**EUB**

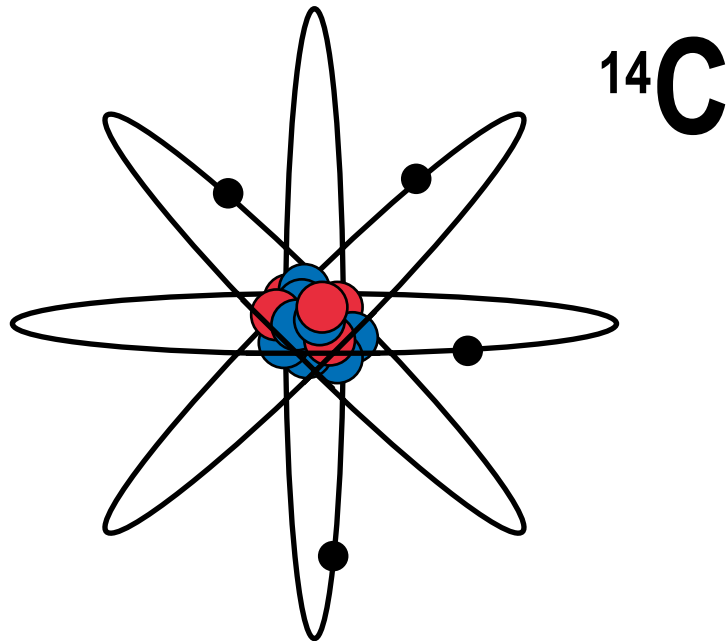# Carbon-14 Dating of Groundwater from Selected Wells in Quaternary and Quaternary-Tertiary Sediments, Athabasca Oil Sands (In Situ) Area, Alberta

$^{14}C$

Alberta Energy and Utilities Board

Alberta Geological Survey

AGS

# Carbon-14 Dating of Groundwater from Selected Wells in Quaternary and Quaternary–Tertiary Sediments, Athabasca Oil Sands (In Situ) Area, Alberta

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# Contents

## Tables

## Figures

## Acknowledgments

# Abstract

The Alberta Geological Survey (AGS) collected samples of groundwater for $^{14}$C-age dating at three sites within the Athabasca Oil Sands (in situ) Area of Alberta. Each site has a nest of piezometers completed at various depths in Quaternary or Quaternary–Tertiary aquifers. Not all of the piezometers at each site were sampled for $^{14}$C-age dating, however. The three Quaternary intertill/intratill aquifer water samples at the first site possess ages of 1558 ± 91 radiocarbon years at 41 m depth, 2402 ± 110 radiocarbon years at 76 m depth and 2532 ± 58 radiocarbon years at 120 m depth. A basal Quaternary aquifer at a second site has a calculated age of 30 880 ± 257 radiocarbon years at a depth of 158 m below ground. A groundwater sample from a Quaternary–Tertiary buried channel aquifer water sample at a third site has a calculated age of 11 186 ± 79 radiocarbon years at 230 m depth.

# 1   Introduction

Between 1999 and 2001, the Alberta Geological Survey conducted a drilling and piezometer-installation program in the Athabasca Oil Sands (in situ) Area of Alberta. Nine piezometers were installed at three sites. The purpose of this program was to collect groundwater samples from the various aquifers for baseline characterization of groundwater conditions in the area prior to extensive oil sands development. This work was jointly funded by the Government of Alberta, through the Alberta Energy and Utilities Board (EUB), and by the Government of Canada through the Ministry of Western Economic Diversification under the Western Economic Partnership Agreement.

Five samples from five of the nine piezometers were submitted for $^{14}C_{DIC}$ analysis. The purpose of this document is to present the results of analyses for $^{14}C_{DIC}$ in the collected groundwater samples and present the calculated radiocarbon ages.

The program study area is located in northeast Alberta and is bounded on the west by the Athabasca River, to the north by the Athabasca and Clearwater rivers, to the east by the Alberta/Saskatchewan border and to the south by the Mostoos Upland (Figure 1). The study area extent, aside from the provincial boundary, was selected to represent natural hydrologic boundaries. The Athabasca and Clearwater rivers are natural drainage boundaries. The Mostoos Upland was selected because it forms the hydrologic divide between the Cold Lake – Beaver River drainage basin to the south and the Athabasca – Clearwater rivers drainage basins to the north. This area encompasses the southeast portion of the EUB-designated Athabasca Oil Sands Area.

# 2   General $^{14}$C Geochemistry

Carbon-14 differs from regular carbon, carbon-12, in that it has two extra neutrons in its nucleus. It forms in the atmosphere through cosmic-ray bombardment of atmospheric gases and in the earth through either neutron activation of nitrogen, or neutron capture of oxygen caused by spontaneous fission of uranium and other elements. Atmospheric testing of nuclear weapons also created carbon-14. Release of $CO_2$ by industrial activities, such as burning fossil fuels (which are too old to have significant levels of carbon-14) has resulted in a relative decrease in the concentration of carbon-14 in the Earth's atmosphere, diluting $^{14}$C by as much as 25 per cent compared to pre-industrial concentrations (Clark and Fritz, 1997, p. 204).

## 2.1   General Principles

Carbon-14 is primarily introduced into groundwater in the soil zone through biological processes. Carbon-14 enters groundwater through the soil zone as the $CO_2$ released by living plants and decaying organic material is dissolved in water and incorporated as dissolved inorganic carbon (DIC). Along the flow path, $^{14}$C concentrations begin to decrease according to radioactive decay principles and through any subsequent dilution or geochemical reaction mechanisms. Dilution, loss, or addition of $^{14}$C through geochemical processes can significantly alter the original $^{14}$C concentration. Processes that will affect $^{14}$C concentrations include

- carbonate dissolution;
- exchange reactions between the $DI^{14}C$ and the aquifer material;
- oxidation of "old" organic matter;
- diffusion of $^{14}$C into the aquifer;
- sulphate reduction;
- incorporation of geogenic $CO_2$ from deep crustal or mantle sources; and
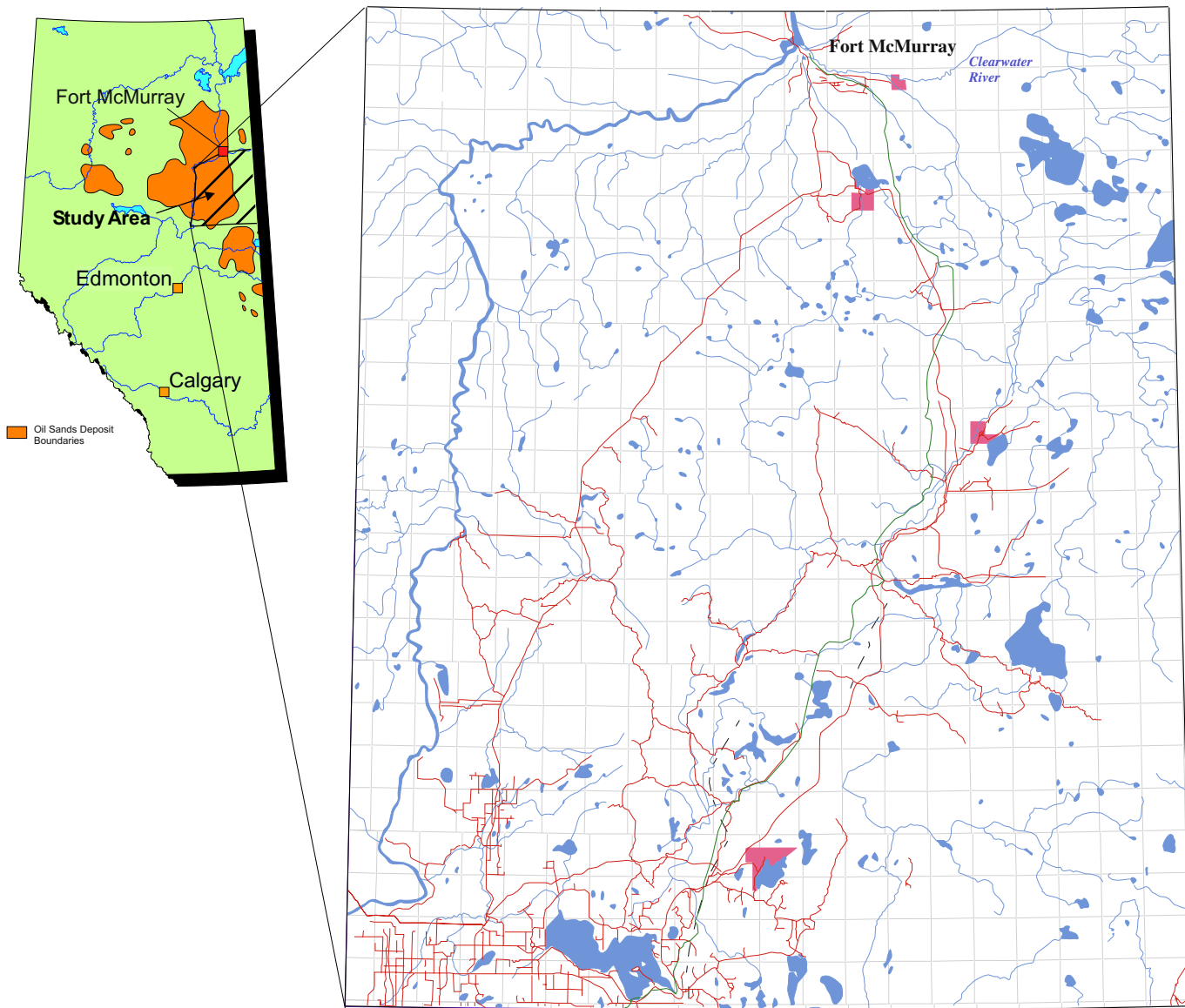- methanogenesis.

**Figure 1. Study area map.**

Carbon-14 can also enter groundwater directly as a component of precipitation. Table 1 contains a summary of $^{14}$C concentrations along the groundwater recharge pathway described above.

**Table 1. $^{14}$C concentrations along the groundwater recharge pathway (Clark and Fritz, 1997, p. 205)**

| Recharge pathway component | $^{14}$C activity (pmC) |
|---|---|
| Atmospheric $CO_2$ | 104.3 |
| Vegetation | 100.0 |
| Soil $CO_2$ | 100.5 |
| DIC (open system) | 102.3 |
| DIC (closed system) | <100 |

## 2.2   Age dating using $DI^{14}C$

The equation for radioactive decay has the form:

$$a_t = a_0\, e^{-\lambda t} \qquad\qquad \text{(Equation 1)}$$

where   $a_t$ = the activity of the species in question at time t

   $a_0$ = the activity of the species in question at time 0

   $\lambda$ = the decay constant (equal to $\ln 2 / t_{1/2}$)

   $t$ = time

The half-life ($t_{1/2}$) is the time interval required for the number of atoms or the activity of a radioactive element to fall from any particular value to one half that value (Friedlander et al., 1981, p. 191). Carbon-14 has a half-life of $5730 \pm 30$ years. With this information, and the determined concentration of $^{14}$C, age dating of materials can be undertaken using the radioactive decay equation.

If no $^{14}$C is gained from outside sources, no $^{14}$C is lost other than through radioactive decay, no DIC dilution occurs, and an original concentration (or activity, $a_o$) of $^{14}$C is known or can be estimated, then Equation 1 can be rearranged to solve for the age of a substance.

$$t = (t_{1/2} / \log 2) \times (\log (a_0/a_t)) \qquad\qquad \text{(Equation 2)}$$

A case in which no $^{14}$C is gained or lost and no DIC dilution occurs is rare (Clark and Fritz, 1997, p. 206). The equation must therefore incorporate a correction factor to account for dilution or addition. The equation then becomes:

$$t = (t_{1/2} / \log 2) \times (\log (qa_0 / a_t)) \qquad\qquad \text{(Equation 3)}$$

where q = dilution factor

A number of models have been proposed to determine this q value.

Dilution by carbonate dissolution:

- The statistical correction model – discussed in Vogel, 1970; Bajjali et al., 1997; and Clark and Fritz, 1997, p. 207.
- The alkalinity correction model – discussed in Tamers, 1975; and Clark and Fritz, 1997, p. 208.
- The chemical mass-balance correction model – discussed in Clark and Fritz, 1997, p. 209

- The $\delta^{13}C$ mixing model – discussed in Pearson, 1965; Pearson and Hanshaw, 1970; and Clark and Fritz, 1997, p.210.
- The matrix exchange model – discussed in Fontes and Garnier, 1979; and Clark and Fritz, 1997, p. 212.

The q value calculations for other processes affecting $^{14}C$ concentrations include

- $^{14}C$ matrix diffusion correction factor - discussed in Maloszewki and Zuber, 1991; and Clark and Fritz, 1997, p. 217;.
- Sulphate reduction correction factor – discussed in Aravena et al., 1995; Bajjali et al., 1997; and Clark and Fritz, 1997, p. 218.
- Incorporation of geogenic $CO_2$ correction factor – discussed in Barnes et al., 1978; Marty and Jambon, 1987; and Clark and Fritz, 1997, p. 220.
- Methanogenesis correction factor –discussed in Clark and Fritz, 1997, p. 220.

After calculation of all q values, a total dilution factor can be calculated. It will be given by:

$q_{tot} = q_{carbonate} + q_{matrix\ diffusion} + q_{sulphate\ reduction} + q_{geogenic} + q_{methanogenesis}$

The age equation then becomes:

$t = (t_{1/2} / \log 2) \times (\log (q_{tot}a_0 / a_t))$ \qquad (Equation 4)

Because of the potential effects on $^{14}C$ concentration listed above, the effective range for age dating of groundwater through the use of $^{14}C$ is limited to about 30 000 years (Clark and Fritz, 1997, p. 201). Clark and Fritz (1997, p. 207–222) give a general description of the models listed above, as well as recommendations on the selection of a model. Careful consideration of the hydrogeological and geochemical conditions at a given site should be considered before selecting a correction-factor calculation model, as not all of the dilution factors will influence all groundwater scenarios.

# 3 Methodology

Samples were collected following the sampling protocols discussed in Lemay (2002). Sample ages were determined using the carbonate dissolution correction-factor calculation proposed by Fontes and Garnier (1979). This method was selected because it required the fewest parameter estimations. It accounts for carbonate dissolution and includes a correction for evaporite dissolution and cation exchange. In addition, it takes into account processes occurring under both open and closed systems.

Corrections were not made for matrix diffusion of $^{14}C$, sulphate reduction, incorporation of geogenic $CO_2$, nor methanogenesis for the following reasons

- The variables necessary to calculate the matrix diffusion of $^{14}C$ (matrix porosity and fissure porosity) for the aquifers in question were not characterized as part of this or any other study.
- Eh measurements indicate that neither methanogenesis nor sulphate reduction are occurring within the aquifers.
- No source of geogenic $CO_2$ appears reasonable given current geological conditions.

For calculation purposes, certain values were assumed since they were not measured, these included

- $\delta^{13}C_{CO2}$ = -23‰ (Clark and Fritz, 1997, p. 205);
- $\delta^{13}C_{carb}$ = 0‰ (Clark and Fritz, 1997, p. 122);
- $A_g$, the $^{14}C$ activity of the soil $CO_2$ taken as 100 pmC; and
- $A_M$, the $^{14}C$ activity of solid taken as 0 pmC.

Certain values had to be calculated, including

- $C_M$, the molal concentration of carbon of inorganic origin as defined by Fontes and Garnier (1979)
  - Taken here to be the sum of the molalities of $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $SO_4^{2-}$ and $Cl^-$
- $C_T$, the molal concentration of the total dissolved inorganic carbon as defined by Fontes and Garnier (1979)
- the isotope fractionation factor, calculated from the work of Bottinga (1968)
- the isotope enrichment factor, calculated based on the method described by Clark and Fritz (1997, p. 31)

Using this information, along with the measured $^{14}C$ concentrations and $\delta^{13}C_{CO2}$ values in the equations defined by Fontes and Garnier (1979), the value of $q_{tot}a_0$ can be calculated. Substituting this information into the radioactive decay equation yields an age for the water sample.

# 4 Results, Observations and Preliminary Interpretations

Sample sites are shown in Figure 2. Calculated ages and sample data are presented in Table 2 and Table 3. Piezometer completion details are presented in Figures 3 to 7. Additional information regarding piezometer completion details can be found in Lemay and Jean (2002).

**Table 2. Results of $\delta^{13}C$ and $^{14}C$ analyses of Quaternary and Quaternary–Tertiary aquifer water samples**

| Piezometer Identification Code | Measured $\delta^{13}C$ (permil) | Corrected $^{14}C/^{12}C$ (pmC) | Calculated $q_{tot}$ correction factor | Age (radiocarbon years) | Minimum Age (radiocarbon years) | Maximum Age (radiocarbon years) |
|---|---|---|---|---|---|---|
| WEPA 00-1-41 | -13.45 | 56.45±0.62 | 0.681536 | 1558 | 1467 | 1649 |
| WEPA 00-1-76 | -13.48 | 51.30±0.68 | 0.685978 | 2402 | 2293 | 2512 |
| WEPA 00-1-120 | -13.95 | 53.10±0.37 | 0.721279 | 2532 | 2474 | 2590 |
| WEPA 00-3-158 | -21.13 | 3.59±0.11 | 1.504546 | 30 880 | 30 631 | 31 137 |
| WR 99-1-230 | -15.20 | 26.45±0.25 | 1.023568 | 11 186 | 11 109 | 11 265 |

**Table 3. Major ions chemistry of Quaternary drift and Quaternary–Tertiary aquifer water samples**

| Piezometer Name | Field pH | Alkalinity* (mg/L $HCO_3^-$) | Alkalinity** (mg/L $HCO_3^-$) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | K (mg/L) | SO$_4$ (mg/L) | Cl (mg/L) | $HCO_3^-$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| WEPA 00-1-41 | 7.44 | 370 | 379 | 82.0 | 24.40 | 11.7 | 3.6 | 5.11 | 1.31 | 379 |
| WEPA 00-1-76 | 7.48 | | 382 | 74.4 | 20.20 | 48.0 | 9.9 | 30.20 | 12.80 | 381 |
| WEPA 00-1-120 | 7.48 | 412 | 410 | 81.5 | 24.50 | 24.2 | 5.1 | 6.08 | 1.83 | 410 |
| WEPA 00-3-158 | 7.67 | 522 | 552 | 32.9 | 11.20 | 182.0 | 4.7 | 54.20 | 6.87 | 552 |
| WR 99-1-230 | 7.72 | 406 | 482 | 64.8 | 18.70 | 98.9 | 5.4 | 38.10 | 0.44 | 482 |

\* Field determined alkalinity
\** Laboratory determined alkalinity

## 4.1 Site WEPA 00-1

Calculated radiocarbon age dates were determined from three intervals at this site. Ages increase with depth from 1558 ± 91 radiocarbon years at 41 m, to 2402 ± 110 radiocarbon years at 76 m, to 2532 ± 58 radiocarbon years at 120 m. This implies an age gradient of approximately 24.5 radiocarbon years/m between the shallowest and intermediate intervals, and an age gradient of approximately 2.9 radiocarbon years/m between the intermediate and deepest intervals.

Figure 2
Locations of piezometers within the
study area

Legend:
- Quaternary drift aquifers water sample locations
- Quaternary/Tertiary buried channel aquifers water sample locations
- Urban centres
- Railway
- Roads
  - 63
  - 881
- Township Range Grid
- Rivers
- Lakes

10  0  10  20  Kilometres

Well Name:                 WEPA 00-1-41
Location (DLS):        06-33-074-09W4M
Latitude:               55.4513766ºN
Longitude:            111.3298244ºW
Datum:                 NAD 83
Surveyed Ground Level:  667.01 m

Lithology        WEPA 00-1-41

(masl)

Oxidized till

Till

Till & Sand

Till

Silt & clay

Till

Sand

Sand

Gravel

Till

Sand

Top of casing elevation: 667.77 m

Drillhole diameter: 14 cm
Bentonite grout: 0 - 35.5 m
5.08 cm diameter Sch 80 PVC pipe

Compressed bentonite pellets:
35.5 - 36.0 m
Sandpack: 36.0 - 41.0 m
PVC 5.08 cm, 3 row, 0.0508 cm
slot size screen: 37.9 - 41.0 m
5.08 cm PVC washdown valve on
screen bottom

Depth (m)

**Figure 3. Piezometer construction details WEPA 00-1-4**1.

Well Name: WEPA 00-1-76
Location (DLS): 06-33-074-09W4M
Latitude: 55.4513830°N
Longitude: 111.3299586°W
Datum: NAD 83
Surveyed Ground Level: 666.99 m

Lithology          WEPA 00-1-76

(masl)

Oxidized till

Till

Till & Sand

Till

Silt & clay

Till

Sand

Sand

Gravel

Till

Sand

Depth (m)

Top of casing elevation: 667.76 m

Drillhole diameter: 14 cm

Bentonite grout: 0 - 71.2 m

5.08 cm diameter Sch 80 PVC pipe

Compressed bentonite pellets:
71.2 - 71.8 m

Sandpack: 71.8 - 79.2 m

PVC 5.08 cm, 3 row, 0.0508 cm
slot size screen: 72.4 - 75.3 m

5.08 cm PVC washdown valve on
screen bottom

**Figure 4. Piezometer construction details WEPA 00-1-76.**
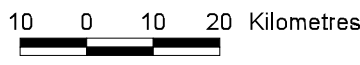
Well Name:                  WEPA 00-1-120
Location (DLS):             06-33-074-09W4M
Latitude:                   55.4513762°N
Longitude:                  111.3298897°W
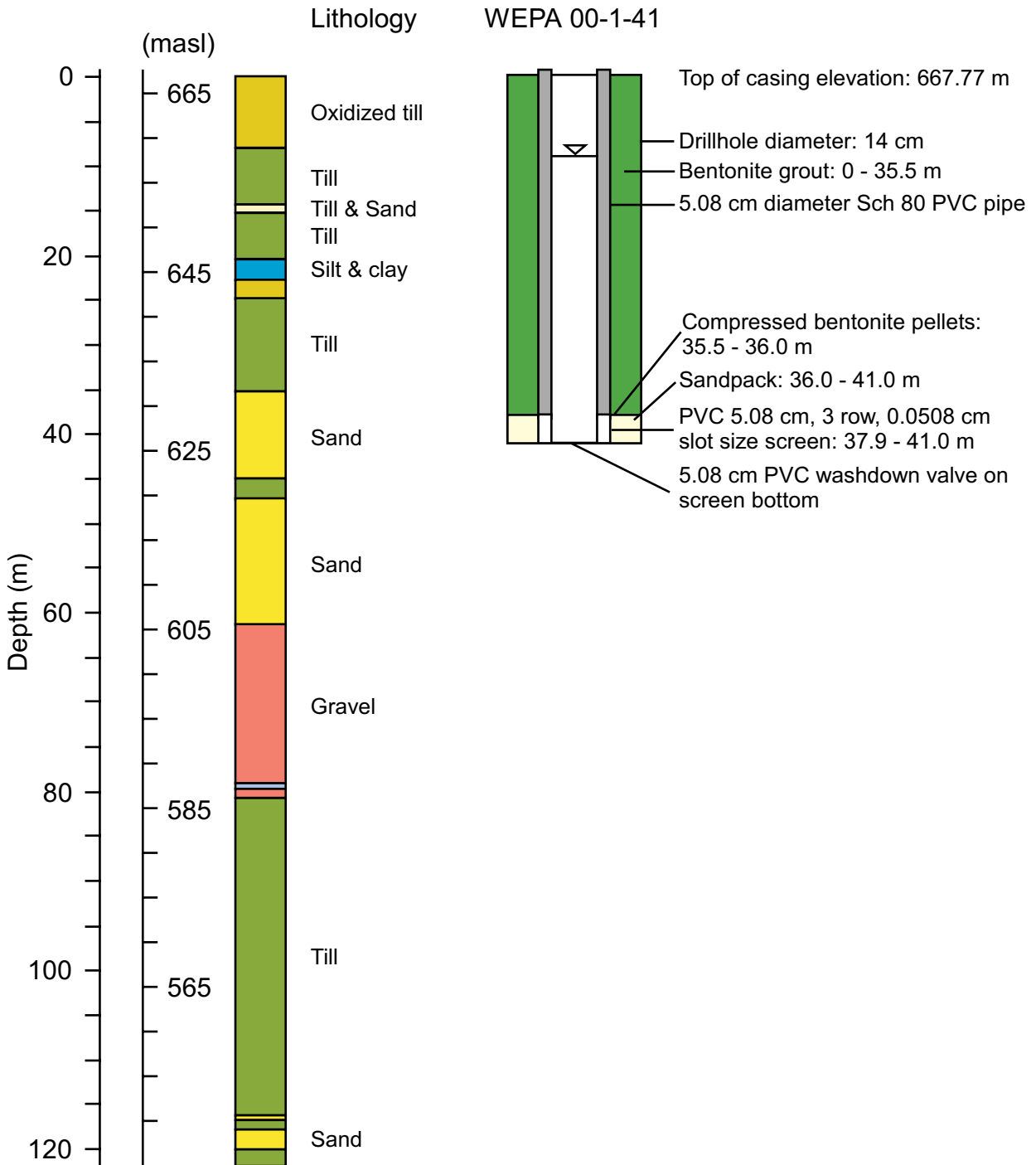Datum:                      NAD 83
Surveyed Ground Level:      666.92 m



**Figure 5. Piezometer construction details WEPA 00-1-120.**

Well Name: WEPA 00-3-158
Location (DLS): 16-04-075-05W4M
Latitude: 55.4729752°N
Longitude: 110.7073340°W
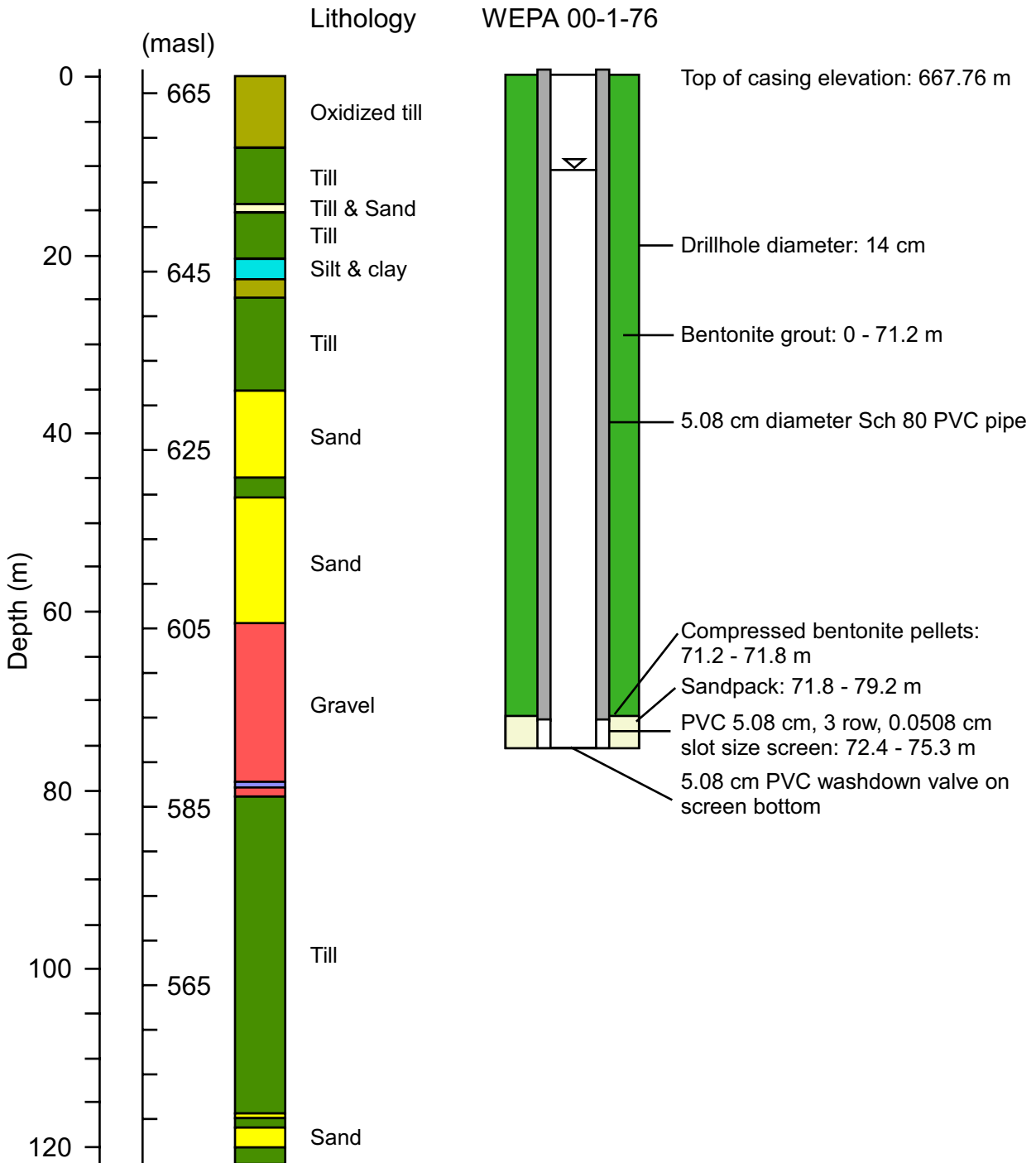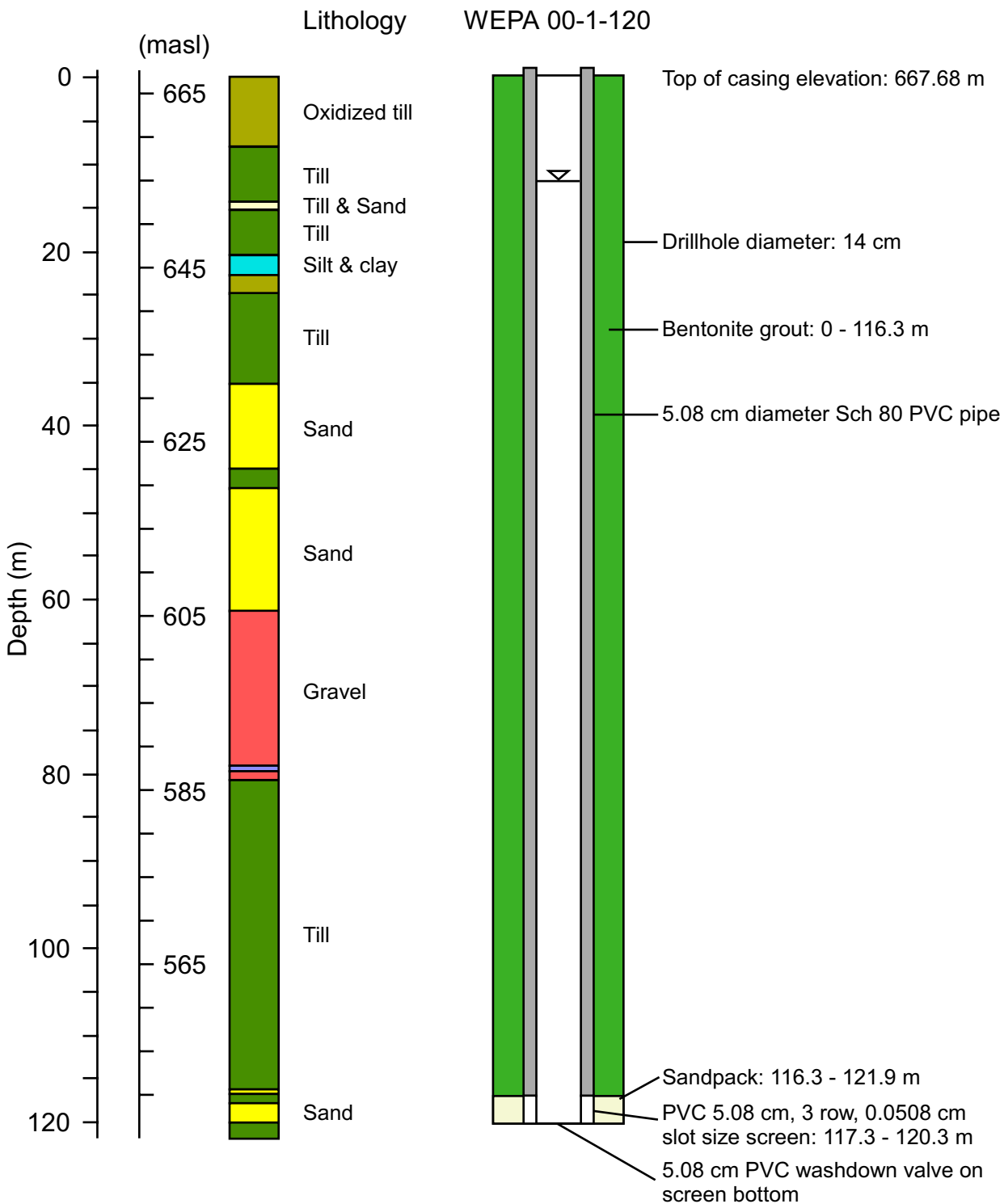Datum: NAD83
Surveyed Ground Level: 648.20 m
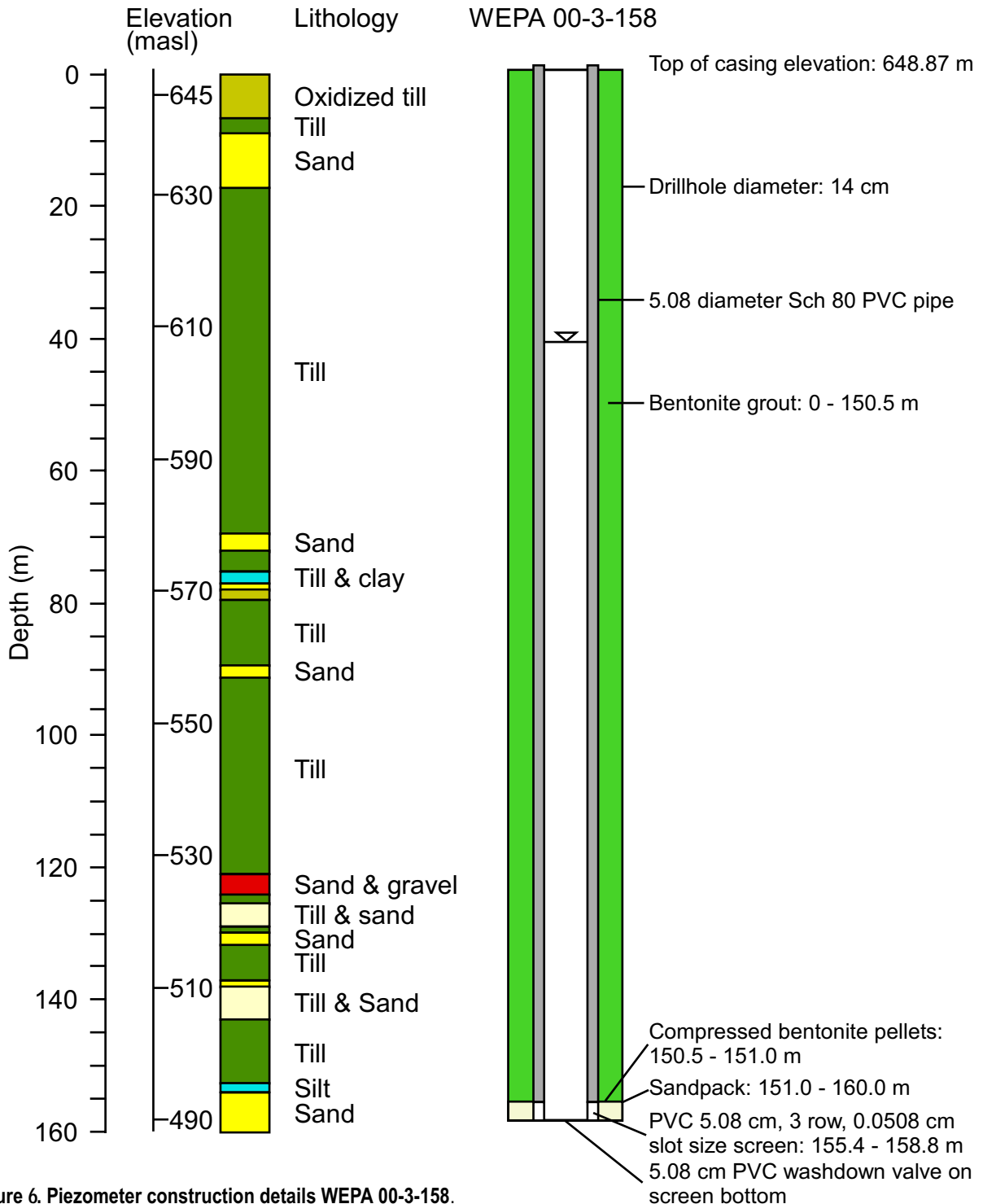


**Figure 6. Piezometer construction details WEPA 00-3-158.**

Well Name: WR99-1-230
Location (DLS): 07-36-77-15W4
Latitude: 55.7143794°N
Longitude: 112.1879148°W
Datum: NAD83
Surveyed Ground Level: 663.07 m

WR 99-1-230

Top of casing elevation: 663.75 m

Drillhole diameter: 14 cm

5.08 cm diameter Sch 80 PVC pipe

Bentonite grout: 0 - 222.4 m

Sandpack: 222.4 - 230.8 m
PVC 5.08 cm, 3 row, 0.0508 cm
slot size screen: 227.5 - 230.6 m
5.08 cm PVC washdown valve on
screen bottom

Lithology column (Elevation masl / Depth m):
- Fill, peat & silt
- Sand
- Till
- Sand
- Silt & clay
- Till
- Sand
- Till
- Sand
- Sand
- Sand
- Till
- Clay
- Sand & gravel
- Silt & clay
- Silt
- Sand
- Sand
- Clay
- Sand & gravel
- Sand & clay
- Sand, silt & clay
- Sand
- Gravel
- Sand
- Sand & gravel

**Figure 7. Piezometer construction details WR99-1-230.**

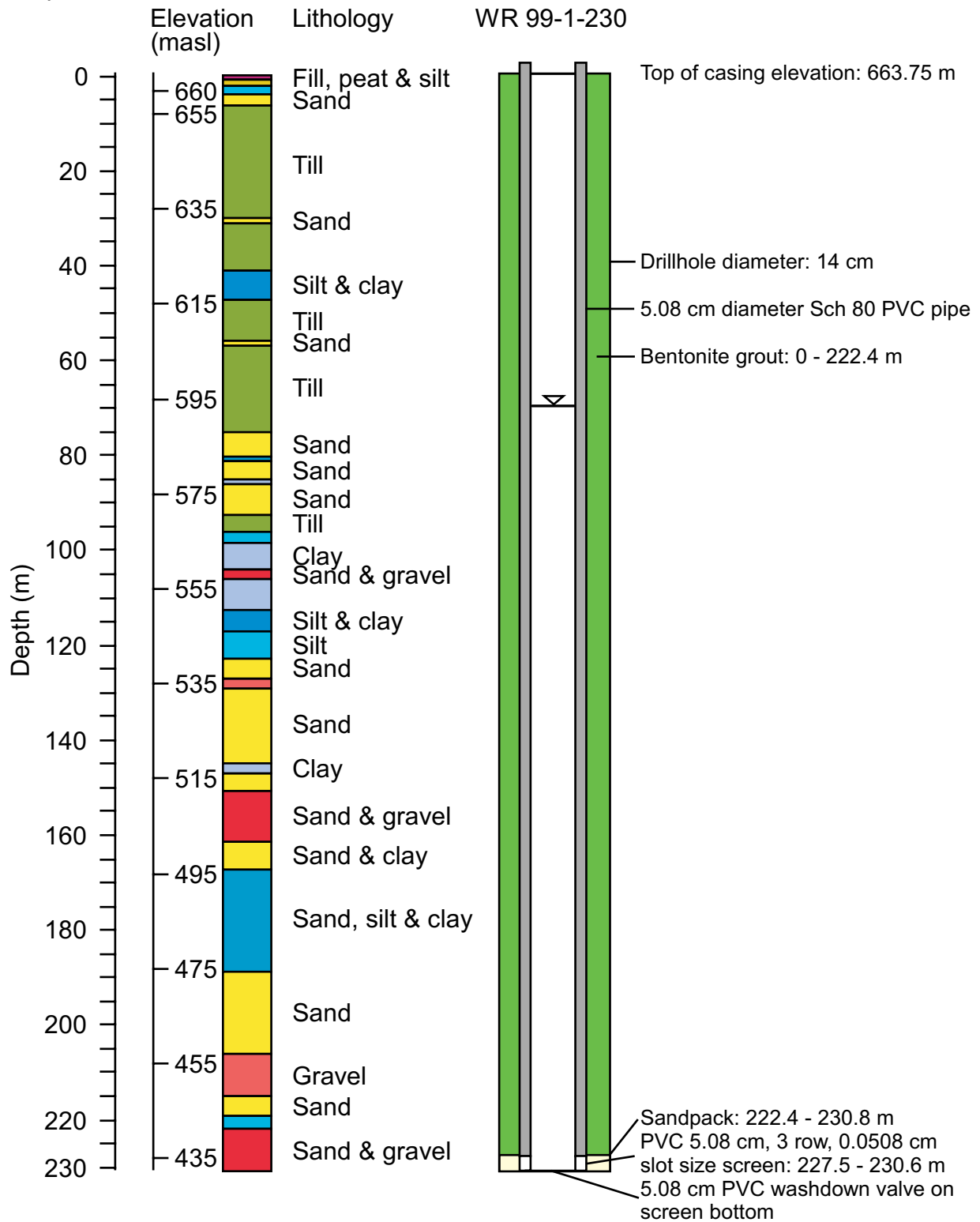Klassen (1989) indicates this area of the southern Canadian Interior Plains was ice-free before approximately 11 000 years ago. The calculated dates of the water samples indicate that the water present in these intervals was recharged since the last glaciation.

## 4.2 Site WEPA 00-3

A groundwater sample was collected from the deepest of three piezometers at this site. The calculated age was 30 880 ± 257 radiocarbon years at 158 m depth. It should be noted that the age for the water sample is very close to the limit of applicability for the $^{14}$C method of age dating water (Clark and Fritz, 1997, p. 201).

According to Klassen (1989), interstadial sediment radiocarbon dates for the southern Canadian Interior Plains are between 22 000 to 43 000 radiocarbon years, setting the minimum and maximum ages for onset of Late Wisconsin glaciation. Most of the southern Canadian Interior Plains apparently were ice-free at this time (Klassen, 1989). Dyke et al. (2002), indicate that Laurentide glacial advance, through central and southern Alberta, started close to the edge of the Canadian Shield, perhaps as late as 22 000 to 23 000 radiocarbon years ago, reaching its maximum limit by 20 000 radiocarbon years ago. Barring any dilution by a source of carbon other than carbonate dissolution, the water sample age indicates the water collected from this piezometer interval was recharged during the onset of the last glaciation or during an interstadial event.

## 4.3 Site WR 99-1

Two piezometers were installed at this site. The first was installed as a water-table piezometer. The second (Figure 7) was installed within a Quaternary–Tertiary buried channel aquifer. Only the second piezometer, completed at a depth of 230 m in a Tertiary–Quaternary buried channel aquifer (Lemay and Jean, 2002) was sampled for the purpose of determining a radiocarbon age. The calculated date is 11 186 ± 79 radiocarbon years.

A supra-till radiocarbon age of 11 300 ± 110 radiocarbon years for a lake bottom mud sample from Mariana Lake, in the Athabasca Oil Sands (in situ) Area of Alberta (Jackson and Pawson, 1984), indicates this area was ice free at this time. The work of Klassen (1989) shows that this area of Alberta was almost entirely covered by ice approximately 12 000 years ago, but by approximately 11 000 years ago, the area was ice free. This indicates the water sampled from this aquifer was recharged near the end of the last glaciation.

# 5 Conclusions

Radiocarbon dates indicate that water in the various aquifers was recharged during different time periods. The ages can be related to periods of glaciation and deglaciation.

The youngest ages were determined for the intertill/intratill aquifers present at site WEPA 00-1. The ages varied between 1558 radiocarbon years to 2532 radiocarbon years and increased with depth. Ice is believed to have retreated from the Athabasca Oil Sands (in situ) Area approximately 11 000 years ago. This implies that recharge of these aquifers occurred since the last glaciation. The age gradient between the shallowest and intermediate piezometers was 24.5 radiocarbon years/m, whereas the age gradient between the intermediate and deepest piezometers was 2.9 radiocarbon years/m.

An age of 11 186 ± 79 radiocarbon years was calculated for the sample collected from the deepest piezometer at site WR 99-1. Ice is believed to have retreated from the Athabasca Oil Sands (in situ) Area approximately 11 000 years ago. This age suggests this aquifer was recharged near the end of the last glaciation. The age is consistent with a radiocarbon date showing this area of Alberta was ice-free at the

time. The groundwater age is also consistent with paleogeographic maps showing Late Wisconsin ice retreat.

The water sample collected from the deepest piezometer at site WEPA 00-3 had a radiocarbon date of 30 880 ± 257 radiocarbon years. The southern Canadian Interior Plains are believed to have been ice-free at the time, indicating that groundwater recharge of this aquifer occurred during the onset of the last glaciation or during an interstadial event.

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