

## Observations and Lessons from the International Static Database (ISD) on Neutralizing Capacity

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### ABSTRACT

Geochemical static tests are a basic component of geochemical assessments and predictions for acidic drainage, and include acid-base accounting and total-metal contents. A key database for such information is the International Static Database (ISD), which currently contains more than 45,000 static-test analyses from over 200 minesites. Such large databases are useful in identifying general trends and, just as important, the percentage of exceptions.

General trends and significant exceptions can be seen in the ISD by comparing one parameter against another. This paper shows that bulk neutralization potential (bulk NP) obtained from acid titration is often a good indicator of neutralizing capacity above values of 10 t CaCO<sub>3</sub>/1000 t. Other types of calculated neutralizing capacity are then compared to bulk NP to determine if they, in fact, reliably represent actual neutralizing capacity and if they can substitute for the more time-consuming and expensive bulk NP. For example, bulk NP correlates better with Carbonate NP (from carbonate analyses) and Total-carbon NP (from total-carbon analyses) than with (Ca+Mg) CaNP (from solid-phase analyses of calcium and magnesium). This means that, in general, (Ca+Mg) CaNP is a less accurate substitute for bulk NP than the other types, and thus requires intensive site-specific justification if a substitution is attempted. This also means that measurement of the frequently less-expensive parameters of total carbon and carbonate can often substitute, within site-specific error bars, for the bulk-NP titration. However, the ISD also shows that non-carbonate minerals make the primary contribution to neutralization in up to 20% of samples, so Carbonate CaNP and Total-carbon CaNP do not always reveal the full neutralizing capacity of a sample.

### INTRODUCTION AND PAST WORK

A variety of techniques and analytical procedures are required for the prediction of environmental problems such as acid rock drainage (ARD) at mining operations. The mining industry and many regulatory agencies have generally accepted that an integrated or “wheel” approach (Figure 1) should be used to predict ARD and metal leaching (Morin and Hutt, 1997; Price et al., 1997; Morin and Hutt, 1999). The “wheel” includes acid-base accounting (ABA) and solid-phase total-metal analyses.

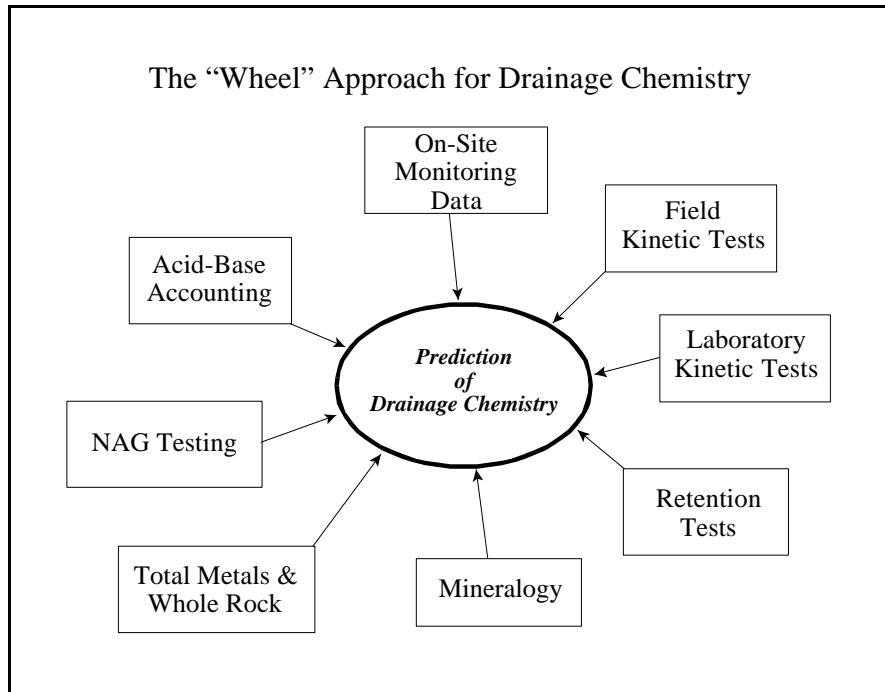
An expanded ABA test can include analyses for total sulphur, sulphide sulphur, acid-leachable sulphate sulphur, bulk neutralization potential (NP), total carbon, carbonate carbon, paste pH, and rinse pH. Total-metal analyses can include metals like calcium and magnesium. From this information, the neutralizing capacities of samples can be measured or calculated in various ways, which is the focus of this paper.

A massive compilation of ABA and other static test data, known as the International Static Database (ISD) (MDAG Publishing, 1999) currently contains more than 45,000 samples from over 200 minesites around the world. Because the ISD is so large, samples cannot be evaluated individually within the limits of this paper. Therefore, scatterplots of one parameter against another are used to concisely identify general trends and significant exceptions.

This approach has been used previously with the ISD. When the ISD was half its current size, Hutt and Morin (1999) examined various ABA criteria for general validity. For example, the assumption that low-sulphur samples (< 0.3% S or < 0.05% S) could not be acidic was shown to be incorrect. Also, based on the comparison to paste pH, there was an assessment of criteria stating that either (1) sulphide-based Net Neutralization Potential (SNNP) = +20 CaCO<sub>3</sub> equivalent/1000 t or (2) sulphide-based Net Potential Ratio (SNPR) = 2.0 correctly separated net-acid-generating from net-acid-neutralizing materials. This showed that these criteria were generally

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**Figure 1** The “Wheel” for prediction of ARD and metal leaching.

reliable for the prediction of acidic or near-neutral conditions (99.5% and 98.0% of samples correctly classified, respectively). The more relaxed criteria of (1) SNNP = 0 CaCO<sub>3</sub> equivalent/1000 t and (2) SNPR = 1.0 separated acidic and near-neutral materials less reliably in 96.5% and 97.9% of samples, respectively. However, numerous samples in the ISD are probably fresh and unweathered, and thus have not generated much acidity. As a result, the estimates of reliability above, based on the comparison to paste pH, are probably maximum and could perhaps decrease if samples were weathered and some additional violations of the criteria appear.

One explanation for the occasional failure of criteria is unavailable neutralization potential (UNP: NP that is measured but unavailable for significant neutralization of acidity to pH > 5.0). UNP is commonly 10 t CaCO<sub>3</sub>/1000 t or less (Hutt and Morin, 1999), but can reach almost 100 t/1000 t in rare circumstances (Morin and Hutt, 1997; Li, 1997). This highlights the error in assuming that all measured NP is available for neutralization.

This paper continues the general examination of the ISD, now greatly expanded, by focussing on neutralizing capacity and some of the ways it can be determined (Table 1).

**Table 1** Types and methods of the neutralizing capacities examined in this paper

Type	Method/Equation for Obtaining Neutralizing Capacities (as t CaCO <sub>3</sub> /1000 t)
Bulk NP	Analytical measurement based on titration with acid
(Ca) CaNP	Calculated from calcium content of sample; = (%Ca/40.08) * 100.09 * 10
(Ca + Mg) CaNP	Calculated from calcium plus magnesium content of sample; = [(%Ca/40.08) + (%Mg/24.31)] * 100.09 * 10
Carbonate CaNP	Calculated from carbonate (CO <sub>2</sub> or CO <sub>3</sub> ) analysis: = (%CO <sub>2</sub> /44.01) * 100.09 * 10 OR = (%CO <sub>3</sub> /60.01) * 100.09 * 10
Total-carbon CaNP	Calculated from total carbon (C) analysis: = (%C/12.01) * 100.09 * 10

## TYPES OF NEUTRALIZING CAPACITIES

One type of neutralizing capacity is referred to here as bulk neutralization potential (bulk NP), which is determined by a titration with acid. Although there are many procedures for the titration (e.g., Lapakko, 1994a), the ISD primarily contains bulk NP determined using the standard Sobek technique (Sobek et al., 1978), with fewer bulk NP values using the modified Sobek procedure.

Bulk NP does not provide detailed information on the forms and reactivities of the neutralizing minerals, but they are sometimes assumed to be quick reacting carbonate minerals such as calcite and dolomite. Slower reacting aluminosilicate minerals are often not considered to contribute significantly to the NP data, but they can in some situations (Morin and Hutt, 1997). These issues are examined further in this paper.

Some minesites will use methods of determining the neutralizing capacity of rock or tailings other than bulk NP, or in addition to bulk NP. This is because many of the other methods are easier, faster, and/or cheaper than conventional bulk NP analyses. For example, the calculation of neutralizing capacity from standard ICP analyses of calcium or from carbon analyses are not unusual (e.g., Downing and Giroux, 1993; Day et al., 2000, these proceedings). Table 1 summarizes the methods examined here.

## BULK NP AND PASTE pH

To determine the amount of measured bulk NP that is available for significant neutralization of acidity, a comparison of bulk NP and paste pH can be made. For example, as discussed previously in another paper on the ISD using 12,838 data points (Hutt and Morin, 1999), numerous samples with bulk NPs of approximately 10 t CaCO<sub>3</sub> equivalent/1000 t or less yielded a pH of less than 5.0, representing unavailable NP (UNP). Apparently 10 t CaCO<sub>3</sub> equivalent/1000 t or less is typical of UNP at many sites.

Figure 2 is an updated comparison of bulk NP and paste pH using 19,232 data points. UNP continues to be around 10 t CaCO<sub>3</sub>/1000 t or less, with exceptions up to 100 t/1000 t in rare circumstances. While high values of UNP have been confirmed (Li, 1997), it remains possible that some analyses are erroneous and this should be kept in mind when attempting any statistical evaluations. In any case, the general observation is that bulk NP accurately represents neutralization capacity above 10 t/1000 t.

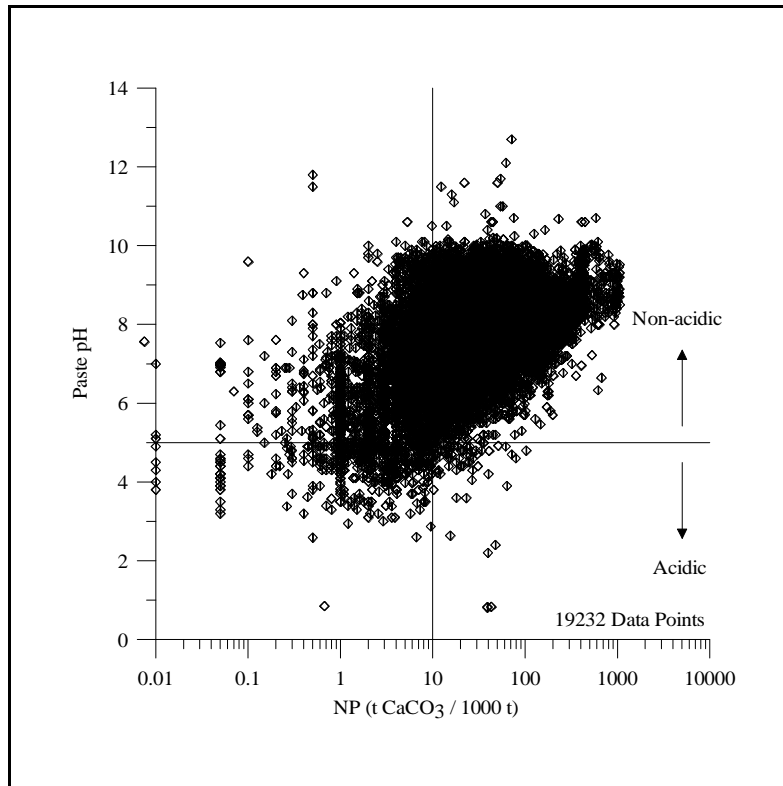


Figure 2 Bulk NP vs Paste pH

### **BULK NP AND (Ca) CaNP**

As discussed above (Table 1), another method of determining the neutralizing capacity of a sample is to calculate it from the calcium content of the material ((Ca) CaNP). This method may be less expensive and faster than conventional bulk NP analyses, as calcium is usually reported as a part of total-metal analyses by ICP (e.g., Downing and Giroux, 1993).

Because the number of samples having both calcium and paste pH measurements are limited, (Ca) CaNP is compared to the more abundant bulk NP as a test of its validity for representing true neutralizing capacity (Figure 3). This shows that (Ca) CaNP frequently either overestimates or underestimates the bulk NP content of a large number of the samples. Therefore, in a general sense, (Ca) CaNP does not correlate well with bulk NP, and thus is not a reliable substitute for bulk NP and is not a reliable indicator of neutralizing capacity.

For overestimates of neutralizing capacity ((Ca) CaNP > bulk NP, Figure 3), a large portion of the calcium content appears to originate from minerals other than quick reacting calcite. Since the determination of total metals requires a much more aggressive digestion than that of conventional bulk NP determinations, it is reasonable that calcium contents would represent a combination of any calcite plus any other less reactive calcium-bearing minerals (e.g., epidote). For underestimates of neutralizing capacity ((Ca) CaNP < bulk NP, Figure 3), the neutralizing capacity of the sample may come from other minerals which are not entirely calcium based. Therefore, (Ca) CaNP at a minesite should not immediately be assumed to represent a valid neutralizing capacity. Instead, any site wishing to substitute bulk NP with (Ca) CaNP should conduct extensive comparisons of calcium content to bulk NP, covering all relevant rock and material types at the site, to establish reliable statistical relationships with bulk NP. Mineralogical examinations would also be warranted to delineate the minerals containing calcium.

### **NP AND (Ca + Mg) CaNP**

Another method of determining the neutralizing capacity of a sample is to calculate CaNP from the calcium plus magnesium content of the sample ((Ca + Mg) CaNP, Table 1). Like (Ca) CaNP content above, this method can be less expensive and faster than conventional bulk NP analyses, as both calcium and magnesium are usually reported as a part of total metal analyses.

Figure 4 is a comparison of bulk NP to (Ca + Mg) CaNP. Compared to Figure 3, (Ca + Mg) CaNP more frequently overestimates the bulk NP content. Because of this, (Ca + Mg) CaNP is generally not a valid indicator of neutralizing capacity and is not an appropriate substitute for bulk NP. Additionally, (Ca + Mg) CaNP frequently underestimates bulk NP, and thus the extent or severity of acidic conditions could be underestimated by using it.

A large portion of the calcium and magnesium contents of many samples appears to originate from minerals other than quick reacting calcite and/or dolomite and, under the more aggressive digestions done during total metals analyses, this would be expected. As with (Ca) CaNP above, reliable correlations between bulk NP and (Ca + Mg) CaNP should be established with an extensive site-specific database and should be supported with mineralogic data.

### **BULK NP AND CARBONATE CaNP**

Carbonate CaNP can be calculated from inorganic carbonate analyses, usually reported as %CO<sub>2</sub> or %CO<sub>3</sub> (Table 1). By comparing bulk NP to carbonate CaNP, the proportion of carbonate within the bulk NP becomes apparent (Figure 5 for arithmetic axes and Figure 6 for logarithmic axes).

Both Figure 5 and 6 show generally good correlations near the 1:1 line and thus in many cases a majority of the bulk NP is made up of carbonate minerals. However, there is still noticeable scatter on either side of the 1:1 line especially at lower levels, due to detection limit effects (visible as straight horizontal and vertical lines of data) as well as to the minor contribution of non-carbonate minerals at low bulk-NP levels. An anomalous cluster of data around a NP of 400 t CaCO<sub>3</sub>/1000 t is due to the mineralogy and geochemistry of one minesite, which reinforces the need for delineating mineralogy as part of proper methodology for drainage-chemistry predictions (Figure 1).

To evaluate further the agreement between Carbonate NP and bulk NP, Table 2 is a summary of statistics related to Figures 5 and 6. If the carbonate CaNP data are within ±10-25% of the bulk NP value, then it is reasonable to conclude that the most of bulk NP of the sample is predominantly derived from carbonate minerals. For bulk NPs greater than 0 t CaCO<sub>3</sub>/1000t, 19.6-36.3% of the ISD samples have Carbonate CaNP within ±10-25% of the bulk NP value (Table 2). However, bulk NP is not typically available for neutralization below roughly 10 t/1000 t (demonstrated above) and thus cannot represent reactive carbonate. When the data are filtered to remove bulk NP values below 10 t/1000 t (Table 2), 26.6-48.8% of samples have Carbonate NP and bulk NP agreeing within ±10-25%, with 78.3% of samples agreeing within ±50%. In all cases, the agreement between the two parameters increases at higher NP levels, indicating high levels of bulk NP are more typically comprised of higher percentages of carbonate minerals.

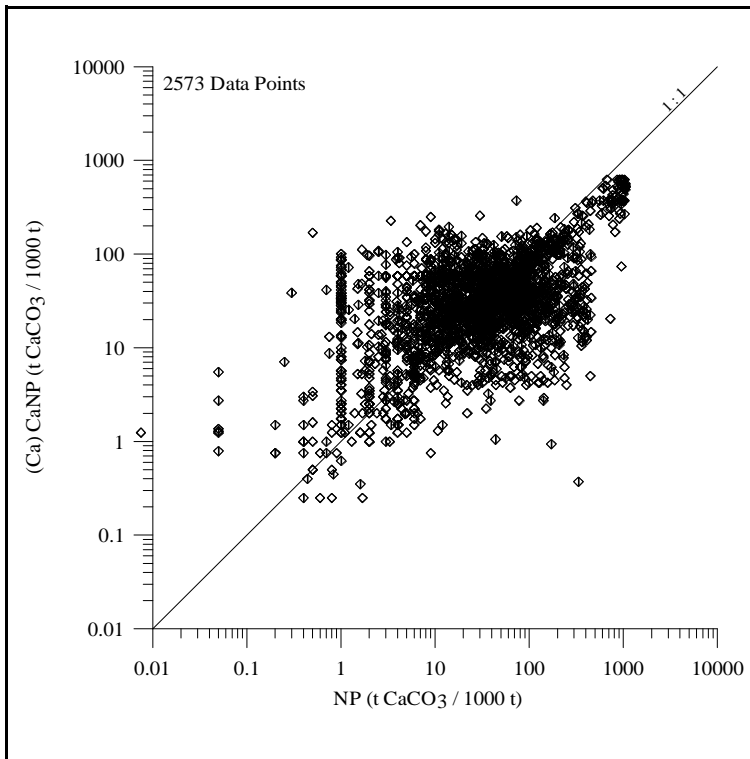


Figure 3 Bulk NP vs (Ca) CaNP

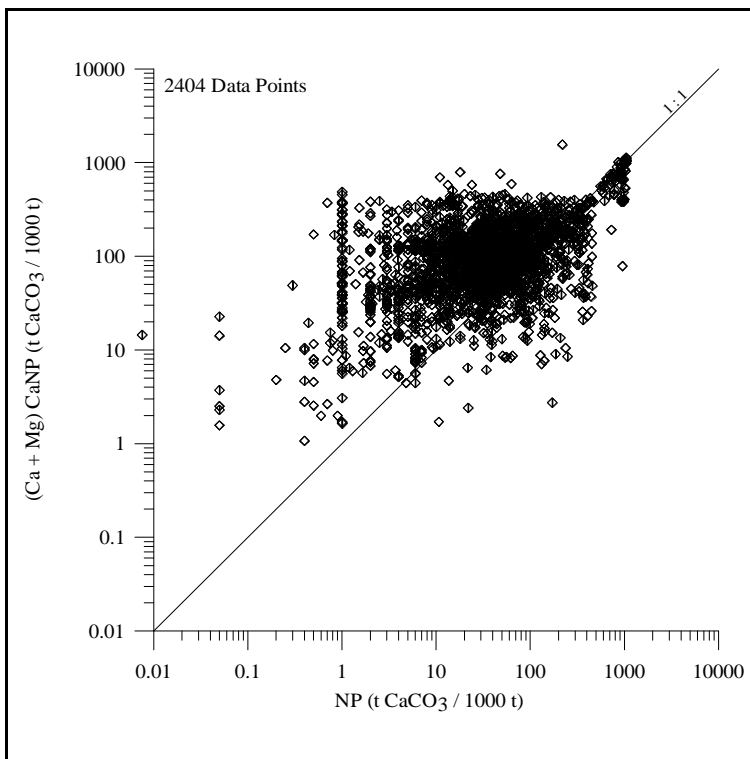


Figure 4 Bulk NP vs (Ca + Mg) CaNP

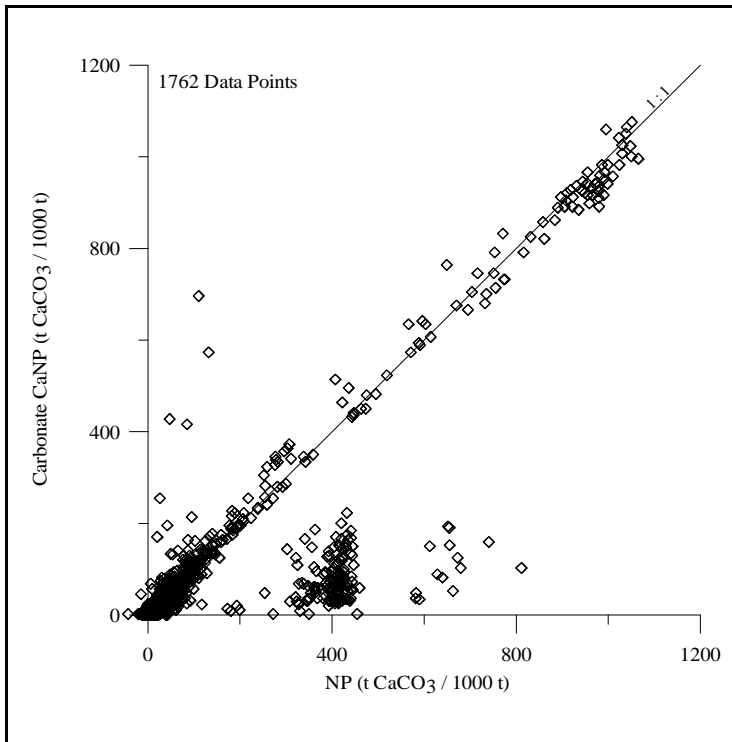


Figure 5 Bulk NP vs Carbonate CaNP (arithmetic)

Table 2 Comparison of bulk NP and Carbonate CaNP

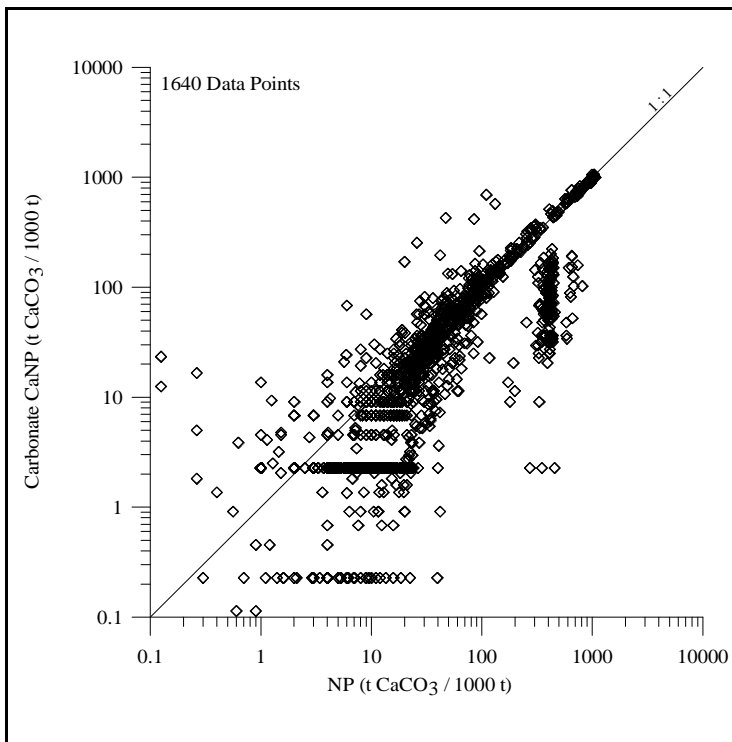


Figure 6 Bulk NP vs Carbonate CaNP (logarithmic)

	% of Samples with Carbonate CaNP Within $\pm 10\%$ of Bulk NP	% of Samples with Carbonate CaNP Within $\pm 25\%$ of Bulk NP	% of Samples with Carbonate CaNP Within $\pm 50\%$ of Bulk NP
All Data	17.8	36.3	69.6
NP > 0	19.6	39.8	76.4
NP \$ 1	20.1	40.7	77.9
NP \$ 10	26.6	48.8	78.3
NP \$ 100	64.2	84.5	88.5

Therefore, the ISD indicates that much of the available bulk NP in most samples consists of carbonate minerals. This justifies the common focus on carbonate minerals when assessing neutralizing capacities (e.g., Lapakko, 1994 a and b). On the other hand, this also means that much of the available bulk NP in up to 20% of the samples consists of relatively fast-neutralizing non-carbonate minerals, which highlights the occasional significant contribution of non-carbonate minerals and non-reactive carbonate minerals to neutralizing capacity (Morin and Hutt, 1997). In any case, Carbonate CaNP frequently correlates well with bulk NP, and is thus frequently a good indicator of neutralizing capacity within site-specific error bars. Further valuable information that can be obtained by comparing bulk NP to Carbonate NP is explained in Morin and Hutt (1997).

#### **BULK NP AND TOTAL CARBON CaNP**

Another common analysis sometimes performed as a part of expanded ABA is total carbon, which can be measured, for example, simultaneously with Leco sulphur on some equipment. Total carbon can then be used calculate Total-carbon CaNP (Table 1). The comparison of bulk NP, as the indicator of neutralizing capacity, to Total-carbon CaNP (Figures 7 and 8) shows correlations similar to those with Carbonate NP (Figures 5 and 6). However, there is a higher frequency of samples where Total-carbon CaNP significantly exceeds bulk NP, which likely reflects of the presence of organic carbon. Also, as with Carbonate CaNP, there is noticeable scatter on either side of the 1:1 line at lower levels due to detection limit effects (visible as vertical and horizontal lines at low bulk NP and low total carbon CaNP values).

Statistics based on Figures 7 and 8 show that Total-carbon CaNP agrees with bulk NP (Table 3) better than Carbonate CaNP (Table 2), except at NP > 100 within  $\pm 10\text{-}25\%$ . This means that Total-carbon CaNP is also a good indicator of neutralizing capacity and can often substitute for bulk NP within site-specific error bars.

**Table 3 Comparison of bulk NP and Total-carbon CaNP**

	Percent of Samples with Total-carbon CaNP Within $\pm 10\%$ of Bulk NP	Percent of Samples with Total-carbon CaNP Within $\pm 25\%$ of Bulk NP	Percent of Samples with Total-carbon CaNP Within $\pm 50\%$ of Bulk NP
All Data	32.0	54.2	75.7
NP > 0	35.8	60.7	84.8
NP \$ 1	35.4	60.5	84.7
NP \$ 10	39.8	68.6	90.0
NP \$ 100	35.9	80.6	95.2

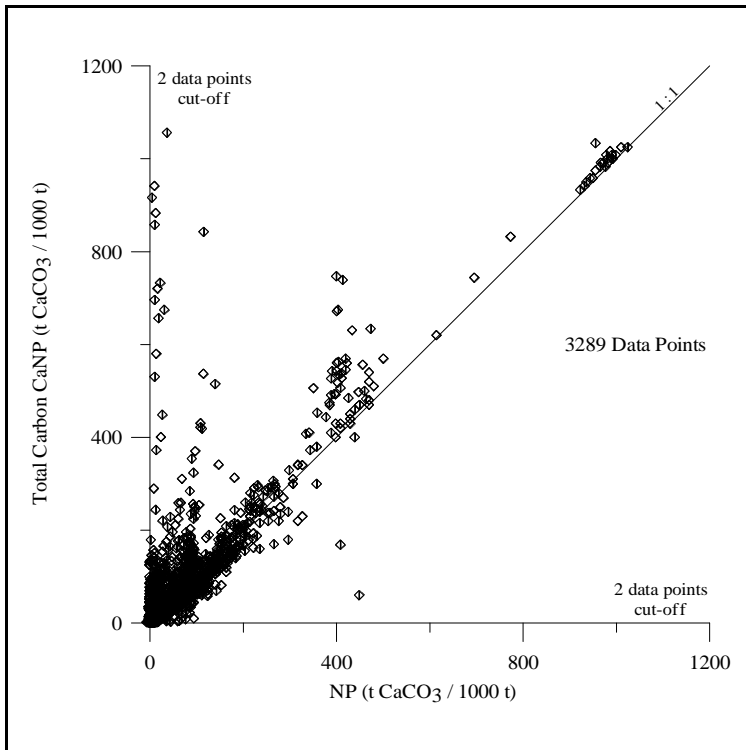


Figure 7 Bulk NP vs Total-carbon CaNP (arithmetic)

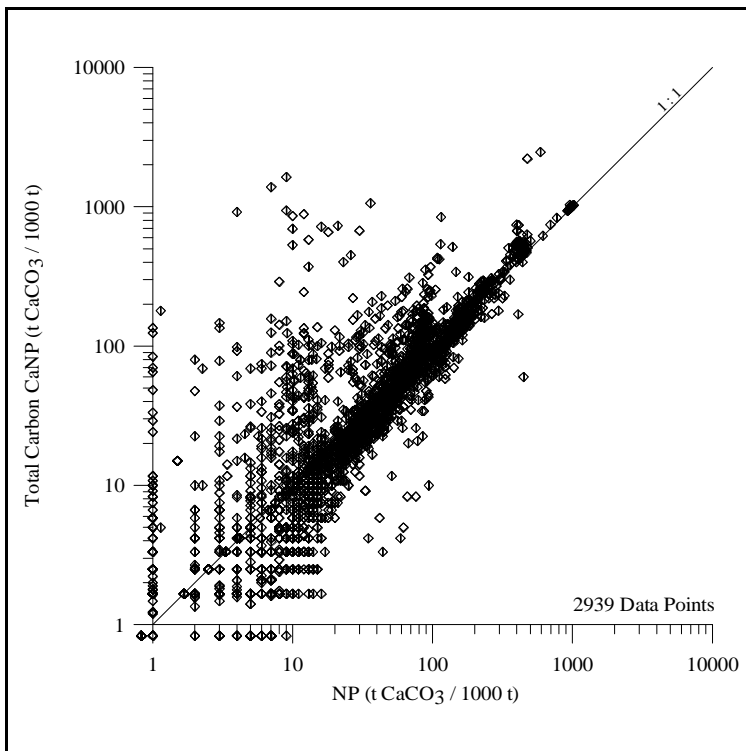


Figure 8 Bulk NP vs Total-carbon CaNP (logarithmic)

## CONCLUSIONS

This paper has used the International Static Database (ISD) to evaluate various types of neutralizing capacities provided by standard geochemical static tests. The comparison of bulk NP to paste pH shows that bulk NP above 10 t/1000 t is a good indicator of neutralizing capacity, although there are a few significant exceptions. The comparison of bulk NP to (Ca) CaNP showed that (Ca) CaNP did not correlate well and thus, in general, is not a good indicator of neutralizing capacity. Furthermore, (Ca + Mg) CaNP showed poorer agreement, and on average tended to overestimate bulk NP. Therefore, a site-specific substitution of these parameters for bulk NP requires intensive site-specific work to justify the substitution.

On the other hand, Carbonate CaNP and Total-carbon CaNP showed good correlations with bulk NP for many samples. As a result, Carbonate CaNP and Total-carbon CaNP are frequently good indicators of neutralizing capacity and good substitutes for bulk NP within site-specific error bars. However, the ISD also shows that non-carbonate minerals make the primary contribution to neutralization in up to 20% of samples, so Carbonate CaNP and Total-carbon CaNP do not always reveal the full neutralizing capacity of a sample.

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