10^{(6-pH)}]$
Anions = $(Br^{-}) + (Cl^{-}) + (NO_3^{-}) + (SO_4^{2-}) + (PO_4^{3-}) + (F^{-}) + (HCO_3^{-}) + [OH^{-}\ (\mu eq\ /L) = 10^{6-(14-pH)}]$

Note: Fluoride (F^{-}) is not currently measured by the HEAL for atmospheric deposition samples.

HCO_3^{-} is calculated based on solution pH and the annual mean concentration of carbon dioxide (CO_2) in the atmosphere as follows:

$$HCO_3^{-}\ (\mu eq/L) = \frac{K_1 K_H\ P_{CO_2} \times (10^6)}{10^{-pH}}$$

Where: K_1 = acid dissociation constant for carbonic acid = $10^{-6.35}$ or 4.467×10^{-7} mol/L (reference 8.3)

K_H = Henry's Law constant for CO_2 = 0.0341 mol/L-atm = (1.5 s/g kg-1 H2O /44.010 g/mol) (Reference 8.1)

P_{CO_2} = Partial pressure of CO_2 (atmospheres)

Note:
K_H = solubility of CO_2 in water at 1 atmosphere/molecular weight of CO_2
Where: solubility of CO_2 in water at 1 atmosphere = 1.50 g CO_2/1kg-atm H_2O
= 1.50 g CO_2/L-atm H_2O
Molecular weight of CO_2 = 44.01g/mol

These references are available at https://hbcp.chemnetbase.com/.

Table 2 Conversion of Ion Concentrations (mg/L) to Micromoles (µmol/L) and Hydrogen Microequivalents (µeq/L)

1 mg/L	hydronium H_3O^+ (MW = 19.02333 g/g-mol) =	**52.56705**	**µmol/L**	=	**52.56705**	**µeq/L**
1 mg/L	ammonium NH_4^+ (MW = 18.03876 g/g-mol) =	**55.4362**	**µmol/L**	=	**55.4362**	**µeq/L**
1 mg/L	calcium Ca^{2+} (MW = 40.078 g/g-mol) =	**24.9513**	**µmol/L**	=	**49.90269**	**µeq/L**
1 mg/L	magnesium Mg^{2+} (MW = 24.305 g/g-mol) =	**41.1438**	**µmol/L**	=	**82.2876**	**µeq/L**
1 mg/L	potassium K^+ (MW = 39.0983 g/g-mol) =	**25.5766**	**µmol/L**	=	**25.57656**	**µeq/L**
1mg/L	sodium Na^+ (MW = 22.98977 g/g-mol) =	**43.4976**	**µmol/L**	=	**43.49761**	**µeq/L**
1 mg/L	hydroxide OH^- (MW = 17.00738 g/g-mol) =	**58.7980**	**µmol/L**	=	**58.79802**	**µeq/L**
1 mg/L	bicarbonate HCO_3^- (MW = 61.01678 g/g-mol) =	**16.3889**	**µmol/L**	=	**16.38894**	**µeq/L**
1 mg/L	chloride Cl^- (MW = 35.452 g/g-mol) =	**28.2076**	**µmol/L**	=	**28.20855**	**µeq/L**
1 mg/L	fluoride F^- (MW = 18.9984 g/g-mol) =	**52.636**	**µmol/L**	=	**52.636**	**µeq/L**
1 mg/L	sulfate SO_4^{2-} (MW =96.0651 g/g-mol) =	**10.4096**	**µmol/L**	=	**20.81922**	**µeq/L**
1 mg/L	nitrate NO_3^- (MW = 62.00506 g/g-mol) =	**16.1288**	**µmol/L**	=	**16.12770**	**µeq/L**
1 mg/L	phosphate PO_4^{3-} (MW = 94.97136 g/g-mol) =	**10.5295**	**µmol/L**	=	**31.58847**	**µeq/L**
1 mg/L	bromide Br^- (MW = 79.904 g/g-mol) =	**12.5150**	**µmol/L**	=	**12.51502**	**µeq/L**

Molecular weights calculated based on "Standard Atomic Weights" , *CRC Handbook of Chemistry and Physics*, 99th Ed., 2018-2019, Section 1. All values are expressed to the full precision in the reference.

Table 3 Atmospheric Concentration of Carbon Dioxide at Mauna Loa Observatory, Hawaii. (See reference 8.2)

Note: The 2017 value is currently used in IPD/CPD calculations. CO2 values prior to and including 2017 have not been updated in this table, which serves as a record of values used in IPD calculations at HEAL.

Year	Mean CO_2 concentration, ppm	Partial Pressure, atm
1997	363.71	$363.71 * 10^{-6}$
1998	366.65	$366.65 * 10^{-6}$
1999	368.33	$368.33 * 10^{-6}$
2000	369.52	$369.52 * 10^{-6}$
2001	371.13	$371.13 * 10^{-6}$
2002	373.22	$373.22 * 10^{-6}$
2003	375.77	$375.77 * 10^{-6}$
2004	377.49	$377.49 * 10^{-6}$
2005	379.80	$379.80 * 10^{-6}$
2006	381.90	$381.90 * 10^{-6}$
2007	383.76	$383.76 * 10^{-6}$
2008	385.59	$385.59 * 10^{-6}$
2009	387.37	$387.37 * 10^{-6}$
2010	389.85	$389.85 * 10^{-6}$
2011	391.63	$391.63 * 10^{-6}$
2012	393.82	$393.82 * 10^{-6}$
2013	396.48	$396.48 * 10^{-6}$
2014	398.61	$398.61 * 10^{-6}$
2015	400.83	$400.83 * 10^{-6}$
2016	404.21	$404.21 * 10^{-6}$
2017	406.53	$406.53 * 10^{-6}$
2018	408.72	$408.72 * 10^{-6}$
2019	411.65	$411.65 * 10^{-6}$
2020	414.21	$414.21 * 10^{-6}$
2021	416.41	$416.41 * 10^{-6}$
2022	418.53	$418.53 * 10^{-6}$

Year	Mean CO_2 concentration, ppm	Partial Pressure, atm
2023	421.08	421.08 * 10^{-6}

Table 4. Conductance Percent Difference (CPD)

$$CPD = \frac{(\text{Calculated Conductance - Measured Conductance})}{\text{Measured Conductance}} \times 100$$

where: Calculated Conductance = $\sum$(Ion Concentration, µeq/L) x $\Lambda_{\pm}$ x 10^{-3}

where: (Ion Concentration, µeq/L) are measured concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NH_4^{+}, [H_3O^{+} (µeq/L) = $10^{(6-pH)}$], Br^{-}, Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}, F^{-}, HCO_3^{-}, and [OH^{-} (mol/L) = $10^{(ph-8)}$] with HCO_3^{-} calculated as indicated in Table 1. Conversion factors are listed in Table 2.

$\Lambda_{\pm}$ = Ionic conductivity, $10^{-4}m^2S\text{-}mol^{-1}$ as listed in Table 5.

Note: Expressing ion concentrations in units of µeq/L converts the ion charge into the correct molar units for the factors in Table 5.

Table 5. Ion conductivity values at 25°C

Ion	$\Lambda_{\pm}$, $10^{-4}m^2S/mol$
1/2 Ca^{2+}	59.47
H^{+}	349.65
K^{+}	73.48
1/2 Mg^{2+}	53.0
NH_4^{+}	73.5
Na^{+}	50.08
Cl^{-}	76.31
F^{-}	55.4
HCO_3^{-}	44.5
NO_3^{-}	71.42
OH^{-}	198
1/3 PO_4^{3-}	92.8
1/2 SO_4^{2-}	80.0
Br^{-}	78.1

From "Ion Conductivity and Diffusion at Infinite Dilution," *CRC Handbook of Chemistry and Physics* , 99th Ed., 2018-2019, Section 5.

7.0 Quality Control and Quality Assurance

7.1 Acceptance criteria for ion balance depends on the total ion concentration:

<60 µeq/L, IPD ± 60%
50 to 100 µeq/L, IPD ± 30%
>100 µeq/L, IPD ± 15%

7.2 Conductivity percent difference has an acceptable range of -40% to 10%.

8.0 References

8.1 "Aqueous Solubility and Henry's Law Constants of Organic Compounds" *CRC Handbook of Chemistry and Physics*, 99th Ed., 2018-2019, Section 5. https://hbcp.chemnetbase.com/documents/30_02/30_02_0001.xhtml?dswid=8856

8.2 "Annual Atmospheric Concentration of Carbon Dioxide and Methane" *CRC Handbook of Chemistry and Physics*, 105th Ed., 2023, Section 10. Accessed 10/9/2024 at https://hbcp.chemnetbase.com/documents/30_09/30_09_0004.xhtml?dswid=7852.

8.3 "Disassociation Constants of Inorganic Acids and Bases," *CRC Handbook of Chemistry and Physics*, 99th Ed., 2018-2019, Section 5. https://hbcp.chemnetbase.com/documents/04_12/04_12_0001.xhtml?dswid=-9341

8.4 "Ion Conductivity and Diffusion at Infinite Dilution," *CRC Handbook of Chemistry and Physics*, 99th Ed., 2018-2019, Section 5.

8.5 "Standard Atomic Weights," *CRC Handbook of Chemistry and Physics*, 99th Ed., 2018-2019, Section 1.

8.3 Central Analytical Laboratory Quality Assurance Report, 2017, Section C.

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