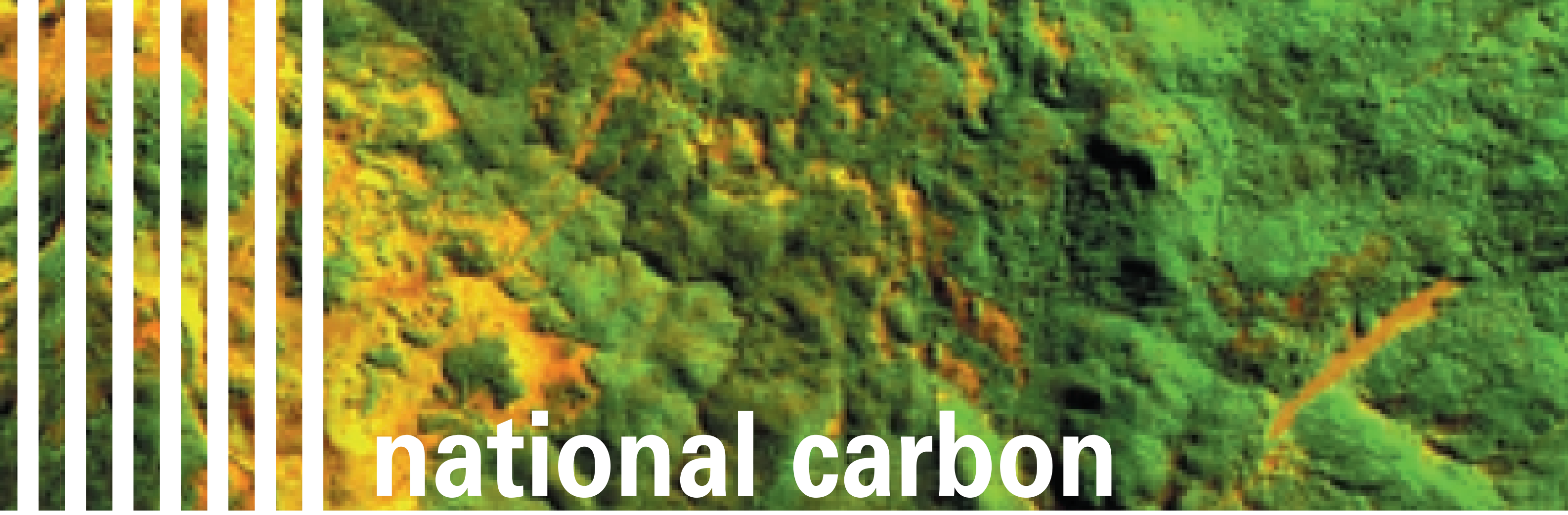

national carbon
accounting system

technical report no. 15

# Carbon Conversion Factors for Historical Soil Carbon Data

Jan O. Skjemstad
Leone R. Spouncer and
Adrian Beech

AUSTRALIAN Greenhouse Office
The lead Commonwealth agency on greenhouse matters

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# CARBON CONVERSION FACTORS FOR HISTORICAL SOIL CARBON DATA

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CSIRO Land and Water, Adelaide

National Carbon Accounting System
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## 1. PROJECT AIMS

The aim of the project was to determine a number of conversion factors for soil total organic carbon (TOC) to allow the conversion of data generated in various soil analytical laboratories over a wide time span to values equivalent to LECO combustion values.

## 2. RATIONALE AND PROCEDURE

Over the past 50 years or so, a range of analytical techniques have been used to estimate soil organic carbon (SOC). The most widely reported procedure is the Walkley and Black (1934) technique which utilises hot chromic acid to oxidise the SOC. In return, the chromic acid is reduced and either the loss of dichromate or the formation of chromate is measured. These measurements can be made either titrimetrically or photometrically. In the original Walkley and Black (W-B) method, the heat of reaction from the addition of concentrated sulphuric acid to a dichromate solution was used to drive the reaction however this heat was inadequate to drive the reaction to completion. The incomplete reaction meant that not all of the SOC was estimated and a recovery of 75% to 80% is widely reported (Piper, 1944). This recovery equates to a factor of 1.3 to convert the W-B data values obtained to values equivalent to the then laborious combustion methods. There have been many modifications to the W-B method since its initial use, including the application of external heat in order to bring the reaction closer to completion. Among various methods, the application of heat is highly variable both in duration and temperature and these result in recovery of SOC of between 75% and 100% compared to modern combustion methods. The difficulty is that in many databases, these modifications are not recognised and so an appropriate conversion factor for any particular modification cannot be readily determined.

To determine what these conversion factors might be, the adopted procedure was to obtain a number of soil samples that had been previously analysed for organic carbon over the past 10-50 years, depending on the laboratory, and compare these with the now widely recognised LECO method. This method determines the amount of carbon converted to $CO_2$ at high temperature (1,200ºC) and so includes all carbon sources in the sample. Since $CaCO_3$ contains carbon which is not organic but will be estimated by the LECO technique, only soils with a pH <7.0 were included in the study.

## 3. LABORATORIES TAKING PART IN THE EXERCISE

All LECO analyses were performed by the Analytical Chemistry Unit at CSIRO, Land and Water, Adelaide. The laboratories from which samples were obtained were:

CSIRO Land and Water

- Adelaide
- Hobart
- Canberra
- Brisbane
- Townsville

Queensland Department of Natural Resources

New South Wales Department of Land and Water Conservation

Victorian Department of Natural Resources and Energy

A comparison study had previously been carried out with Agriculture Western Australia.

## 4. SAMPLE PROTOCOLS

The samples covered a time span equal to that which was to be used to determine the initial soil C values for the IBRA regions of Australia. The samples were spread as evenly as possible across this time period, depending on sample availability, so that any changes in conversion factors due to methodological changes could also be determined. These soil samples were from both surface and subsoils but were from no deeper than 30cm in the profile and did not contain $CaCO_3$. The inclusion of a range of soil types was not essential for this exercise but C values were generally less than 6%. In some cases, soils with higher carbon values were included and some estimates of conversion factors were made with and without these samples.

The time periods over which the original analyses were conducted varied among laboratories. For the State Departments, most analyses were recent while CSIRO data was available from the early 1960s. Recent samples were not obtained from the CSIRO laboratories because they had either closed down or converted to the LECO method. There appeared to be little point in re-analysing samples that had already been analysed by the LECO method.

Samples were air dried and ground to <2mm. Subsamples of 10-20g were provided along with an estimate of TOC and a time (year) of analysis. In some cases, the material provided was >>2 mm. Although these samples were ground to <2 mm for the LECO analysis, the coarseness of the samples resulted in poor subsampling and errors were likely to be large.

## 5. CONVERSION FACTORS BY STATE

### A) QUEENSLAND

### CSIRO Townsville (99 samples, 1963 to 1984)

In the Townsville laboratory, the W-B method was used prior to 1984. Post-1984, soil samples were sent to Adelaide for LECO analysis.

A plot of %C LECO vs %C W-B (Fig. 1) shows an $R^2$ of 0.793 with a slope of 1.26. The poor $R^2$ results from a considerable number of outliers where the ratio %C LECO/%C W-B was >2 or <0.5 (Fig. 2). The origin of these large differences is not clear but it must be assumed that in these cases some problem with sample numbering was involved. It is highly unlikely that these differences could arise from analytical error alone. Even poor subsampling is unlikely to cause such large differences. These 6 samples were therefore removed from the analyses which improved the $R^2$ to 0.891 with a slope of 1.19 (Fig. 3). Figure 2 also shows that prior to 1968, the %C LECO/%C W-B is closer to 1.0 than the average 1.19. On this basis, the samples were split into before and after 1968 and plotted %C LECO vs %C W-B. The before 1968 samples gave a slope of 0.995 with an $R^2$ of 0.971 (Fig. 4) and the data from samples after 1968 gave a slope of 1.24 and an $R^2$ of 0.893 (Fig. 5).

Further enquiries uncovered that the data entered into the database for the Townsville soils prior to 1968 had been corrected for the W-B under-recovery by multiplying the W-B result by 1.3 but that the method used had been recorded as the W-B method. This explains the apparent high recovery of the W-B method prior to 1968.

**Recommendation**

- No correction factor to be applied prior to and including 1968, unless it can be demonstrated that a correction factor has not already been applied.
- Correction factor of 1.24 to be used for all other data up to and including 1984.
- No correction factor to be applied after 1984.

### CSIRO Brisbane (90 samples, 1960 to 1976)

In the Brisbane laboratory, a W-B method was used until 1976. Prior to 1968, the standard W-B method was employed but subsequently the analyses were performed in smaller flasks which resulted in higher reaction temperatures. Post-1976, samples were analysed by a LECO method and no correction is required.

For the Brisbane samples, a plot of %C LECO vs %C W-B (Fig. 6) shows an $R^2$ of 0.93 with a slope of 1.21. A plot of the ratio %C LECO/%C W-B also shows some scatter, but two populations appear to be present; samples 1 to 41 and 42 to 90 (Fig. 7). This discontinuity corresponds to a change in the W-B technique in 1968. Plotting samples 1-41 and 42-90 separately, gives slopes of 1.32 (Fig. 8) and 0.982 (Fig. 9), respectively. This demonstrates that the original W-B method used, prior to 1968 gave a correction factor of 1.32, similar to the figure often quoted in the literature, but post-1968, the W-B and LECO methods, on average, agree.

**Recommendation**

- Correction factor of 1.32 to be used prior to and including 1968.
- No correction factor applied after 1968.

### Queensland Department of Natural Resources (173 samples, 1980 to 1999)

A comparison of the data from QDNR with the LECO method showed a high degree of variability with a slope of 1.16 and an $R^2$ of 0.866 (Fig. 10). A plot of the ratio %C LECO/%C W-B also shows high variability but indicates a general decline in the ratio from 1980 to 1999 (samples 1 to 173). The first 50 samples represent the years 1980-1982 inclusive, and these show a higher ratio than the remainder (1.34). The remaining samples cover the time period 1988-1999 and show an average ratio of 1.07. Because of the noise in the data, it is difficult to determine where actual change in ratio has occurred but even into the late 1980s (to sample 70), the ratio is much higher than 1.0. The average ratio for 1988-1991 is 1.19. Because the samples do not cover the full time span, it is not possible to determine if a change occurred within or at the beginning or end of the gap in samples and more samples need to be analysed to determine where the change actually occurred.

**Recommendation**

- Correction factor of 1.34 to be used prior to and including 1987.
- Correction factor of 1.07 to be used after 1987.

## B) NEW SOUTH WALES

### CSIRO Canberra (85 samples, 1968 to 1984)

The data from the Canberra samples showed good agreement with a slope of 0.989 and an $R^2$ of 0.927 (Fig. 12). Figure 13 shows that the ratio near 1.0 was consistent across the whole period with a few exceptions near the 1984 end. Removing these few samples from the analysis had no effect on the overall results. Further investigation found that the data entered into the database for the Canberra soils had been corrected for the W-B under-recovery by multiplying the W-B result by 1.3 but that the method used had been recorded as the W-B method. This explains the apparent high and consistent recovery of the W-B method.

**Recommendation**

- No correction factor applied.

### New South Wales Department of Land and Water Conservation (110 samples, 1990 to 1998)

The data from the NSW samples showed considerable scatter ($R^2$ = 0.892) with a slope of 1.13 (Fig. 14). A plot of ratio with time (Fig. 15) showed that the ratio was relatively constant with time. A factor of 1.13 is consistent with modifications that improve efficiency of the W-B method. This might be achieved through the use of smaller reaction vessels or application of some external heating.

**Recommendation**

- Correction factor of 1.13 to be used.

### C) VICTORIA

#### Victorian Department of Natural Resources and Energy (116 samples, 1961 and 1991 to 1999)

The samples from DNRE were in two groups; a small group of 12 samples from 1961 and the remainder from 1991 to 1999 inclusive. Comparing the LECO and W-B data from these samples also shows considerable scatter ($R^2 = 0.831$) with a slope of 0.992 (Fig. 16). Because of the scatter in the %C LECO/%C W-B ratios (Fig. 17), it is not possible to determine whether there has been any significant change in ratio with time.

**Recommendation**

- No correction factor to be used.

### D) TASMANIA

#### CSIRO Hobart (54 samples, 1960 to 1964)

Only a small set of samples from the CSIRO Hobart laboratories was available. Figure 18 shows a plot of LECO vs W-B data. There is generally good agreement with an $R^2 = 0.912$ and a slope of 0.992 despite a few apparent outliers. Figure 19 shows some scatter in the ratio but this seems consistent across the time span. Again, the consistent ratio close to 1.0 indicates that a correction factor was applied despite no indication in the database. Because the Hobart laboratory was closed in the early 70s, this could not be corroborated through further investigation.

- No correction factor to be used.

### E) SOUTH AUSTRALIA

#### CSIRO Adelaide (86 samples, 1960 to 1974)

A plot of LECO vs W-B data for the Adelaide data is given in Figure 20. There is good agreement with an $R^2 = 0.982$ and a slope of 1.02. Figure 21 shows some scatter in the ratio with a few apparent outliers giving ratios >2.0 and <0.5. There is some indication that the ratio increased at about sample 50 but investigations failed to find any evidence that there had been a change in methodology at this time. Again, further inquiries determined that all W-B data had been corrected with a factor of 1.3 prior to inclusion in the database.

**Recommendation**

- No correction factor to be used.

### F) WESTERN AUSTRALIA

#### Agriculture Western Australia

Previous work with BRS had already developed a correction factor of 1.12 for about 300 samples from WA with an $R^2 = 0.98$.

**Recommendation**

- Correction factor of 1.12 to be used.

## 6. CONCLUSIONS AND RECOMMENDATIONS

The large amount of scatter in the data is of considerable concern. In a few cases, this results from mislabeling or misidentification of samples. In the vast majority of cases however these cannot adequately explain the scatter. The most likely explanation is poor subsampling so that the subsamples analysed in the original laboratories were not representative of those sent to the ACU group in Adelaide. This could be tested by sending the subsamples back to the respective laboratories for analyses provided these laboratories were still in operation and were continuing to use the W-B method. Despite the scatter encountered in some of the data, the slope of the regression lines developed between the LECO and W-B methods should be adequate for the purposes of determining initial soil carbon condition. Some confidence can be gained from the fact that the data that had already been corrected consistently gave slopes close to 1.0. Also, those data that were derived from the original W-B method but were not corrected, gave correction factors of 1.32 and 1.34. It is therefore recommended that the correction factors summarized in the following table should be used to determine soil total organic carbon.

## 7. SUMMARY OF CORRECTION FACTORS

| Laboratory | Correction Factor | Comments |
|---|---|---|
| QUEENSLAND | | |
| CSIRO Townsville | 1.00 | Prior to and including 1968 |
| | 1.24 | 1969 and up to and including1984 |
| CSIRO Brisbane | 1.32 | Prior to and including 1968 |
| | 1.00 | 1969 and subsequent years |
| QDNR | 1.34 | Prior to and including 1987 |
| | 1.07 | 1988 and subsequent years |
| | | |
| NSW | | |
| CSIRO Canberra | 1.00 | For all years |
| DLWC | 1.13 | For all years |
| | | |
| VICTORIA | 1.00 | For all years |
| | | |
| TASMANIA | | |
| CSIRO Hobart | 1.00 | For all years |
| | | |
| SOUTH AUSTRALIA | | |
| CSIRO Adelaide | 1.00 | For all years |
| | | |
| WESTERN AUSTRALIA | | |
| AgWA | 1.12 | For all years |

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Walkley, A and L.A. Black. (1934). *An examination of the Dgtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method*. Soil Science 37: 29-38.

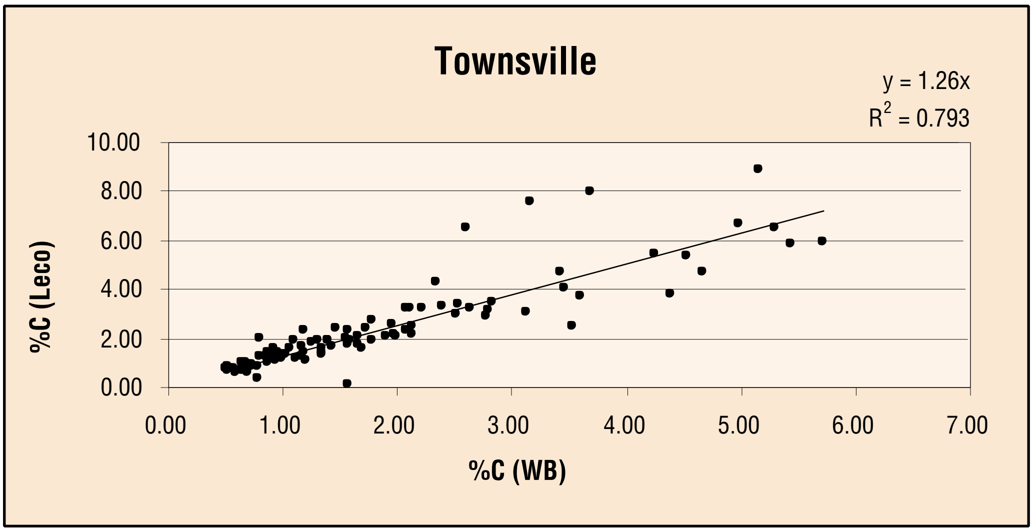


**Figure 1. Relationship of W-B data from CSIRO Townsville laboratory with LECO data from CSIRO ACU, Adelaide.**

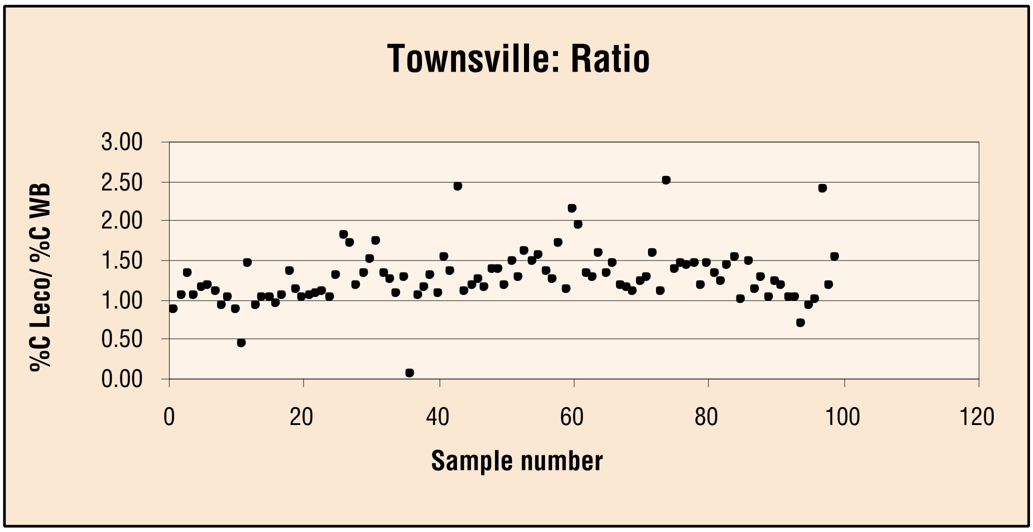


**Figure 2. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1963 to 1984 inclusive.**

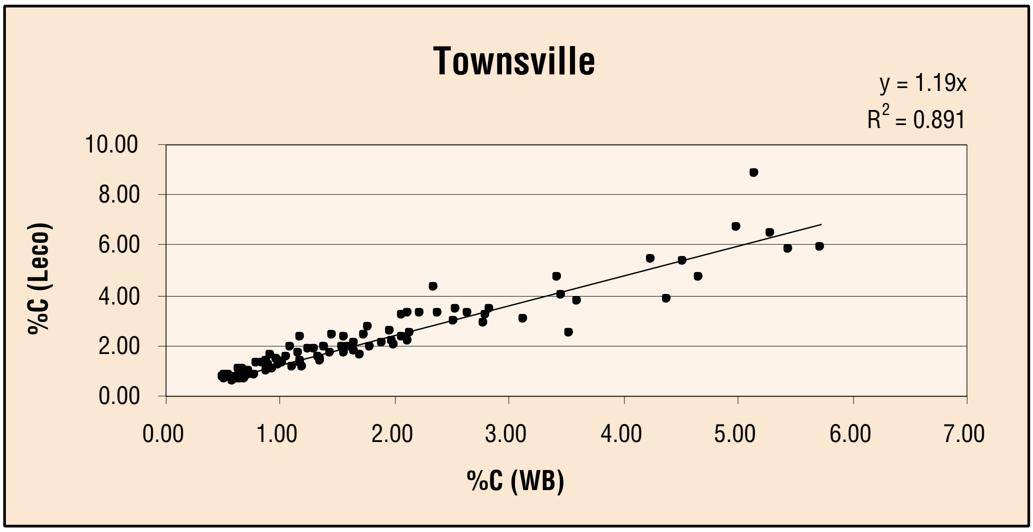


**Figure 3. Relationship of W-B data from CSIRO Townsville laboratory with LECO data from CSIRO ACU, Adelaide with 6 outliers removed.**

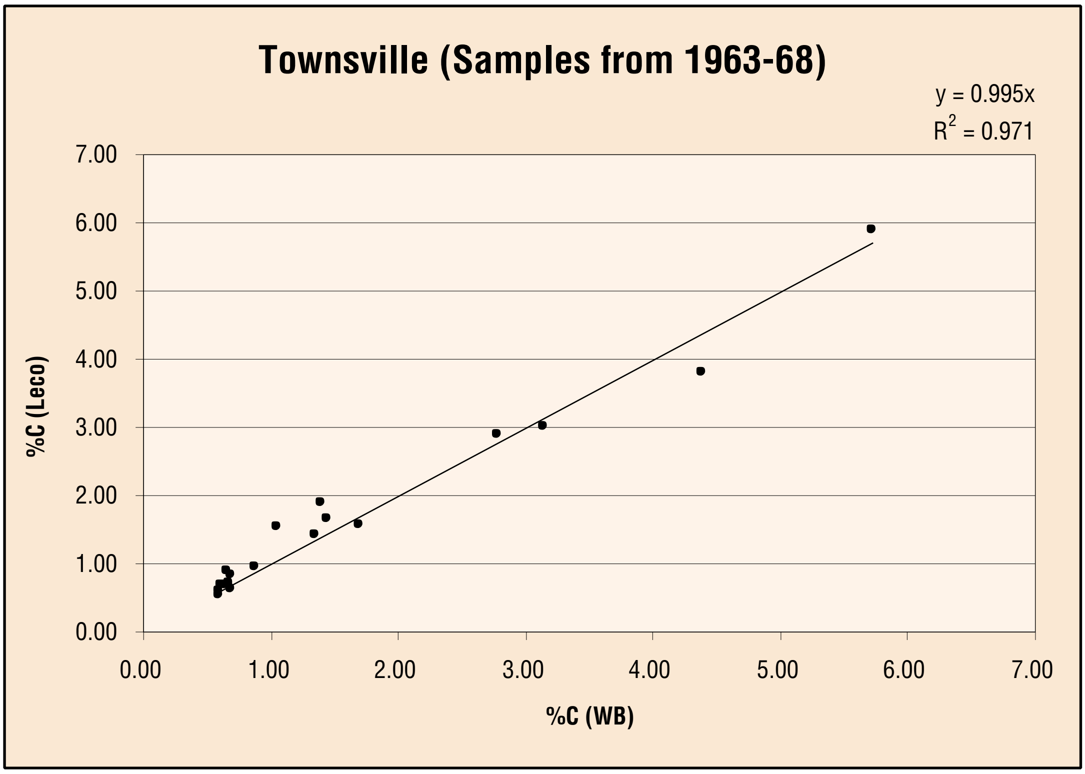


**Figure 4. Relationship of W-B data from CSIRO Townsville laboratory with LECO data from CSIRO ACU, Adelaide for the period 1963 to 1968 inclusive.**

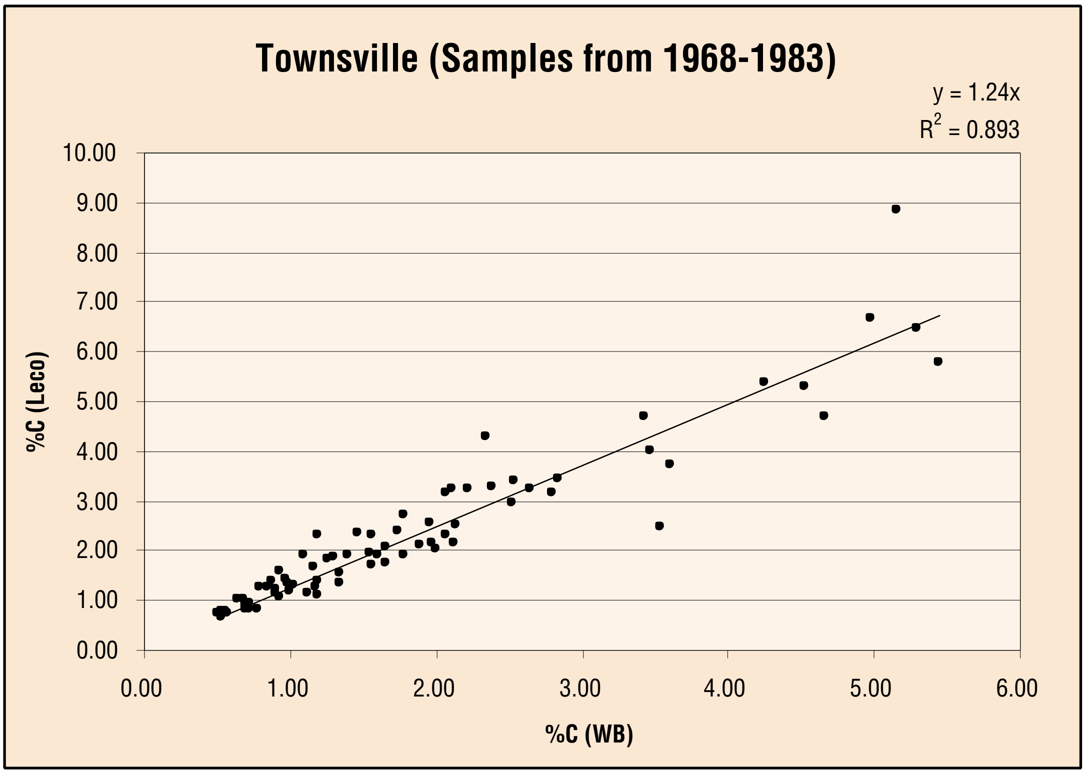


**Figure 5. Relationship of W-B data from CSIRO Townsville laboratory with LECO data from CSIRO ACU, Adelaide for the period 1969 to 1984 inclusive.**

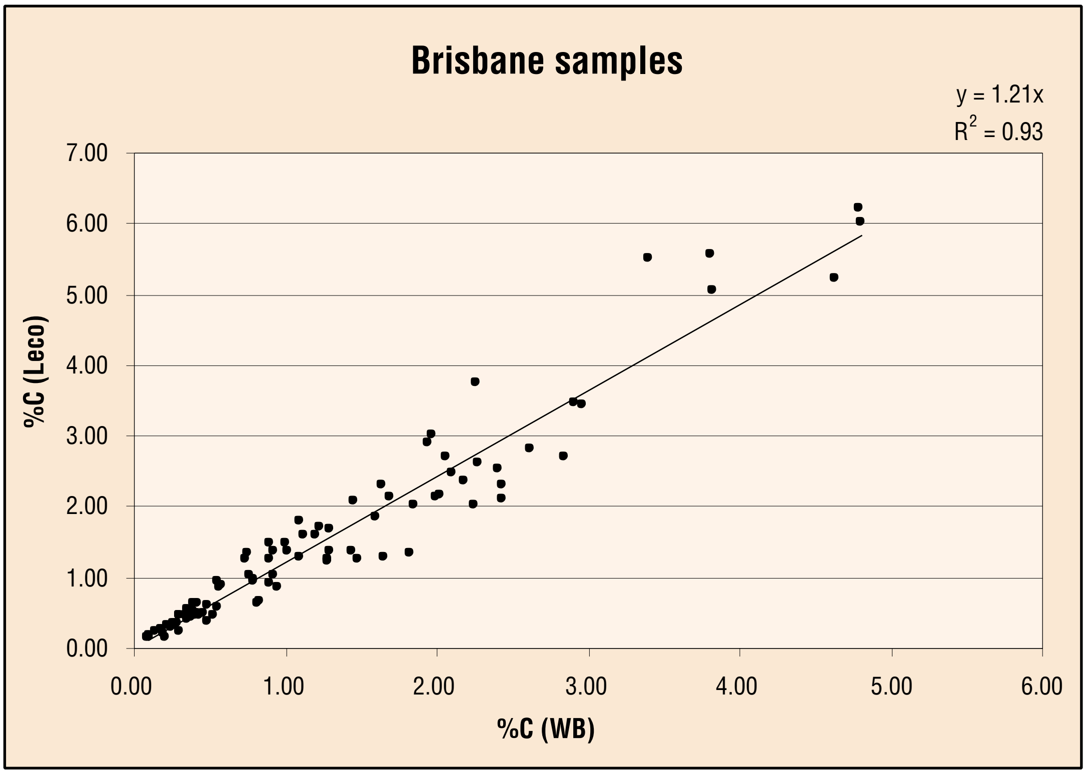


**Figure 6. Relationship of W-B data from CSIRO Brisbane laboratory with LECO data from CSIRO ACU, Adelaide.**

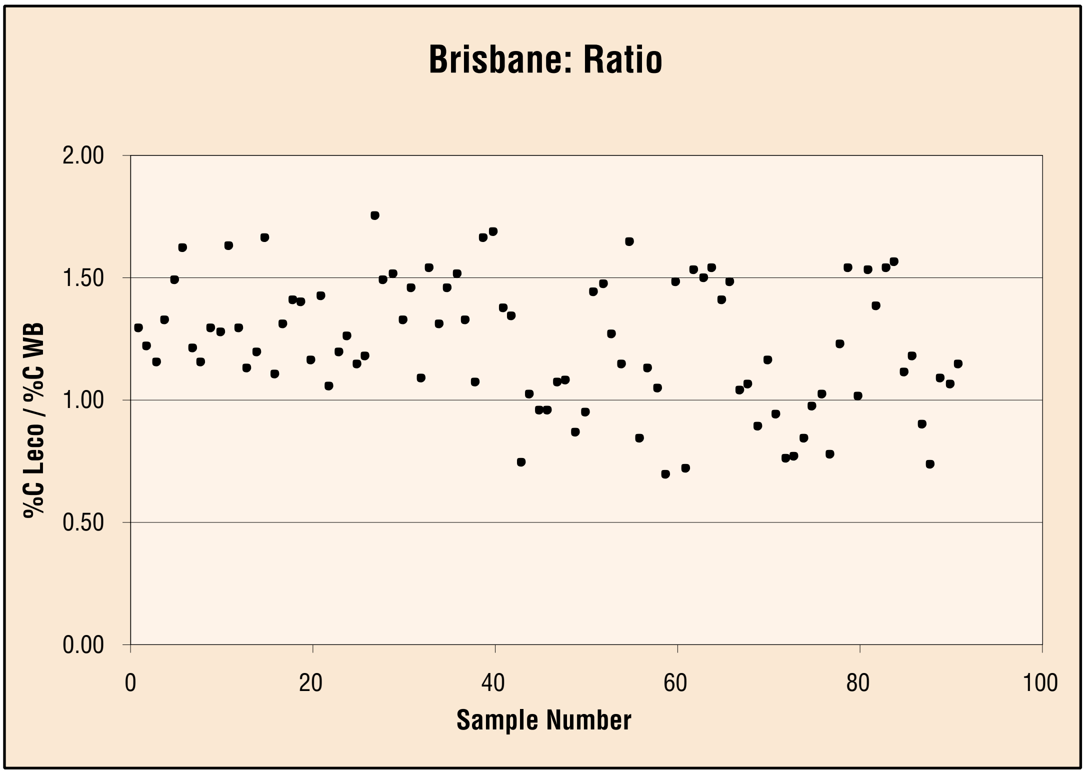


**Figure 7. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1960 to 1976 inclusive.**

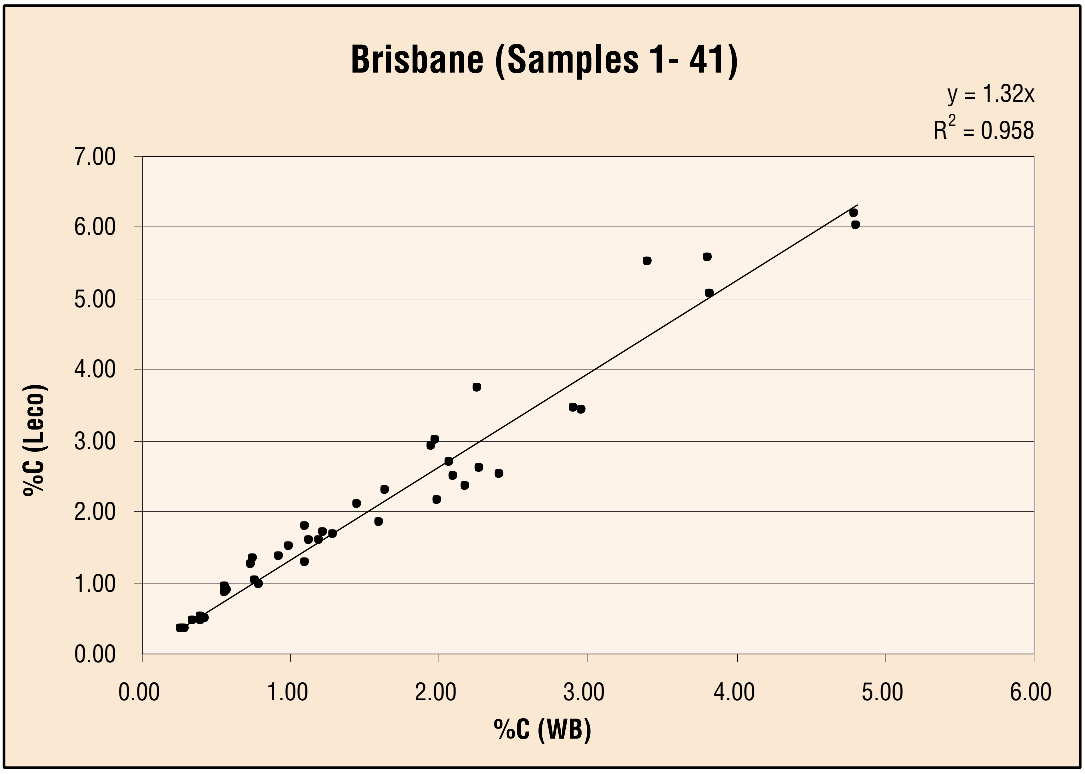


**Figure 8. Relationship of W-B data from CSIRO Brisbane laboratory with LECO data from CSIRO ACU, Adelaide for the period 1960 to 1968 inclusive.**

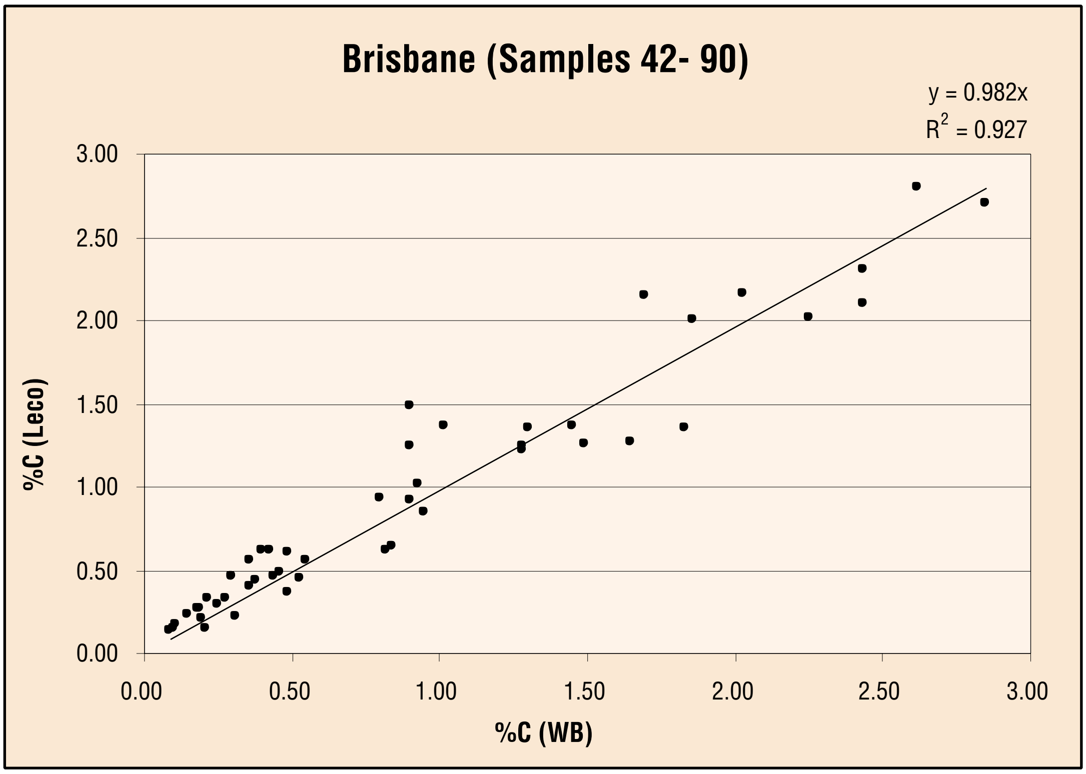


**Figure 9. Relationship of W-B data from CSIRO Brisbane laboratory with LECO data from CSIRO ACU, Adelaide for the period 1969 to 1976 inclusive.**

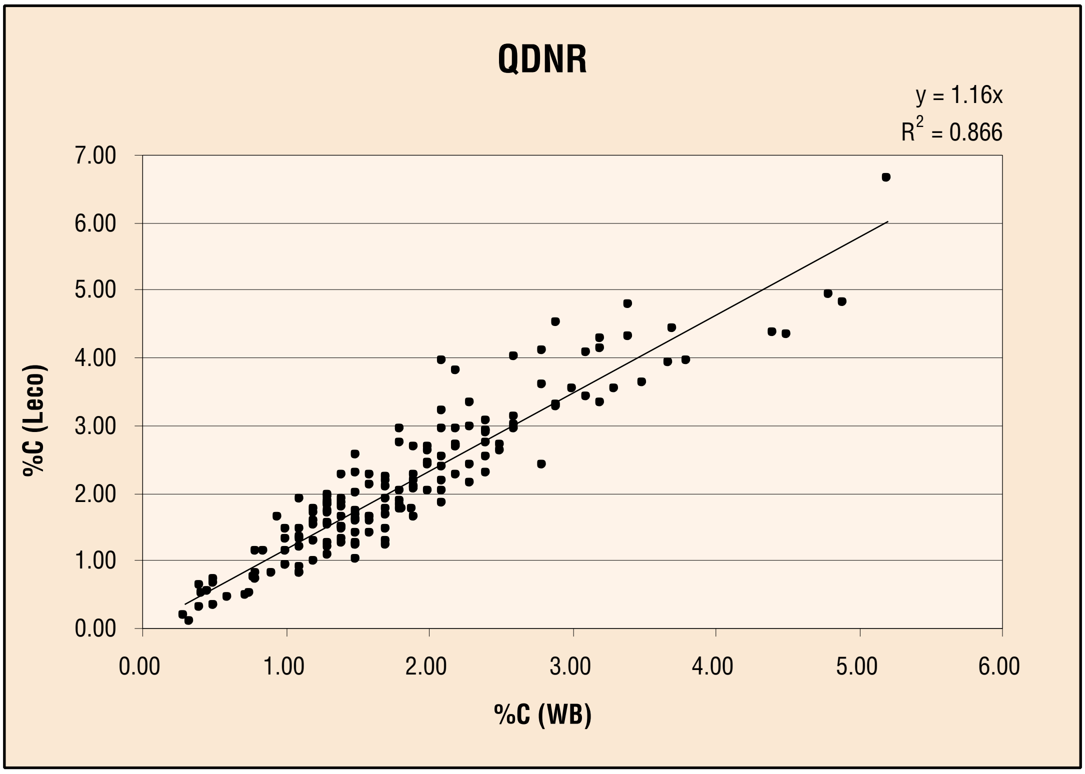


**Figure 10. Relationship of W-B data from QDNR Brisbane laboratory with LECO data from CSIRO ACU, Adelaide.**

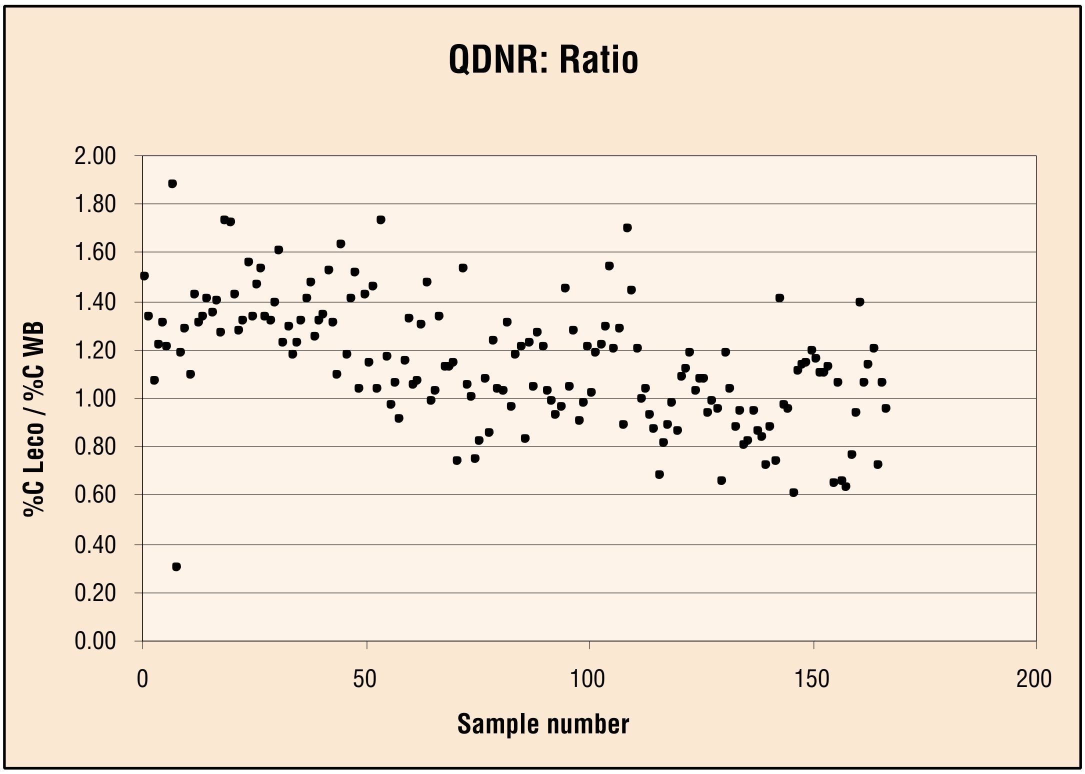


**Figure 11. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1980 to 1999 inclusive.**

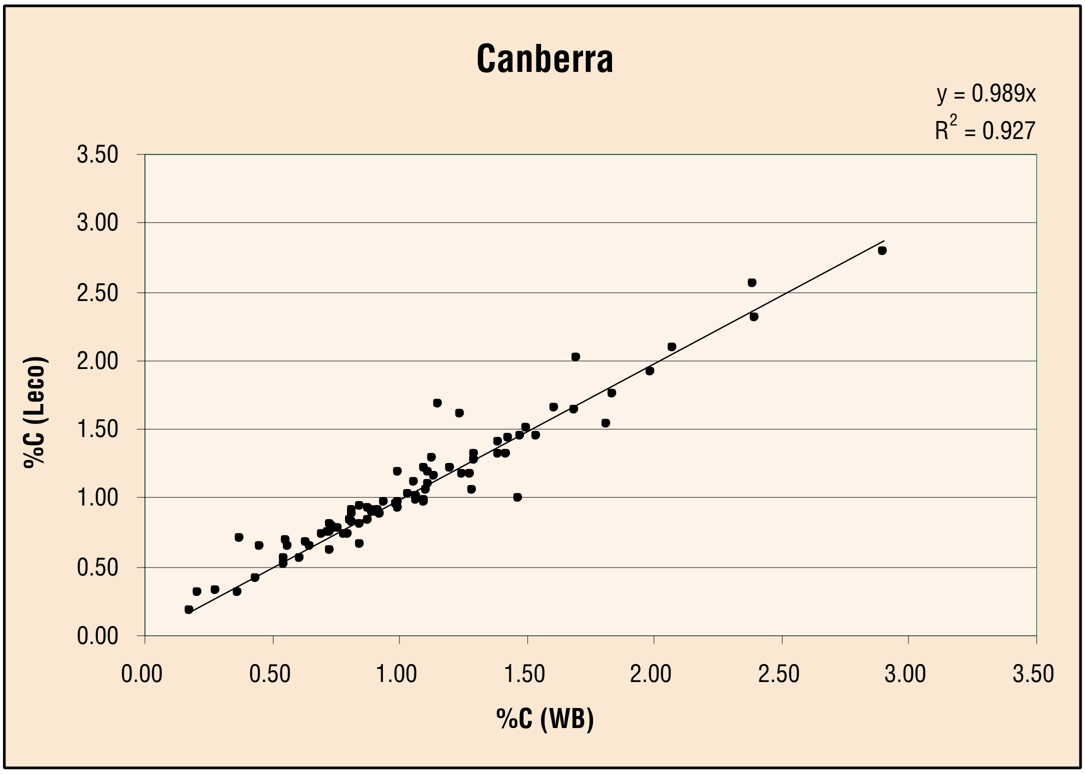


**Figure 12. Relationship of W-B data from CSIRO Canberra laboratory with LECO data from CSIRO ACU, Adelaide.**

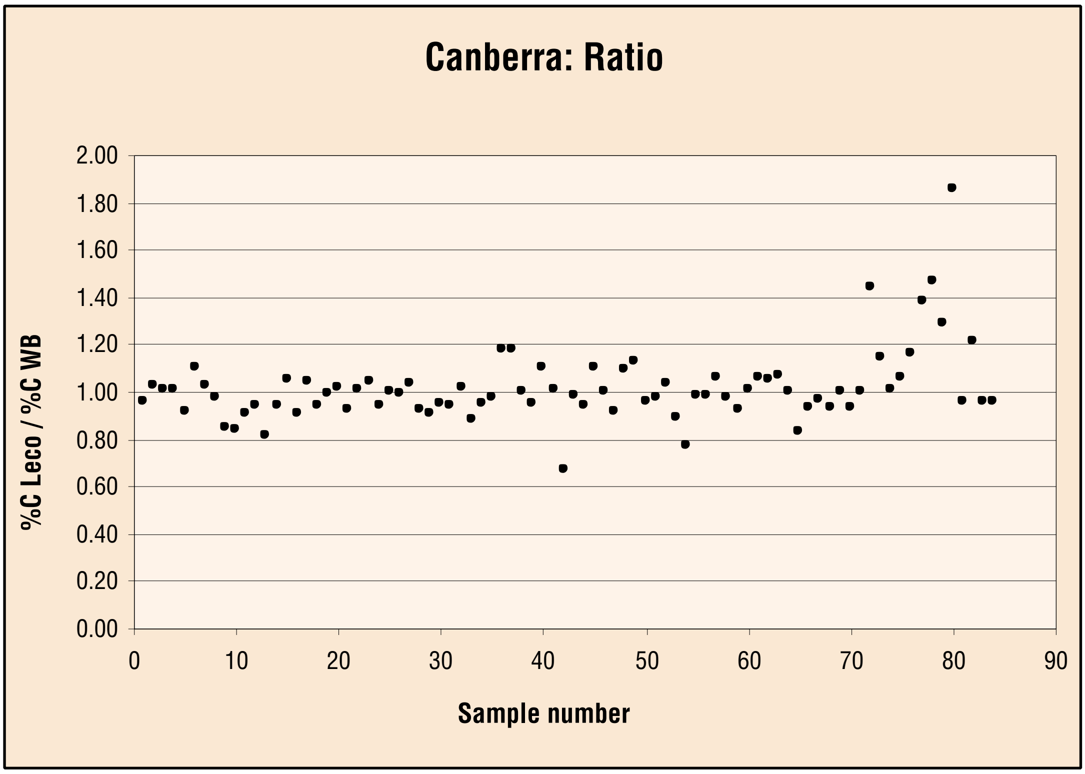


**Figure 13. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1968 to 1984 inclusive.**

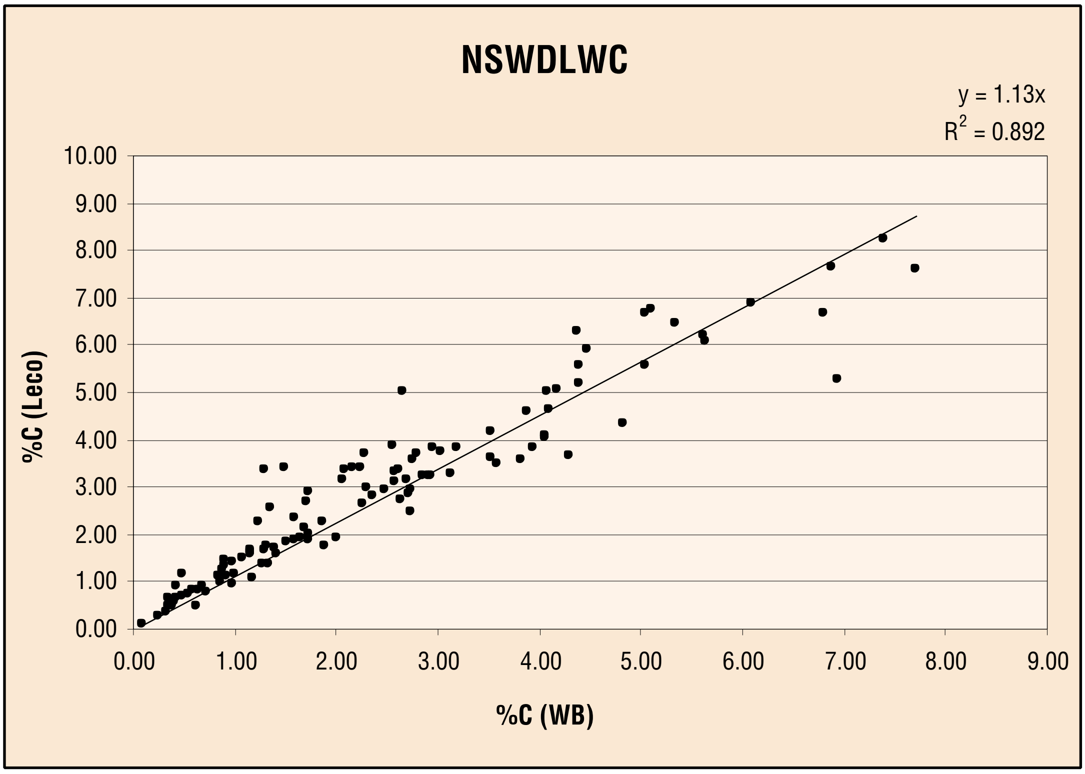


**Figure 14. Relationship of W-B data from NSWDLWC laboratory with LECO data from CSIRO ACU, Adelaide.**

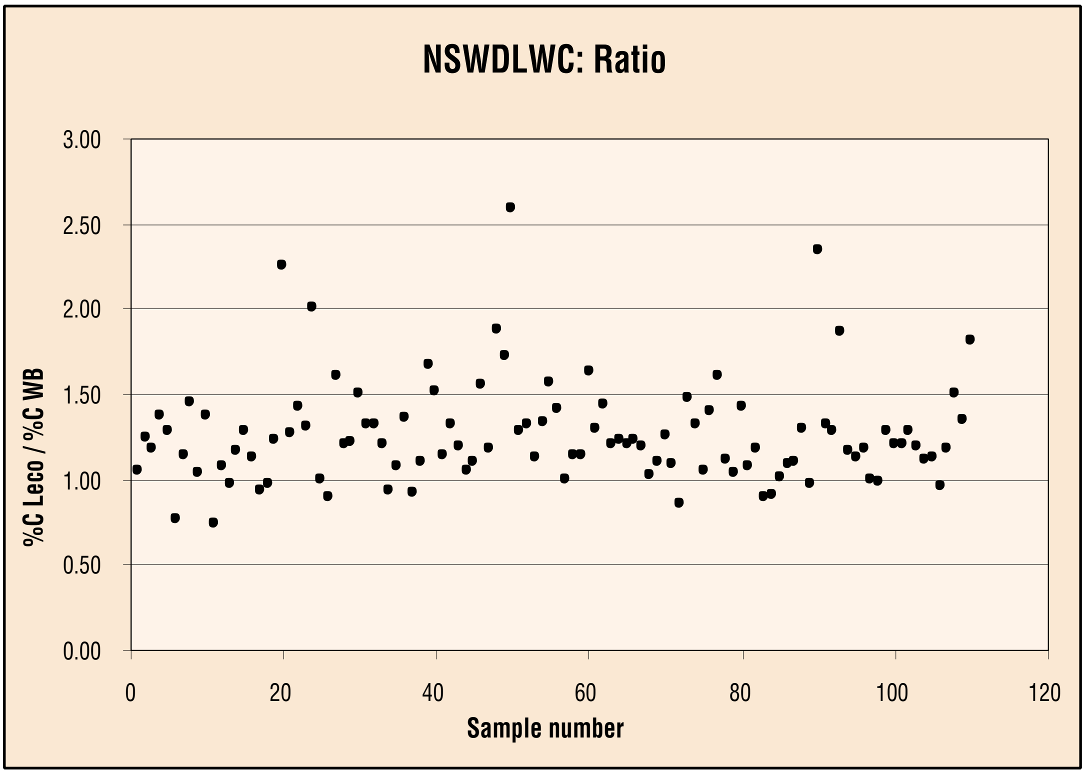


**Figure 15. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1990 to 1998 inclusive.**

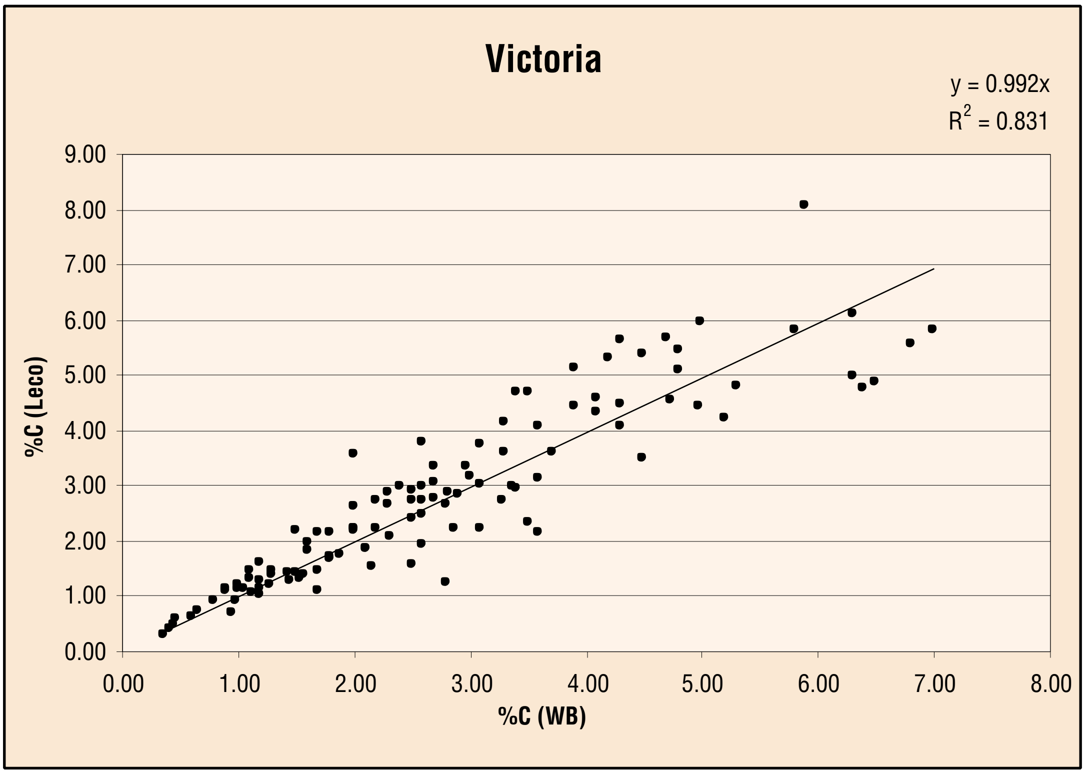


**Figure 16. Relationship of W-B data from VDNRE laboratory with LECO data from CSIRO ACU, Adelaide.**

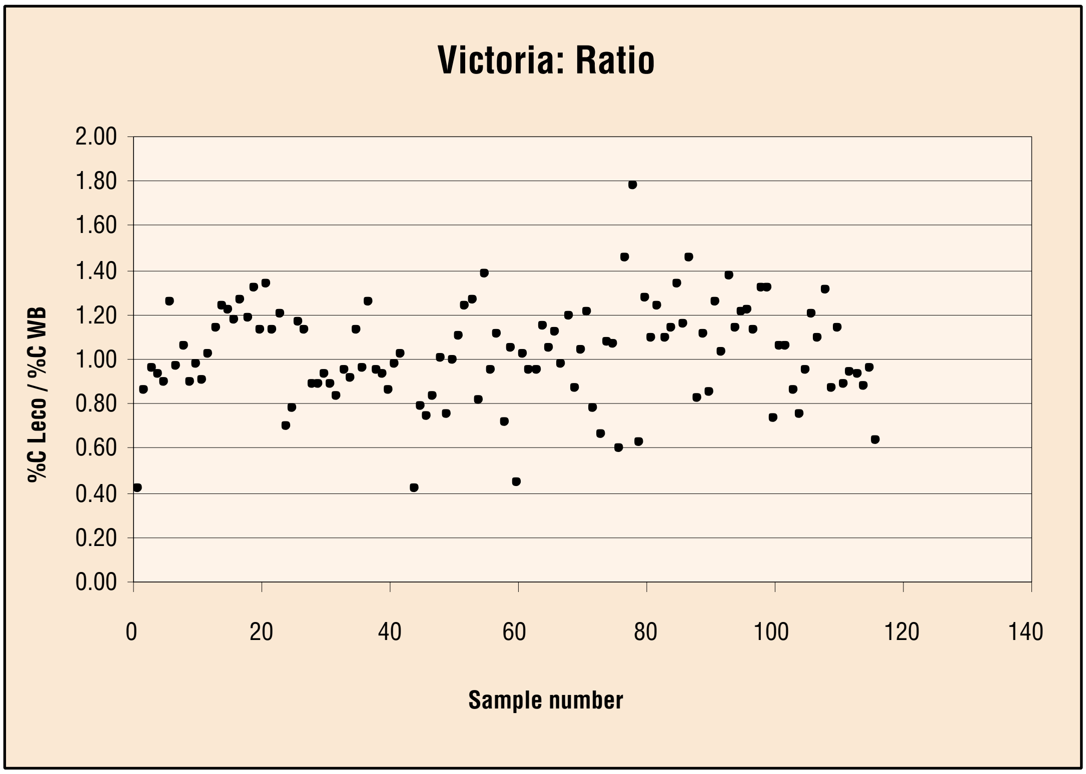


**Figure 17. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1961 to 1999 inclusive.**

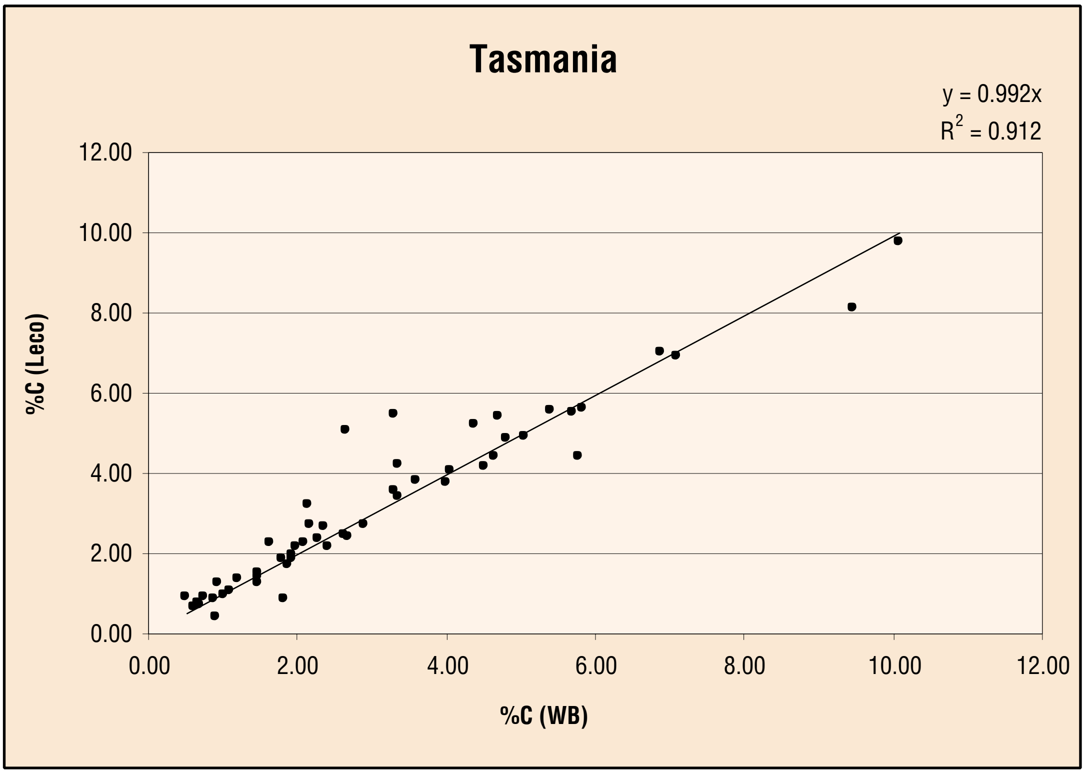


**Figure 18. Relationship of W-B data from CSIRO Hobart laboratory with LECO data from CSIRO ACU, Adelaide.**

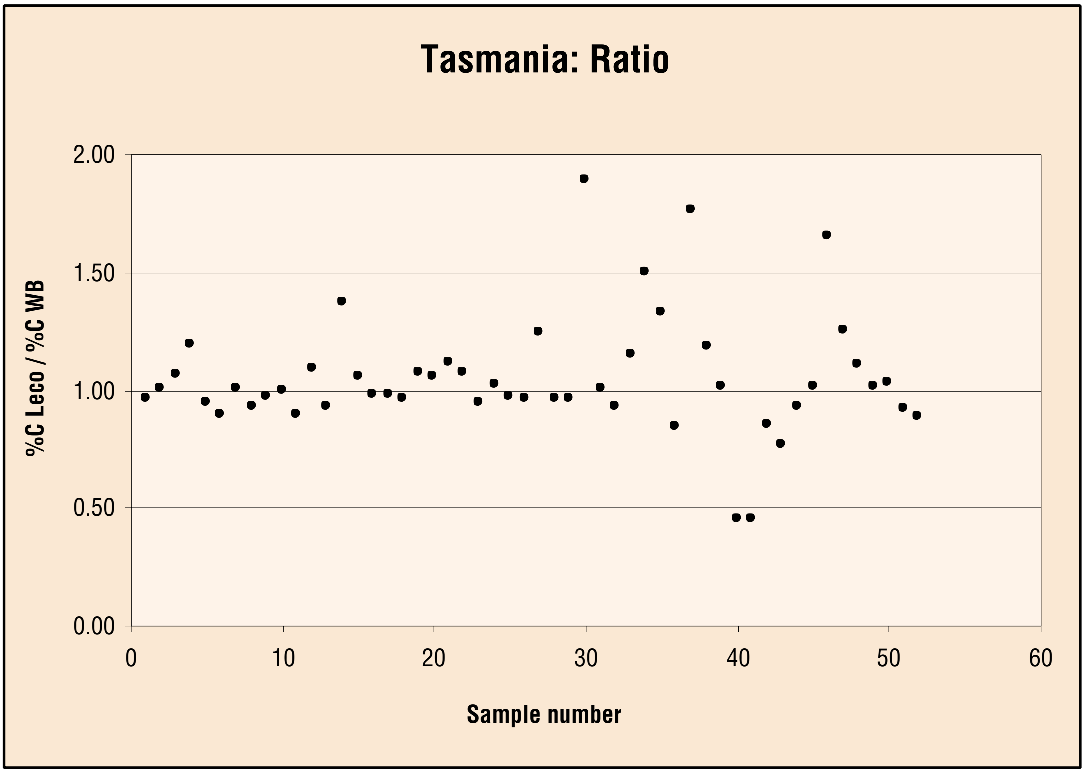


**Figure 19. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1960 to 1964 inclusive.**

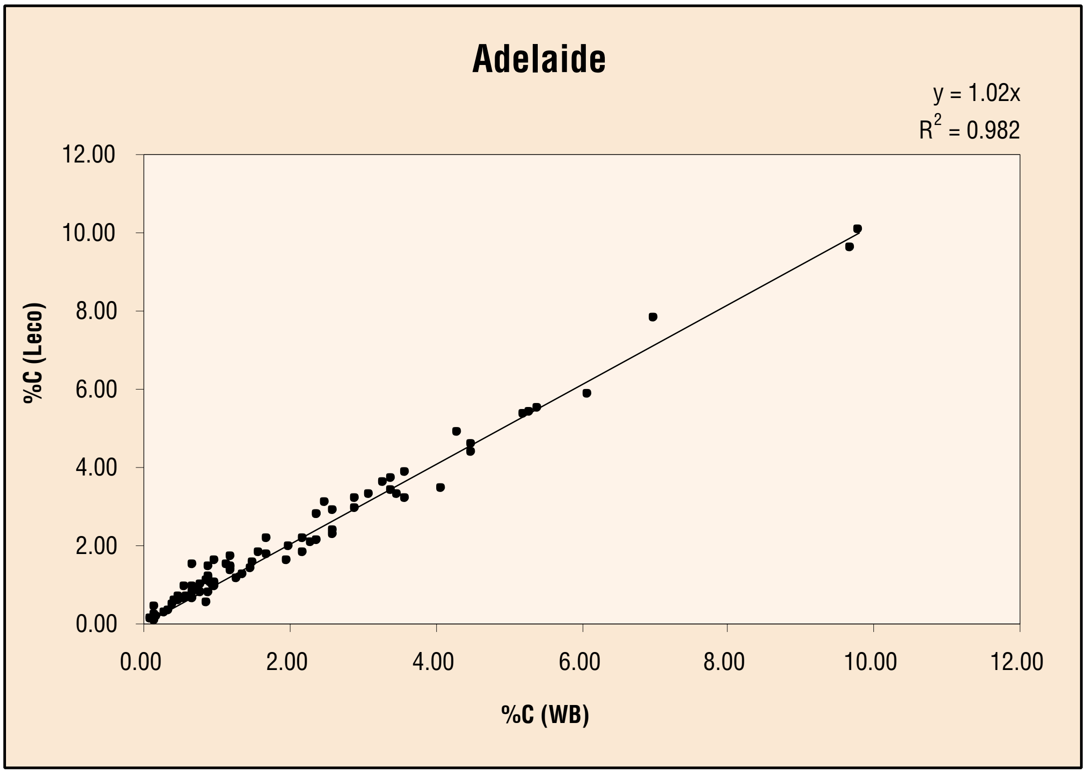


**Figure 20. Relationship of W-B data from CSIRO Adelaide laboratory with LECO data from CSIRO ACU, Adelaide.**

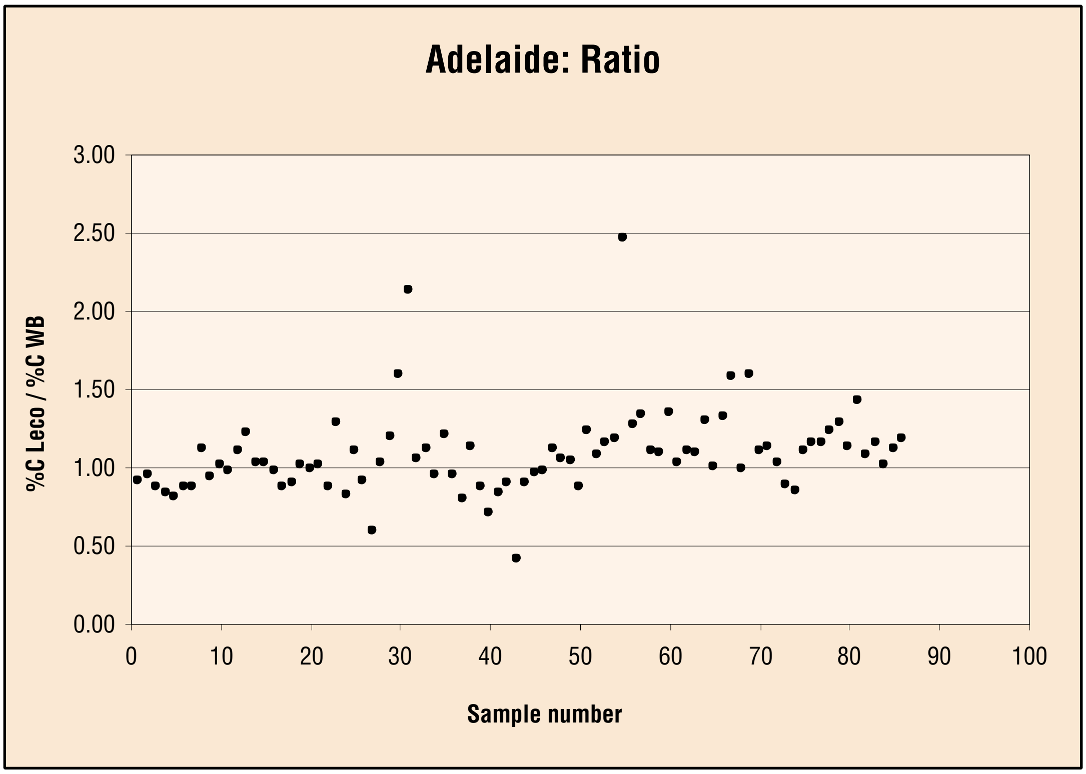


**Figure 21. Changes in LECO/W-B ratio with sample number. Sample numbers were arranged in increasing order from 1960 to 1974 inclusive.**

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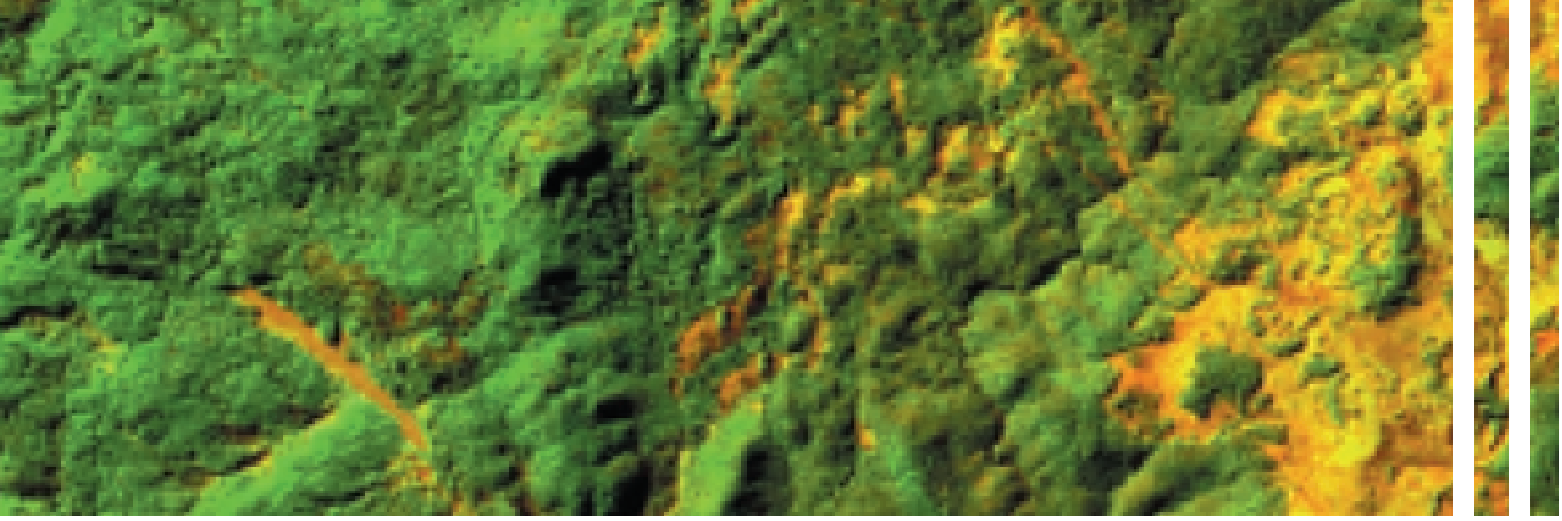

The National Carbon Accounting System provides a complete accounting and forecasting capability for human-induced sources and sinks of greenhouse gas emissions from Australian land based systems. It will provide a basis for assessing Australia's progress towards meeting its international emissions commitments.

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