Sensitivity Analysis

2024-05-30

This report is to document the sensitivity of the TUV model, and the subsequent calculation of water quality guidelines for PAHs, to variation in certain TUV parameters.

Input parameters

The input parameters for the calculation of light attenuation through water for the TUV model are:

- Vertical Attenuation Coefficient at wavelength `wvl`: $kvat = k_d e^{-Sk(ref\_wvl - wvl)}$
  - **`Kd`** Light attenuation coefficient (set directly or calculated from DOC)
  - **`Sk`** (default `0.018`)
  - **`ref_wvl`** Reference wavelength for `Kd` (default `305`)
- **`depth_m`** Water depth in m
- **`lat`** Latitude in decimal degrees
- **`lon`** Longitude in decimal degrees
- **`elev_m`** Surface elevation, m above sea level
- **`year`** Year
- **`month`** Month
- **`day`** Day
- **`tzone`** Timezone Local Time - UTC (default `0`; UTC)
- **`tstart`** Start time, hours local time (default `0`)
- **`tstop`** Stop time, hours local time (default `23`)
- **`tsteps`** Number of time steps (default `24`)
- **`albedo`** Surface albedo (default `0.07`)
- **`o3_tc`** Ozone column, Dobson Units (DU) - Looked up in climatology (recommended default `300`)
- **`so2_tc`** SO2 column, DU (default `0`)
- **`no2_tc`** NO2 column, DU (default `0`)
- **`taucld`** Cloud optical depth (default `0`)
- **`zbase`** Cloud base, km (default `4`)
- **`ztop`** Cloud top, km (default `5`)
- **`tauaer`** Aerosol optical depth at 550 nm - Looked up in climatology (recommended default `0.235`)
- **`ssaaer`** Aerosol single scattering albedo (default `0.990`)
- **`alpha`** Aerosol Angstrom exponent(default `1.0`)
- **`wvl_start`** Starting wavelength, nm (default `279.5`)
- **`wvl_end`** End wavelength, nm (default `420.5`)

- **`wvl_steps`** Number of wavelength intervals (default `141`)
- **`nstr`** TUV run type; use –2 for fast, 4 for slightly more accurate (default `-2`)

Those currently under consideration for sensitivity analysis are:

- **`Kd`** Light attenuation coefficient - includes use of **`DOC`** for calculating `Kd`
- **`albedo`** Surface albedo (default `0.07`)
- **`o3_tc`** Ozone column, Dobson Units (DU) - Looked up in climatology (recommended default `300`)
- **`tauaer`** Aerosol optical depth at 550 nm - Looked up in climatology (recommended default `0.235`)
- **`ssaaer`** Aerosol single scattering albedo (default `0.990`)
- **`lat`** Latitude in decimal degrees
- **`elev_m`** Surface elevation, m above sea level
- **`depth_m`** Water depth in m
- **`nstr`** TUV run type; use –2 for fast, 4 for slightly more accurate (default `-2`)

The analyses are conducted at three different sample lakes (Southern Interior, Vancouver Island, Northeast), using two PAHs (Anthracene and Benzo[a]pyrene).

For each analysis, we will test a range of reasonable values for the parameter of interest, and plot the PLC50 value calculated across that range. To look at the relative effect of that parameter on the photoxicity of the PAH, we also plot the ratio of PLC50:NLC50.

Initially, sensitivity analyses will be univariate (varying the input of interest while holding the others constant). If there are significant interactions expected between certain variables, these can be explored.

Basic usage of the `pahwq` package

To start, we will demonstrate a typical straightforward use case at a single site.

To calculate the acute phototoxic water quality guideline (PLC50) for Anthracene at 0.25 m depth in Okanagan Lake on June 21, 2023, with a measured DOC of 5 g/m^3, you would use the following code:

First, set up the options for the model run:

```
library(pahwq)

set_tuv_aq_params(
  depth_m = 0.25,
  lat = 49.601632,
  lon = -119.605862,
  elev_m = 342,
  DOC = 5,
  date = "2023-06-21",
  tzone = -8,
```

```
  albedo = 0.05
)
```

After setting them, you can view the options that will be used by TUV. Some are set via the function inputs, some are looked up (e.g., `o3_tc`, `tauaer`) or calculated (e.g., `kd(305)` is calculated from the input `DOC`).

```
view_tuv_aq_params()
#> a,b,c for: kvdom = a exp(-b(wvl-c)). a = kd(305), b = Sk, c = wavelength, wvl
= 305: 20.11 0.018 305
#> ydepth, m: 0.25
#> lat, negative S of Equator: 49.601632
#> lon, negative W of Greenwich (zero) meridian: -119.605862
#> surface elevation, km above sea level: 0.342
#> timezone: Local Time - UTC: -8
#> iyear: 2023
#> imonth: 6
#> iday: 21
#> tstart, hours local time: 0
#> tstop, hours local time: 23
#> number of time steps: 24
#> surface albedo: 0.05
#> o3_tc  ozone column, Dobson Units (DU): 359.937
#> so2_tc SO2 column, DU: 0
#> no2_tc NO2 column, DU: 0
#> taucld - cloud optical depth: 0
#> zbase - cloud base, km: 4
#> ztop - cloud top, km: 5
#> tauaer - aerosol optical depth at 550 nm: 0.0641989811085006
#> ssaaer - aerosol single scattering albedo: 0.99
#> alpha - aerosol Angstrom exponent: 1
#> starting wavelength, nm: 279.5
#> end wavelength, nm: 700.5
#> number of wavelength intervals: 421
#> nstr, use -2 for fast, 4 for slightly more accurate: -2
#> out_irrad_y, T/F, planar spectral irradiance at ydepth: T
#> out_aflux_y, T/F, scalar spectral irradiance (actinic flux)  at depth: F
#> out_irrad_ave, T/F, planar irrad., averaged 0-ydepth: F
#> out_aflux_ave, T/F, scalar, ave 0-ydepth: F
#> out_irrad_atm, T/F, planar, in atmosphere: F
#> out_aflux_atm, T/F, scalar, in atmosphere: F
```

Run the TUV model and get the results. The results show the underwater irradiance at the specified depth, at each wavelength and time step.

```
run_tuv()
```

```
# Get the results
tuv_res <- get_tuv_results(file = "out_irrad_y")
head(tuv_res)
#>    wl wavelength_start wavelength_end Kd_lambda t_00.00.00 t_01.00.00
#> 1 280            279.5          280.5      31.5          0          0
#> 2 281            280.5          281.5      31.0          0          0
#> 3 282            281.5          282.5      30.4          0          0
#> 4 283            282.5          283.5      29.9          0          0
#> 5 284            283.5          284.5      29.3          0          0
#> 6 285            284.5          285.5      28.8          0          0
#>  t_02.00.00 t_03.00.00 t_04.00.00 t_05.00.00 t_06.00.00 t_07.00.00 t_08.00.00
#> 1          0          0   3.16e-38   1.00e-37   1.90e-37   4.44e-37   7.97e-34
#> 2          0          0   3.21e-35   1.02e-34   1.94e-34   4.63e-34   6.16e-31
#> 3          0          0   3.74e-32   1.18e-31   2.27e-31   5.57e-31   5.39e-28
#> 4          0          0   1.84e-30   5.80e-30   1.12e-29   2.79e-29   2.25e-26
#> 5          0          0   2.19e-28   6.92e-28   1.35e-27   3.47e-27   2.16e-24
#> 6          0          0   1.75e-26   5.52e-26   1.09e-25   2.90e-25   1.36e-22
#>  t_09.00.00 t_10.00.00 t_11.00.00 t_12.00.00 t_13.00.00 t_14.00.00 t_15.00.00
#> 1   3.54e-29   2.17e-26   6.84e-25   2.05e-24   6.97e-25   2.26e-26   3.79e-29
#> 2   1.04e-26   3.65e-24   8.57e-23   2.34e-22   8.72e-23   3.79e-24   1.11e-26
#> 3   3.42e-24   6.74e-22   1.17e-20   2.90e-20   1.19e-20   6.97e-22   3.62e-24
#> 4   8.16e-23   1.16e-20   1.69e-19   3.97e-19   1.72e-19   1.20e-20   8.61e-23
#> 5   3.71e-21   3.41e-19   3.95e-18   8.62e-18   4.00e-18   3.51e-19   3.90e-21
#> 6   1.08e-19   6.33e-18   5.78e-17   1.17e-16   5.85e-17   6.49e-18   1.13e-19
#>  t_16.00.00 t_17.00.00 t_18.00.00 t_19.00.00 t_20.00.00 t_21.00.00 t_22.00.00
#> 1   8.93e-34   4.49e-37   1.91e-37   1.01e-37   3.22e-38          0          0
#> 2   6.83e-31   4.68e-34   1.95e-34   1.02e-34   3.27e-35          0          0
#> 3   5.92e-28   5.63e-31   2.28e-31   1.19e-31   3.81e-32          0          0
#> 4   2.46e-26   2.83e-29   1.13e-29   5.83e-30   1.87e-30          0          0
#> 5   2.34e-24   3.51e-27   1.36e-27   6.97e-28   2.23e-28          0          0
#> 6   1.46e-22   2.94e-25   1.09e-25   5.55e-26   1.78e-26          0          0
#>   t_23.00.00
#> 1          0
#> 2          0
#> 3          0
#> 4          0
#> 5          0
#> 6          0
```

We can inspect and verify the inputs that were used in the model run:

```
tuv_run_params(tuv_res)
#> a,b,c for: kvdom = a exp(-b(wvl-c)). a = kd(305), b = Sk, c = wavelength, wvl
= 305
#>                                                                          "20.11
0.018 305"
```

```
#>                                                                    ydepth,
m
#>                                                                     "0.25"
#>                                                          lat, negative S of
Equator
#>                                                               "49.601632"
#>                                          lon, negative W of Greenwich (zero)
meridian
#>                                                             "-119.605862"
#>                                              surface elevation, km above sea
level
#>                                                                   "0.342"
#>                                                    timezone: Local Time
- UTC
#>                                                                      "-8"
#>                                                                    iyear
#>                                                                   "2023"
#>                                                                   imonth
#>                                                                      "6"
#>                                                                     iday
#>                                                                     "21"
#>                                                          tstart, hours
local time
#>                                                                      "0"
#>                                                           tstop, hours
local time
#>                                                                     "23"
#>                                                        number of time
steps
#>                                                                     "24"
#>                                                                  surface
albedo
#>                                                                   "0.05"
#>                                             o3_tc  ozone column, Dobson
Units (DU)
#>                                                                "359.937"
#>                                                               so2_tc SO2
column, DU
#>                                                                      "0"
#>                                                               no2_tc NO2
column, DU
#>                                                                      "0"
#>                                                 taucld - cloud optical
depth
#>                                                                      "0"
#>                                                          zbase - cloud
base, km
#>                                                                      "4"
```

```
#>                                                                    ztop - cloud
top, km
#>                                                                          "5"
#>                                                tauaer - aerosol optical depth at
550 nm
#>                                                             "0.0641989811085006"
#>                                               ssaaer - aerosol single scattering
albedo
#>                                                                       "0.99"
#>                                                        alpha - aerosol Angstrom
exponent
#>                                                                          "1"
#>                                                            starting wavelength,
nm
#>                                                                      "279.5"
#>                                                                end wavelength,
nm
#>                                                                      "700.5"
#>                                                            number of wavelength
intervals
#>                                                                        "421"
#>                                    nstr, use -2 for fast, 4 for slightly more
accurate
#>                                                                         "-2"
#>                                out_irrad_y, T/F, planar spectral irradiance at
ydepth
#>                                                                          "T"
#>              out_aflux_y, T/F, scalar spectral irradiance (actinic flux)  at
depth
#>                                                                          "F"
#>                                   out_irrad_ave, T/F, planar irrad., averaged
0-ydepth
#>                                                                          "F"
#>                                             out_aflux_ave, T/F, scalar, ave
0-ydepth
#>                                                                          "F"
#>                                              out_irrad_atm, T/F, planar, in
atmosphere
#>                                                                          "F"
#>                                              out_aflux_atm, T/F, scalar, in
atmosphere
#>                                                                           "F"
```

Next, calculate the site-specific light absorption (P_{abs}) for Anthracene from the TUV results. The `p_abs()` function uses a lookup table to get the molar absorption coefficient table for the specified PAH.

```
(Pabs <- p_abs(tuv_res, "Anthracene"))
#> [1] 448.6275
```

Finally, calculate PLC50 in ?g/L, supplying the P_{abs} value.

```
plc50(Pabs, pah = "Anthracene")
#> [1] 2.133157
```

We can compare the PLC50 to the NLC50 to see the effect of the photoxicity of the PAH:

```
nlc50("Anthracene")
#> [1] 58.40685
```

A shortcut:
If you don't need to inspect every step of the way, the above process can be completed in two function calls:

```
tuv_res <- tuv(
  depth_m = 0.25,
  lat = 49.601632,
  lon = -119.605862,
  elev_m = 342,
  DOC = 5,
  date = "2023-06-21",
  tzone = -8,
  albedo = 0.05
)

plc50(tuv_res, "Anthracene")
#> [1] 2.133157
```

Sensitivity Analysis: Setup

We'll start by loading the packages we need and getting some data from B.C. EMS:

Show/Hide Code

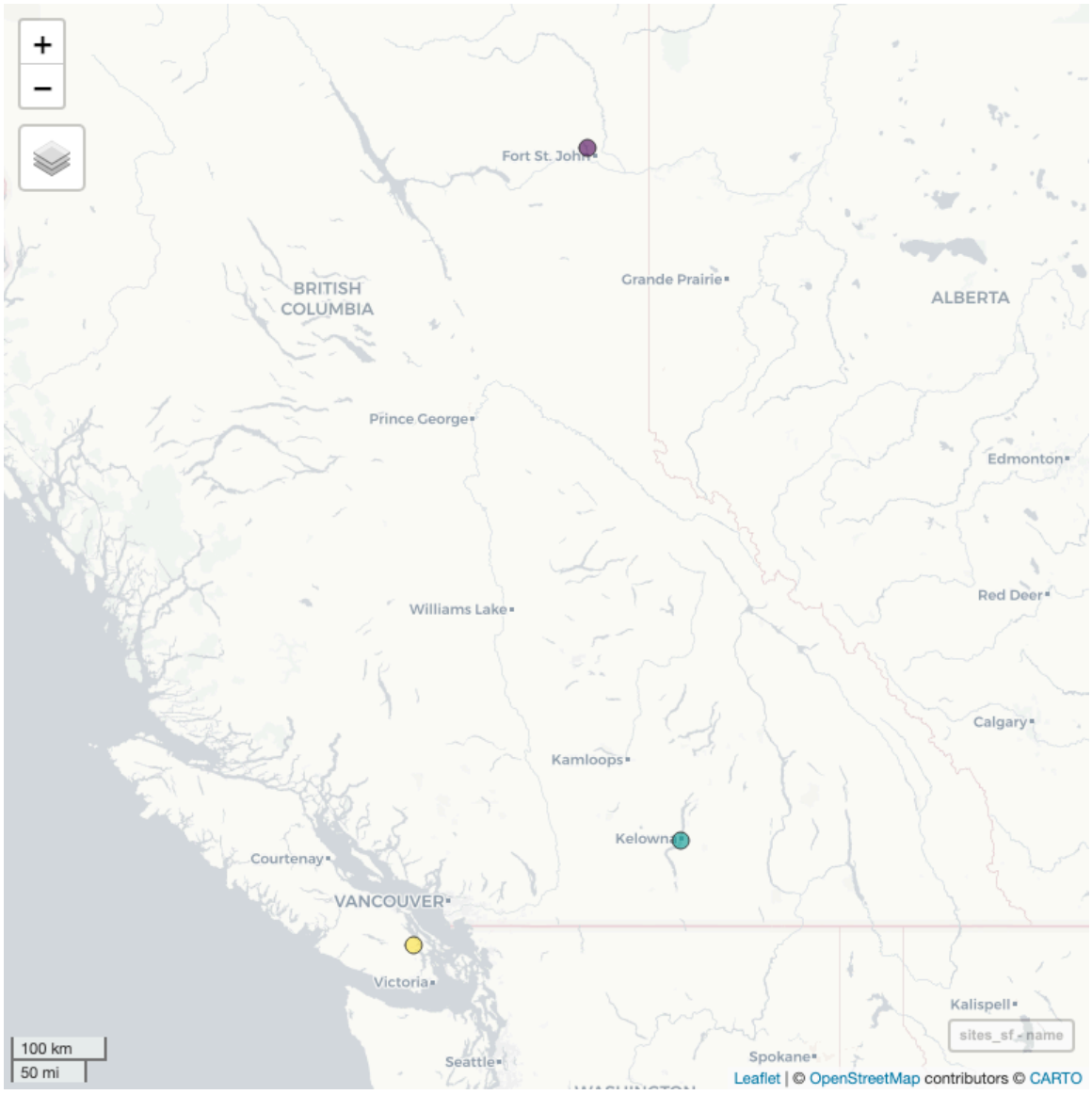
```
library(sf)
library(mapview)
library(rems)
library(dplyr)
library(ggplot2)
library(ggrepel)
library(latex2exp)

con <- connect_historic_db()
```

```
db <- attach_historic_data(con)
sites_sf <- db |>
  filter(
    EMS_ID %in% c("0500236", "E207466", "0400390"),
    # grepl("(CHARLIE L)|(OKANAGAN)|(QUAMICHAN)", MONITORING_LOCATION),
    COLLECTION_START > as.Date("2020-01-01"), PARAMETER_CODE == "1103"
  ) |>
  collect() |>
  st_as_sf(coords = c("LONGITUDE", "LATITUDE"), crs = 4326, remove = FALSE) |>
  filter(!is.na(RESULT)) |>
  arrange(desc(COLLECTION_START)) |>
  group_by(EMS_ID, MONITORING_LOCATION, LONGITUDE, LATITUDE) |>
  mutate(doc_min = min(RESULT), doc_max = max(RESULT)) |>
  slice(1) |>
  select(emsid = EMS_ID,
         name = MONITORING_LOCATION,
         lon = LONGITUDE,
         lat = LATITUDE,
         date = COLLECTION_START,
         DOC = RESULT,
         doc_min,
         doc_max) |>
  left_join(
    tribble(
      ~ emsid, ~elev_m,
      "E207466", 25,
      "0400390", 693,
      "0500236", 342
    ), by = join_by("emsid")
  ) |>
  ungroup() |>
  relocate(elev_m, .after = lat)

disconnect_historic_db(con)
```

Locations

Show/Hide Code

```
mapview(sites_sf, zcol = "name", legend = FALSE)
```



Okanagan Lake, Okanagan

- EMS ID: 0500236
- Region: Okanagan
- Latitude: 49.8614 N
- Longitude: 119.5134 W
- Site Depth: 70.1 m
- Maximum Lake Depth: 232 m
- Lake Elevation: 342 m
- Lake Surface Area: 350.08 sq km

Charlie Lake, Peace

- EMS ID: 0400390

- Region: Peace
- Latitude: 56.3125 N
- Longitude: 120.9642 W
- Site Depth: 13 m
- Maximum Lake Depth: 13 m
- Lake Elevation: 693 m
- Lake Surface Area: 17.56 sq km

Quamichan Lake, Vancouver Island

- EMS ID: E207466
- Region: Vancouver Island
- Latitude: 48.8003 N
- Longitude: 123.6625 W
- Site Depth: 7 m
- Maximum Lake Depth: 8 m
- Lake Elevation: 25 m
- Lake Surface Area: 2.88 sq km

Prepare the data for comparisons, including setting the date to be the same for all sites:

Show/Hide Code

```
sites <- sites_sf |>
  st_drop_geometry() |>
  mutate(date = "2023-08-01")
gt(sites)
```

emsid	name	lon	lat	elev_m	date	DOC	doc_min	doc_max
0400390	CHARLIE LAKE DEEP STATION 1.2 KM EAST OF PARK	−120.9642	56.3125	693	2023-08-01	14.00	0.96	15.40

emsid	name	lon	lat	elev_m	date	DOC	doc_min	doc_-max
0500236	OKANAGAN L D/S KELOWNA STP (DEEP)	−119.5134	49.8614	342	2023-08-01	4.26	4.06	5.17
E207466	QUAMICHAN LAKE; CENTRE	−123.6625	48.8003	25	2023-08-01	6.61	6.37	11.80

Basic analysis using defaults

To perform the sensitivity analysis, we need to define a function, `multi_plc50()` that allows us to do repeated runs of the TUV model and PLC50 calculation using a range of inputs at multiple sites:

Show/Hide Code

```
multi_plc50 <- function(df, site = "name", pah, varying, vals = NULL, ...)
{
          if     (!varying     %in%     union(names(tuv_aq_defaults()),
names(formals(set_tuv_aq_params)))) {
    stop(varying, " is not a valid argument for `set_tuv_aq_params()`")
  }

  if (!is.null(vals)) {
    var_df <- data.frame(vals)
    names(var_df) <- varying

    df <- df |>
      select(!any_of(varying)) |>
      dplyr::cross_join(var_df)
  }

  df |>
    rowwise() |>
    mutate(
      tuv_res = list(calc_tuv(
          date = date,
          lat = lat,
```

```
          lon = lon,
          elev_m = elev_m,
          varying = .data[[varying]],
          vary_var = varying,
          ...
        ))
    ) |>
    cross_join(data.frame(PAH = pah)) |>
    mutate(
      timing = attr(tuv_res, "timing"),
      Pabs = p_abs(tuv_res, PAH),
      plc50 = plc50(Pabs, pah = PAH),
      nlc50 = nlc50(PAH),
      plc_nlc_ratio = plc50 / nlc50
    ) |>
    ungroup()
}

calc_tuv <- function(date, lat, lon, elev_m, varying, vary_var, ...) {
  args <- c(
    varying,
    list(
      depth_m = 0.25,
      date = as.Date(date),
      lat = lat,
      lon = lon,
      elev_m = elev_m
    ),
    ...
  )
  names(args)[1] <- vary_var

  # allow overriding of one of the core args by one supplied in 'varying',
  # this will keep the first of duplicated argument names, which will
  # be the one in 'varying'
  args <- args[unique(names(args))]

  do.call("set_tuv_aq_params", args)

  t <- system.time(run_tuv(quiet = TRUE))
  res <- get_tuv_results(file = "out_irrad_y")
  attr(res, "timing") <- unname(t["elapsed"])
  res
}
```

We then use the `multi_plc50()` function to calculate P_{abs}, PLC50, and ratio of PLC50:NLC50 for Anthracene using recorded DOC values at the three sites. This also uses the utility of pahwq to look up ozone column and aerosol optical depth from climatologies based on latitude, longitude, and month.

Show/Hide Code

```r
diff_DOC <- multi_plc50(sites, pah = c("Anthracene", "Naphthalene"),
varying = "DOC")
```

emsid	name	lon	lat	elev_m	date	DOC	PAH	timing	Pabs	plc50	nlc50	plc_nlc_ratio
0400390	CHARLIE L DEEP STATION 1.2 KM EAST OF PARK	-120.9642	56.3125	693	2023-08-01	14.00	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0400390	CHARLIE L DEEP STATION 1.2 KM EAST OF PARK	-120.9642	56.3125	693	2023-08-01	14.00	Naphthalene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0500236	OKANAGAN L D/S KELOWNA STP (DEEP)	-119.5134	49.8614	342	2023-08-01	4.26	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0500236	OKANAGAN	-119.5134	49.8614	342	2023-08-01	4.26	Naphthalene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

emsid	name	lon	lat	elev_m	date	DOC	PAH	timing	Pabs	plc50	nlc50	plc_nlc_ratio
	L D/ S KELOWNA STP (DEEP)											
E207466	QUAMICHAN LAKE: CENTRE	-123.6625	48.8003	[illegible]	[illegible]-08-01	6.61	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
E207466	QUAMICHAN LAKE: CENTRE	-123.6625	48.8003	[illegible]	[illegible]-08-01	6.61	Naphthalene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

To compare the sites using the same input parameters other than location (lat, lon, elevation), we modify the data to set a constant [DOC] (DOC = 5), and calculate P_{abs}, PLC50, and ratio of PLC50:NLC50 for Anthracene using constant DOC = 5:

Show/Hide Code

```
same_DOC <- sites |>
  mutate(DOC = 5) |>
  multi_plc50(pah = "Anthracene", varying = "DOC")
```

emsid	name	lon	lat	elev_m	date	DOC	PAH	timing	Pabs	plc50	nlc50	plc_nlc_ratio
0400390	CHARLIE L DEEP STATION 1.2 KM EAST OF PARK	[illegible]	[illegible]	[illegible]	[illegible]-08-01	5	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

emsid	name	lon	lat	elev_m	date	DOC	PAH	timing	Pabs	plc50	nlc50	plc_nlc_ratio
[illegible]	OKANAGAN L D/S KELOWNA STP (DEEP)	[illegible]	49.8614	[illegible]	[illegible]	5	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	QUAMICHAN LAKE; CENTRE	[illegible]	[illegible]	[illegible]	[illegible]	5	Anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Light Attenuation Coefficicent (k_d)

The TUV model calculates the light attenuation coefficient $k_d(\lambda)$ for each wavelength, based on a reference $k_d\left(\lambda_{ref}\right)$, where λ_{ref} is the reference wavelength.

$k_d\left(\lambda_{ref}\right)$ at 305nm ($k_{d,305}$) can be estimated from Dissolved Organic Carbon concentration [DOC] using the equation:

$k_{d,305} = a_{305}[DOC]^{b_{305}} + 0.13$; a_{305} = 2.76 and b_{305} = 1.2 from D. P. Morris *et al.* [1]; Equation 4-1a in P. Jourabchi [2]

For the sensitivity analysis for k_d, it is more interpretable to supply a range of k_d values to the TUV model directly, even though in practice it is more likely to use [DOC] to estimate k_d.

We will test the sensitivity to k_d using sample values from Table 3 (P. Jourabchi [2]), from 0.08 to 275:

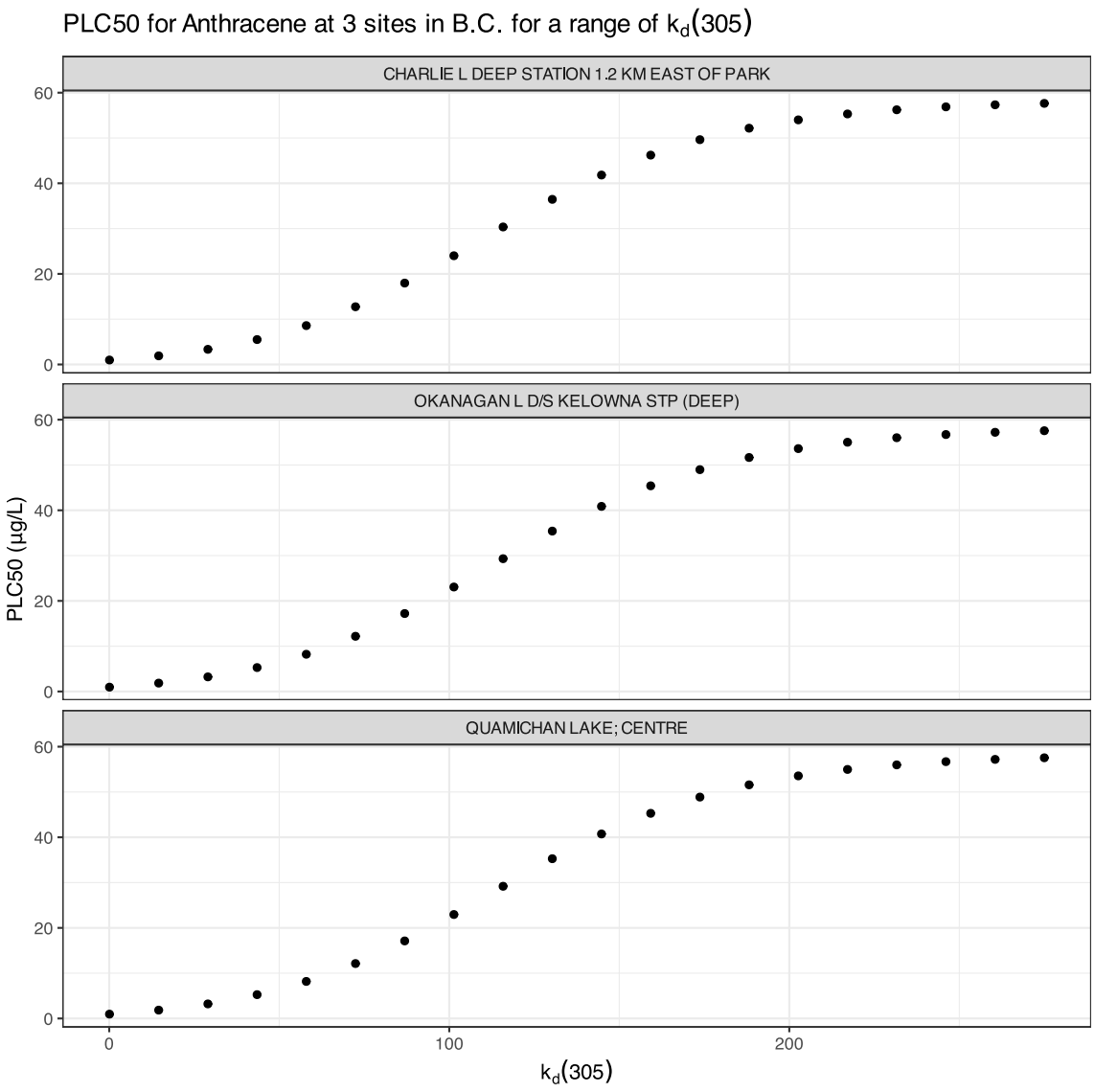
Show/Hide Code

```
kd_vals <- seq(0.08, 275, length.out = 20)
```

Effect of varying k_d on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

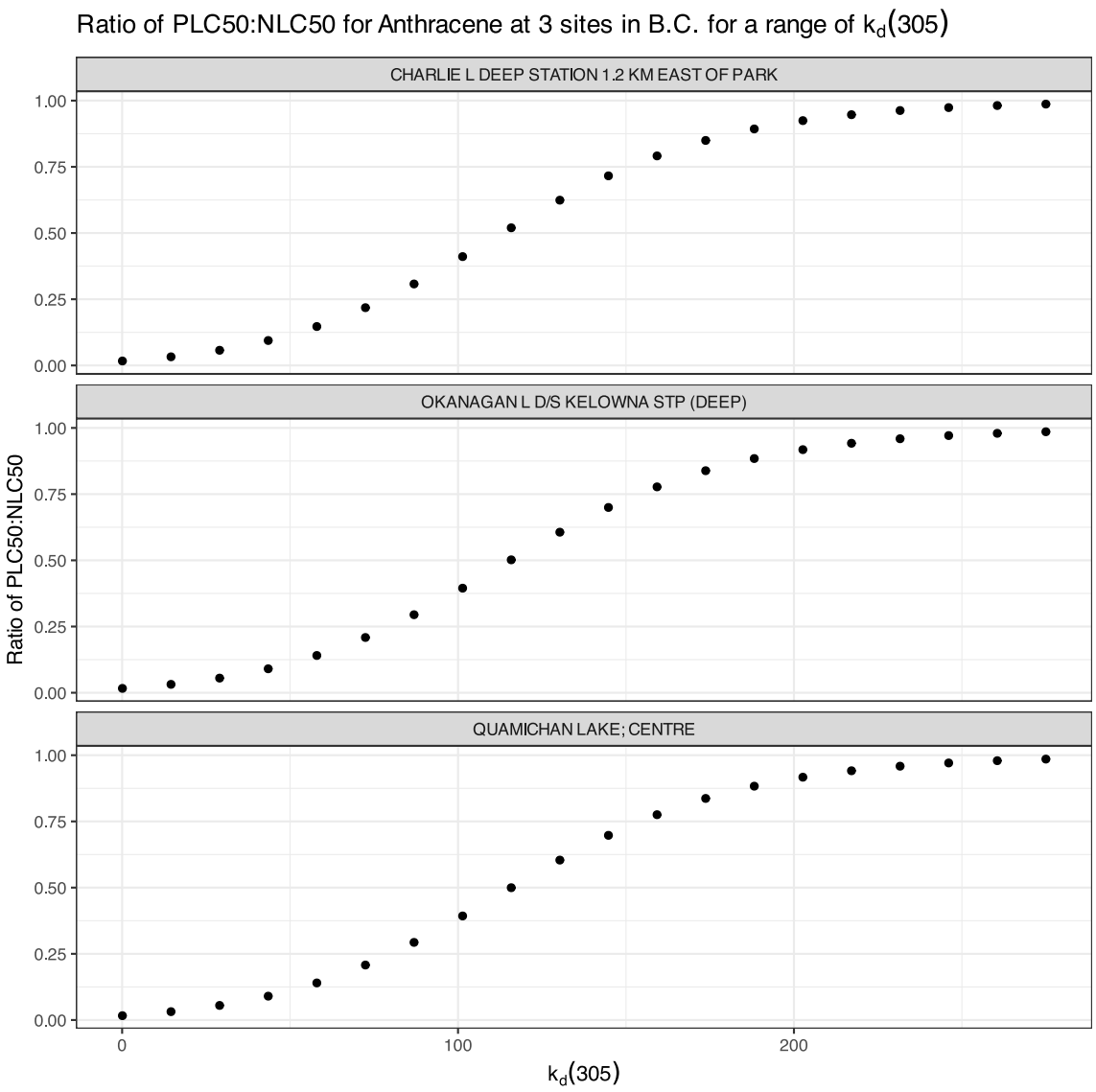
```r
kd_test_a <- multi_plc50(sites,
                         pah = "Anthracene",
                         varying = "Kd_ref",
                         vals = kd_vals,
                         Kd_wvl = 305,
                         o3_tc = 300,
                         tauaer = 0.235)

ggplot(kd_test_a, aes(x = Kd_ref, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = TeX(r"(PLC50 for Anthracene at 3 sites in B.C. for a range of
$k_d(305)$)"),
    x = TeX(r"($k_d(305)$)"),
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(kd_test_a, aes(x = Kd_ref, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = TeX(r"(Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C.
for a range of $k_d(305)$)"),
    x = TeX(r"($k_d(305)$)"),
```

```
    y = "Ratio of PLC50:NLC50"
  )
```



For Anthracene, the ratio of PLC50:NLC50 approaches 1 when $k_d(305)$ is ~ 250 — in other words at that level of k_d, PLC50 is nearly the same as NLC50, indicating that the light is attenuated to such an extent that the phototoxicity of Anthracene is not activated at the light levels when $k_d(305)$ >= 250.

According to the above equation for estimating k_d from [DOC]:

$$250 = 2.76[DOC]^{1.23} + 0.13$$

[DOC] ~= 40

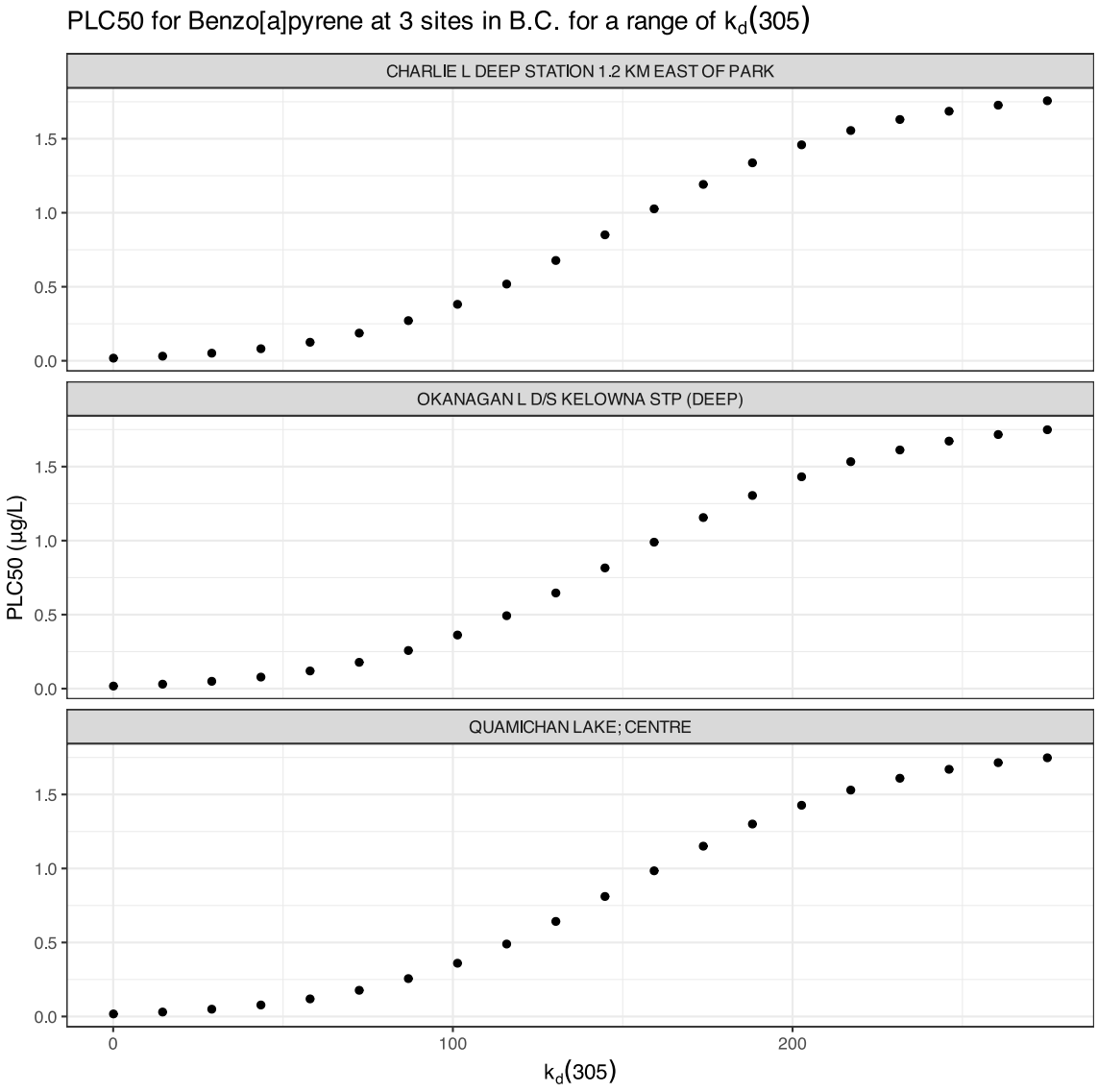
Therefore $k_d(305)$ of ~250 is representative of light attenuation when [DOC] is ~40. This is a significantly higher DOC concentration than observed in our three sample lakes, and is outside the range for which the above equation is recommended (it is recommended for [DOC] between 0.2 and 23 mg/L).

Effect of varying k_d on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

We will use the same input values as we did for Anthracene:

Show/Hide Code

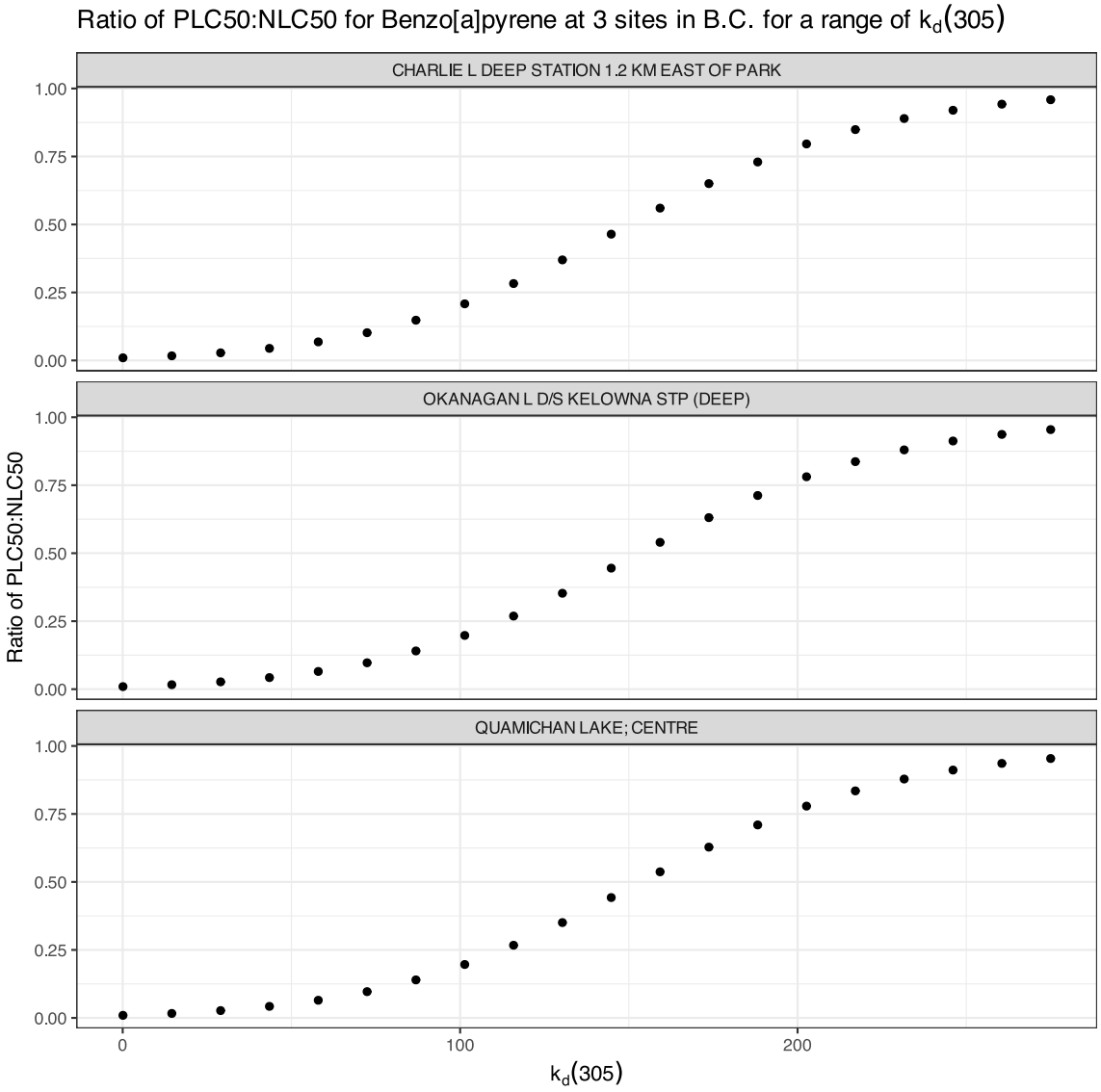
```
kd_test_b <- multi_plc50(sites,
                         pah = "Benzo[a]pyrene",
                         varying = "Kd_ref",
                         vals = kd_vals,
                         Kd_wvl = 305,
                         o3_tc = 300,
                         tauaer = 0.235)

ggplot(kd_test_b, aes(x = Kd_ref, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
     title = TeX(r"(PLC50 for Benzo\[a\]pyrene at 3 sites in B.C. for a
range of $k_d(305)$)"),
    x = TeX(r"($k_d(305)$)"),
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(kd_test_b, aes(x = Kd_ref, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = TeX(r"(Ratio of PLC50:NLC50 for Benzo\[a\]pyrene at 3 sites
in B.C. for a range of $k_d(305)$)"),
    x = TeX(r"($k_d(305)$)"),
```

```
    y = "Ratio of PLC50:NLC50"
  )
```



Surface Albedo (`albedo`)

We test surface albedo values from 0.05 to 0.1 (typical for water), and include the suggested default of 0.7:

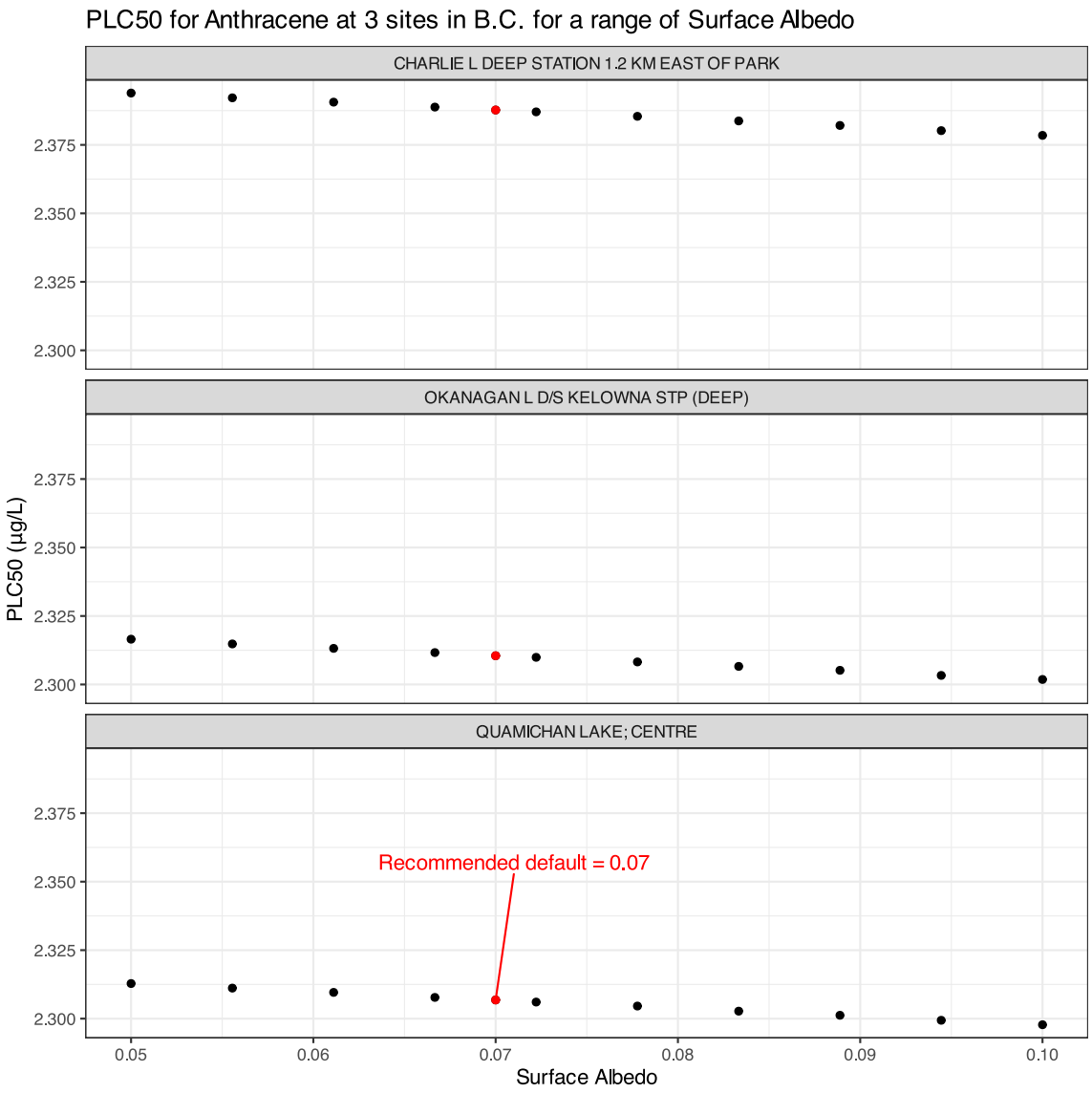
```
albedo_vals <- c(seq(0.05, 0.1, length.out = 10), 0.07)
```

For this and the remaining analyses, we will set DOC = 5 for all sites to ensure a constant k_d value. We can then test the range of surface albedo values at all three sites for Anthracene and Benzo[a]pyrene.

Effect of varying Surface Albedo on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

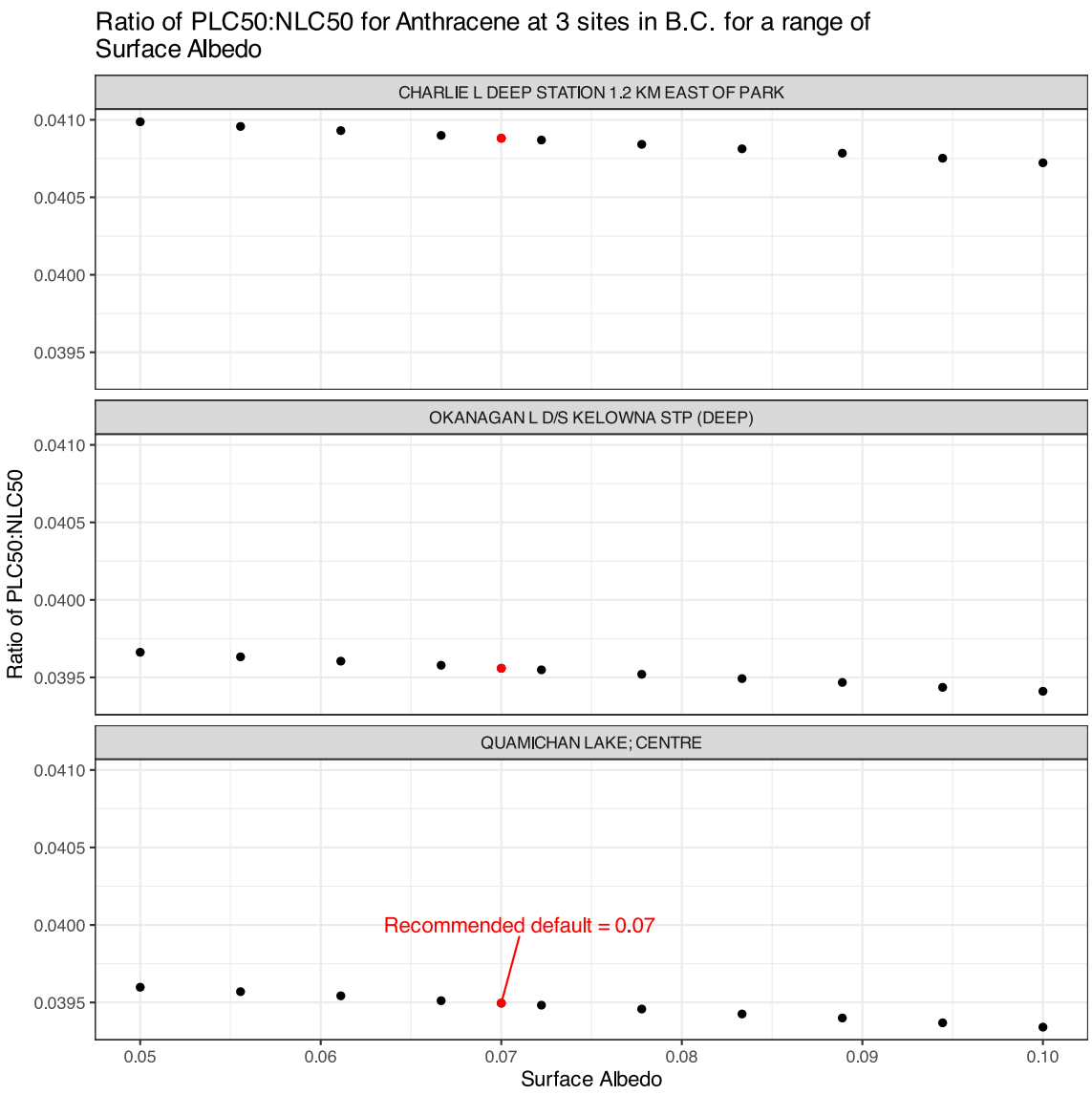
```
albedo_test_a <- multi_plc50(sites,
                             pah = "Anthracene",
                             varying = "albedo",
                             vals = albedo_vals,
                             DOC = 5,
                             o3_tc = 300,
                             tauaer = 0.235)

ggplot(albedo_test_a, aes(x = albedo, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(albedo_test_a, albedo == 0.07),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(albedo_test_a, albedo == 0.07, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.07",
    nudge_x = 0.001,
    nudge_y = 0.05
  ) +
  labs(
   title = "PLC50 for Anthracene at 3 sites in B.C. for a range of Surface
Albedo",
    x = "Surface Albedo",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(albedo_test_a, aes(x = albedo, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(albedo_test_a, albedo == 0.07),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(albedo_test_a, albedo == 0.07, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.07",
    nudge_x = 0.001,
    nudge_y = 0.0005
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nSurface Albedo",
    x = "Surface Albedo",
    y = "Ratio of PLC50:NLC50"
  )
```

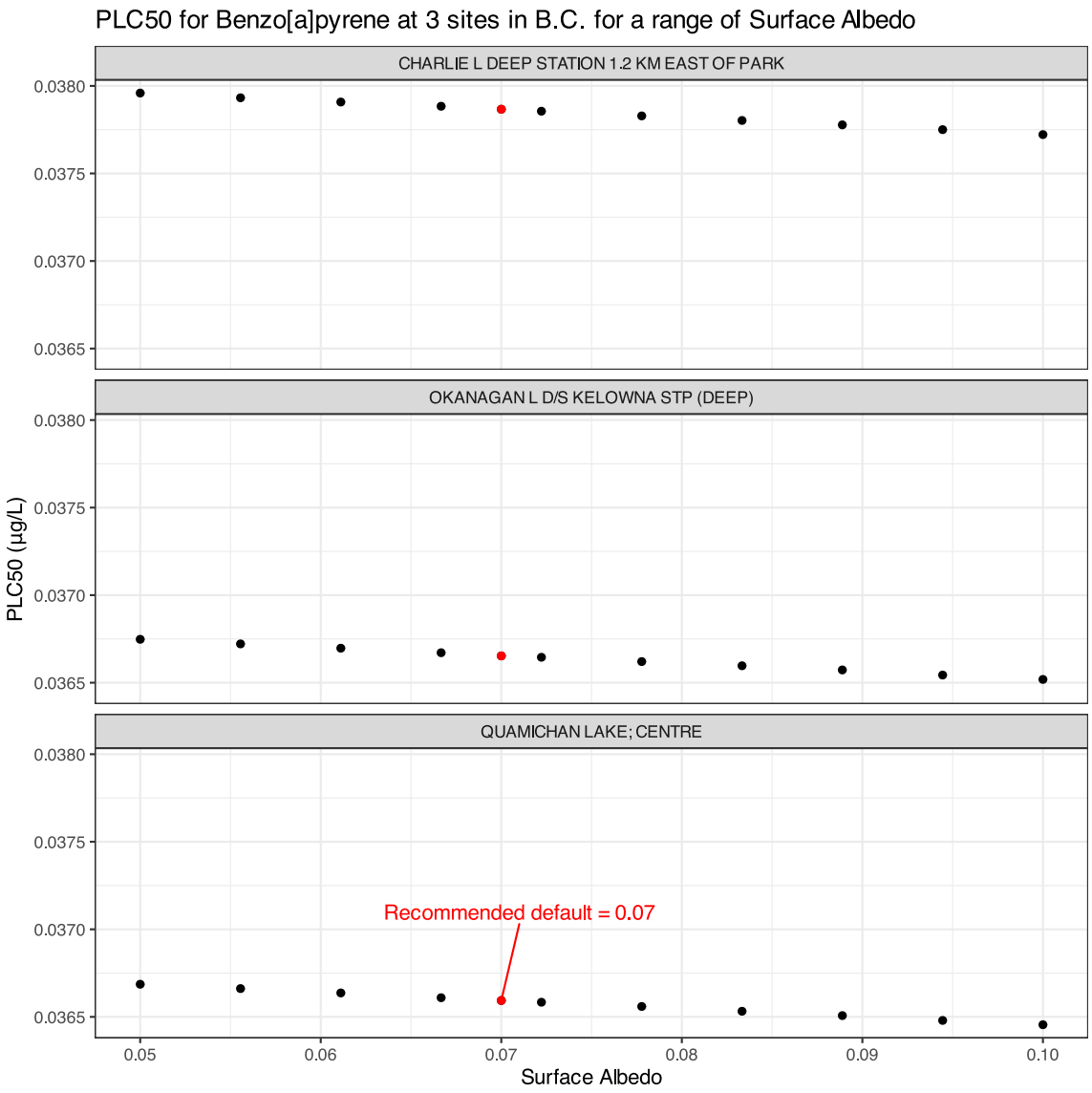


Effect of varying Surface Albedo on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
albedo_test_b <- multi_plc50(sites,
                             pah = "Benzo[a]pyrene",
                             varying = "albedo",
                             vals = albedo_vals,
                             DOC = 5,
                             o3_tc = 300,
                             tauaer = 0.235)
```

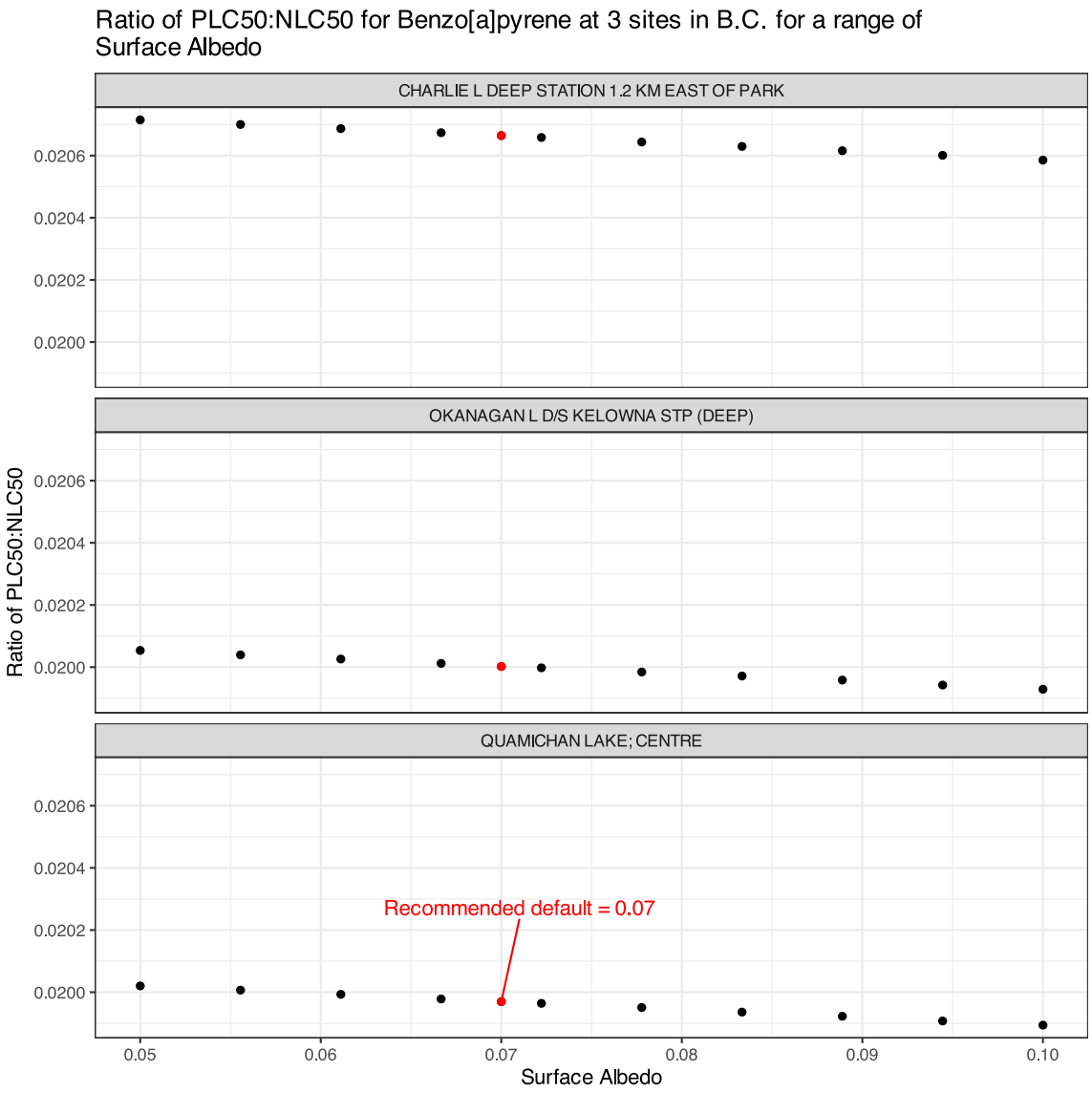
```
ggplot(albedo_test_b, aes(x = albedo, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(albedo_test_b, albedo == 0.07),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(albedo_test_b, albedo == 0.07, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.07",
    nudge_x = 0.001,
    nudge_y = 0.0005
  ) +
  labs(
    title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range of
Surface Albedo",
    x = "Surface Albedo",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(albedo_test_b, aes(x = albedo, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(albedo_test_b, albedo == 0.07),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(albedo_test_b, albedo == 0.07, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.07",
    nudge_x = 0.001,
    nudge_y = 0.0003
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nSurface Albedo",
    x = "Surface Albedo",
    y = "Ratio of PLC50:NLC50"
  )
```



Ozone Column (`o3_tc`)

The pahwq package currently uses average monthly ozone column data from 1980-1991 from J. P. F. Fortuin and H. Kelder [3], which is bundled with the TUV model. Based on latitude and longitude and month, the ozone column value is looked up and supplied to the TUV model. This default behaviour can be overridden by supplying a value to the `o3_tc` argument in the `set_tuv_aq_params` function. In the absence of climatological data, the recommended default value is 300 DU (P. Jourabchi [2]).

To test the sensitivity of PLC50 to ozone column, a range of values is tested from 280-420 DU, which are typical values in middle to Northern latitudes. See NASA's 'Ozone Watch' page for more information on atmospheric ozone.

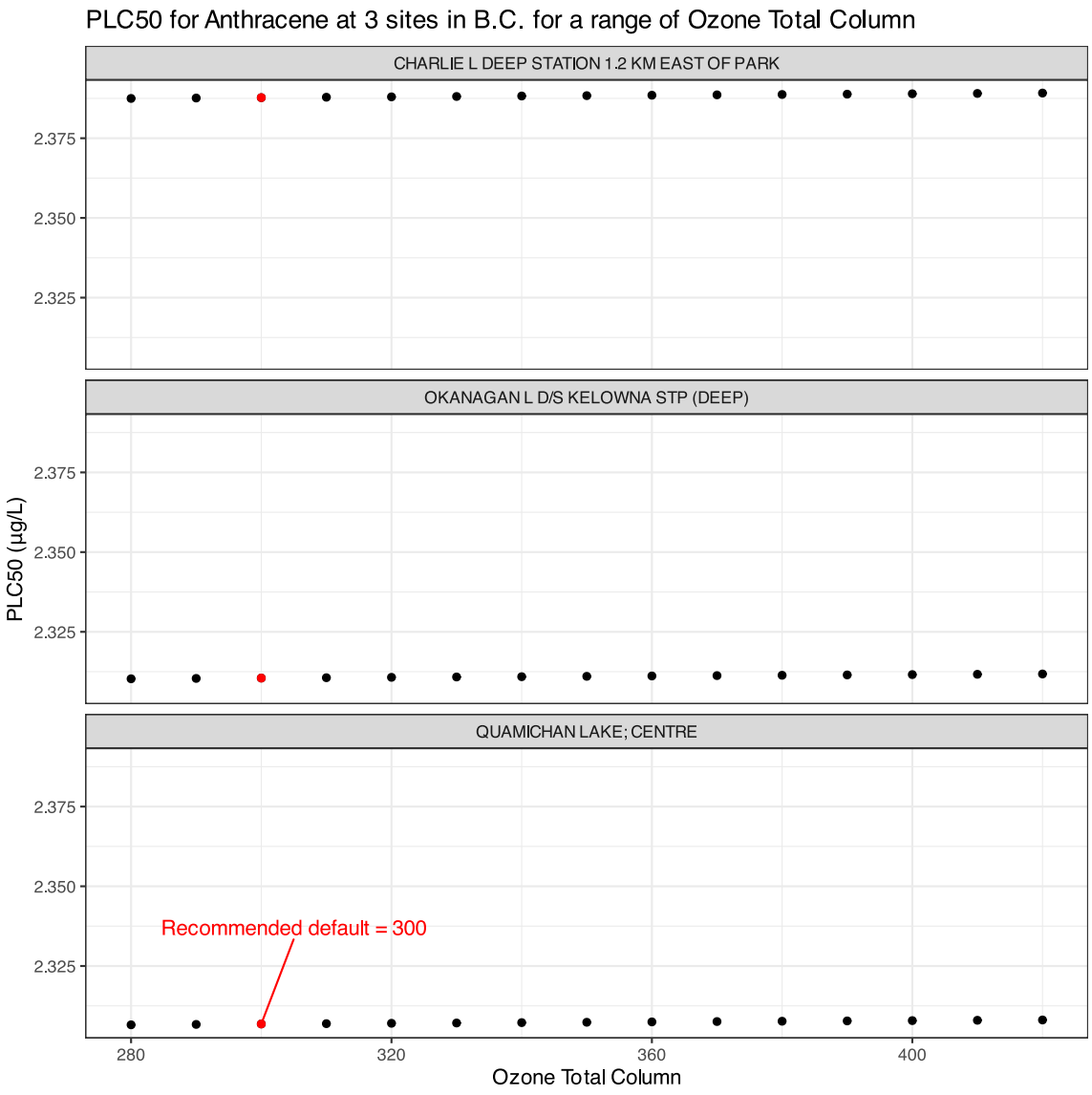
Show/Hide Code

```
ozone_vals <- seq(280, 420, by = 10)
```

Effect of varying Ozone Total Column on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

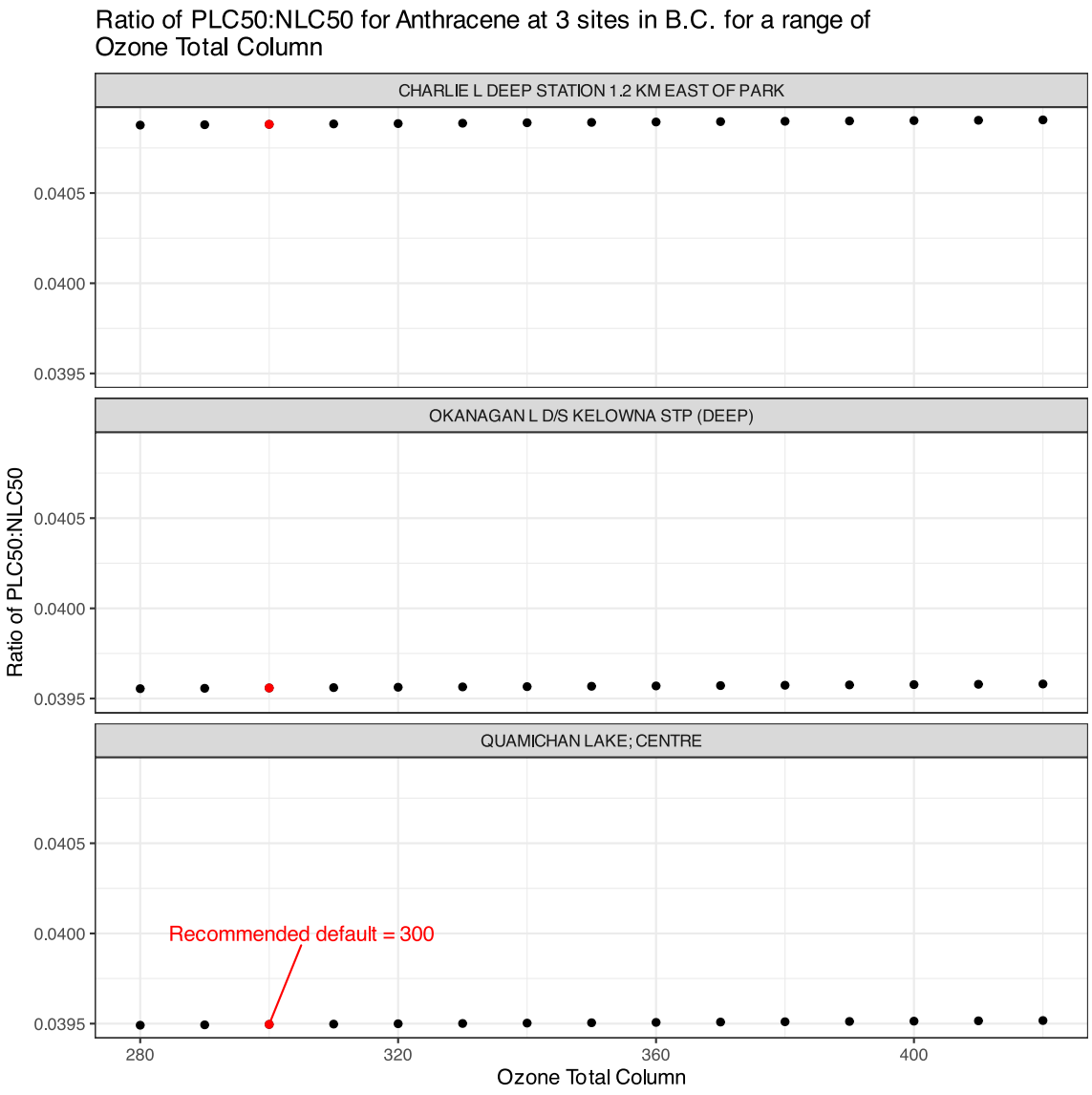
```
ozone_test_a <- multi_plc50(sites,
                            pah = "Anthracene",
                            varying = "o3_tc",
                            vals = ozone_vals,
                            DOC = 5,
                            tauaer = 0.235)

ggplot(ozone_test_a, aes(x = o3_tc, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ozone_test_a, o3_tc == 300),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(ozone_test_a, o3_tc == 300, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 300",
    nudge_x = 5,
    nudge_y = 0.03
  ) +
  labs(
    title = "PLC50 for Anthracene at 3 sites in B.C. for a range of Ozone
Total Column",
    x = "Ozone Total Column",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(ozone_test_a, aes(x = o3_tc, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ozone_test_a, o3_tc == 300),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(ozone_test_a, o3_tc == 300, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 300",
    nudge_x = 5,
    nudge_y = 0.0005
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nOzone Total Column",
    x = "Ozone Total Column",
    y = "Ratio of PLC50:NLC50"
  )
```

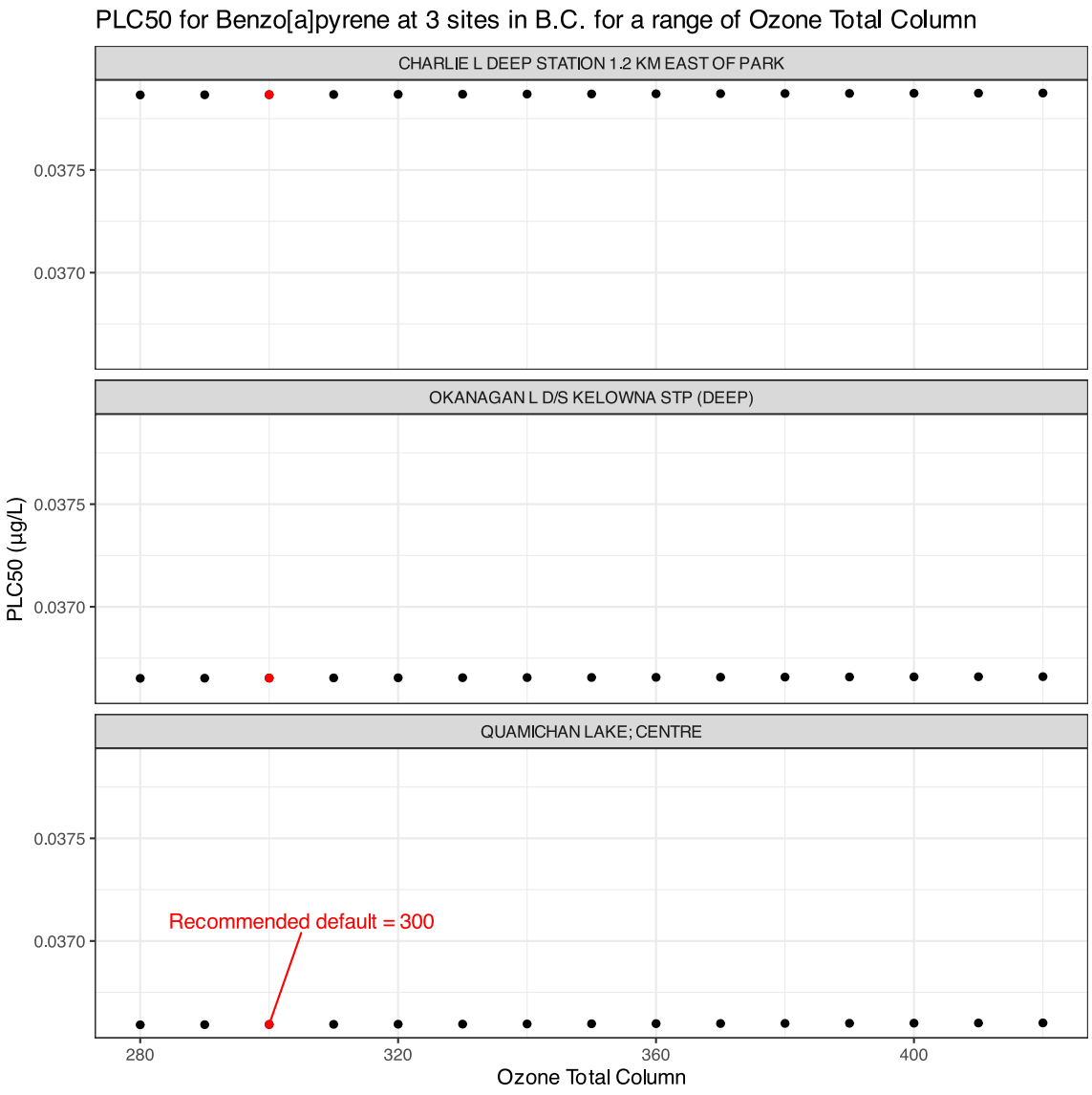


Effect of varying Ozone Total Column on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
ozone_test_b <- multi_plc50(sites,
                            pah = "Benzo[a]pyrene",
                            varying = "o3_tc",
                            vals = ozone_vals,
                            DOC = 5,
                            tauaer = 0.235)
```

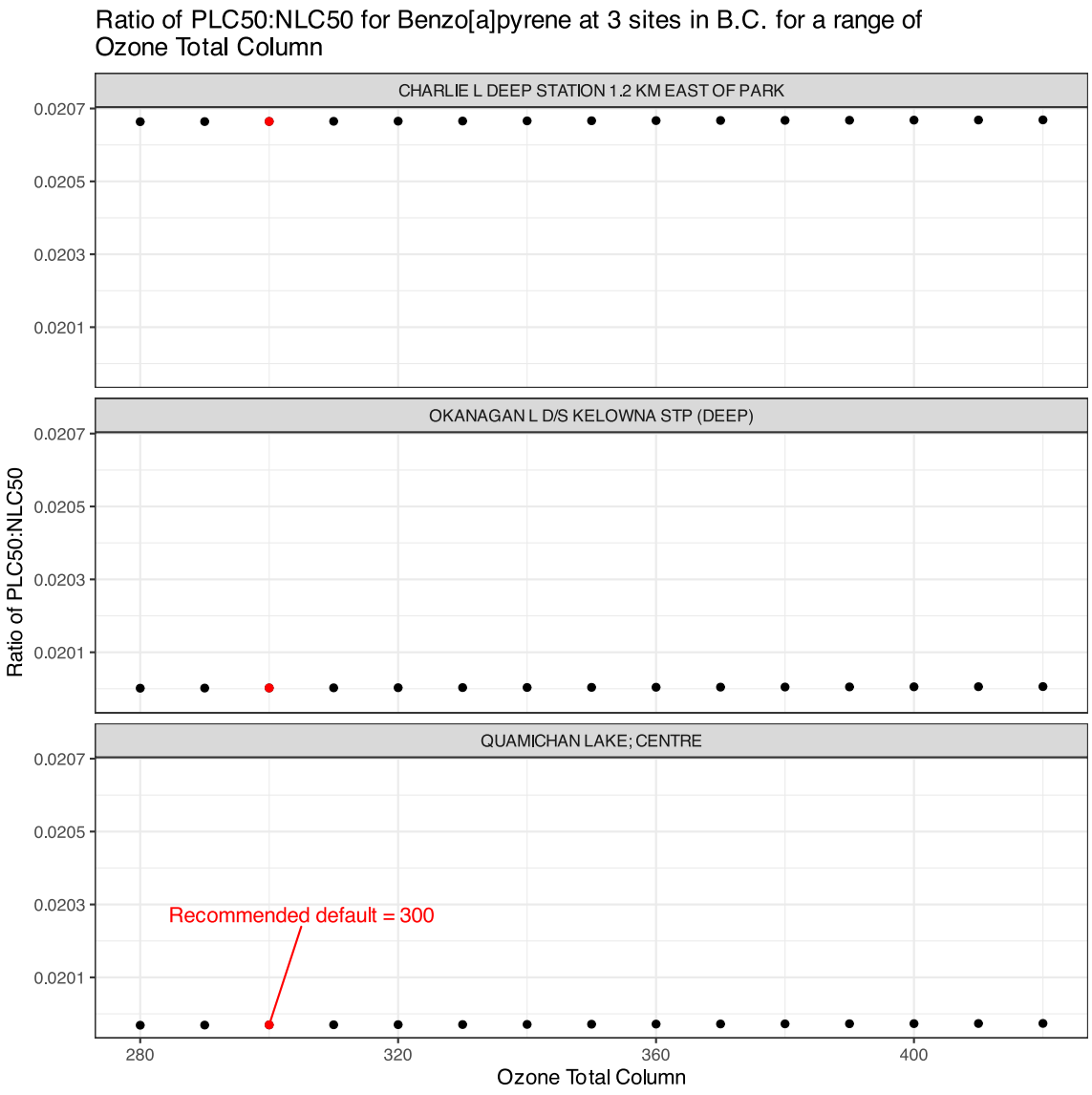
```r
ggplot(ozone_test_b, aes(x = o3_tc, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ozone_test_b, o3_tc == 300),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(ozone_test_b, o3_tc == 300, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 300",
    nudge_x = 5,
    nudge_y = 0.0005
  ) +
  labs(
    title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range of
Ozone Total Column",
    x = "Ozone Total Column",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(ozone_test_b, aes(x = o3_tc, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ozone_test_b, o3_tc == 300),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(ozone_test_b, o3_tc == 300, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 300",
    nudge_x = 5,
    nudge_y = 0.0003
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nOzone Total Column",
    x = "Ozone Total Column",
    y = "Ratio of PLC50:NLC50"
  )
```



Aerosol Optical Depth (`tauaer`)

The pahwq package currently uses average monthly aerosol optical depth data from 2002 to 2023, obtained from MODIS/Aqua satellite data. Based on latitude and longitude and month, the AOD value is looked up and supplied to the TUV model. This default behaviour can be overridden by supplying a value to the `tauaer` argument in the `set_tuv_aq_params` function. In the absence of climatological data, the recommended default value is 0.235 (P. Jourabchi [2]).

To test the sensitivity of PLC50 to AOD, a range of values is tested from 0.1 (clear skies with maximum visibility) to 1.0 (very hazy skies). See the NASA Earth Observatory page on aerosols.

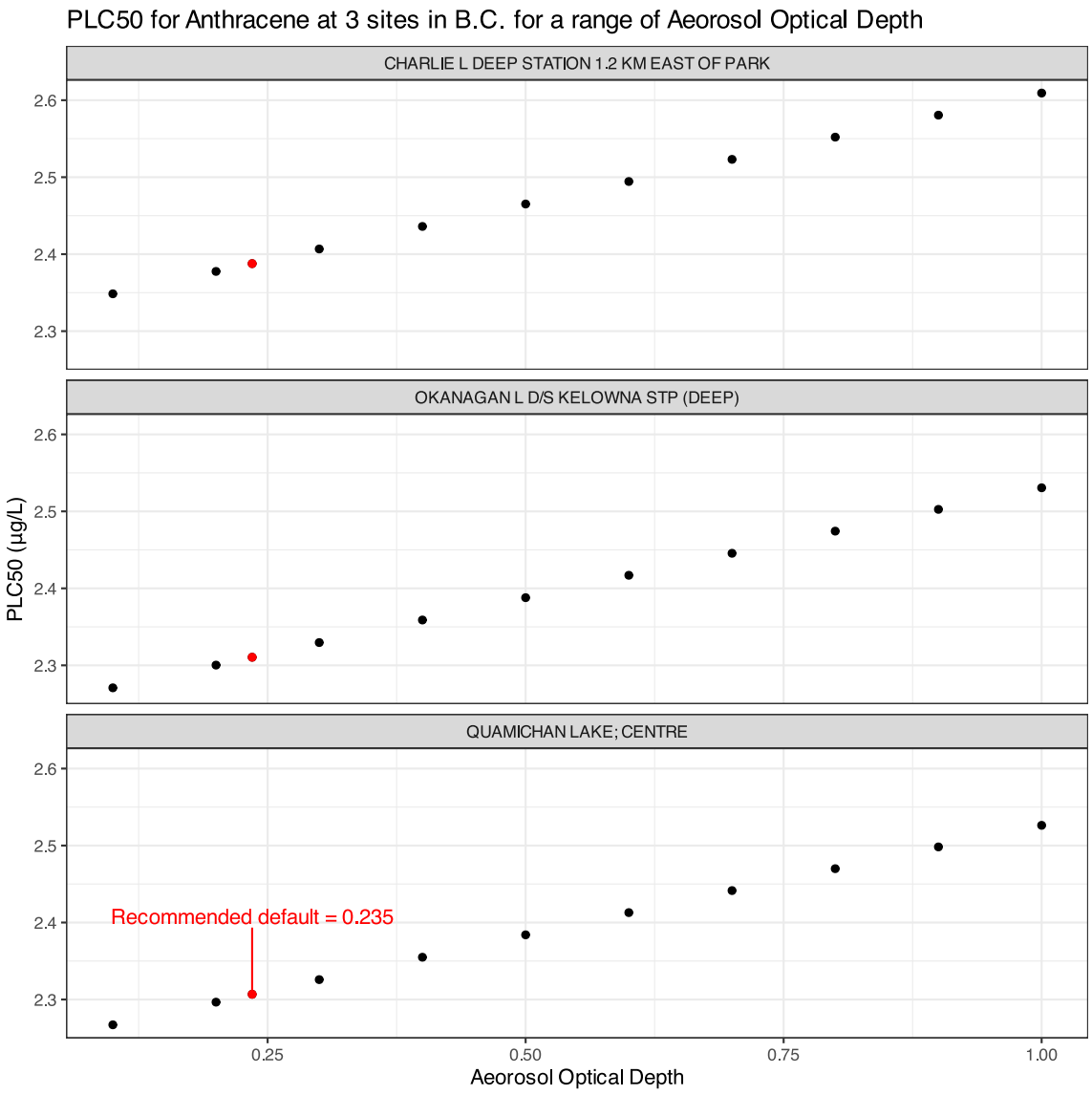
Show/Hide Code

```
aod_vals <- c(seq(0.1, 1.0, length.out = 10), 0.235)
```

Effect of Varying Aerosol Optical Depth (AOD) on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

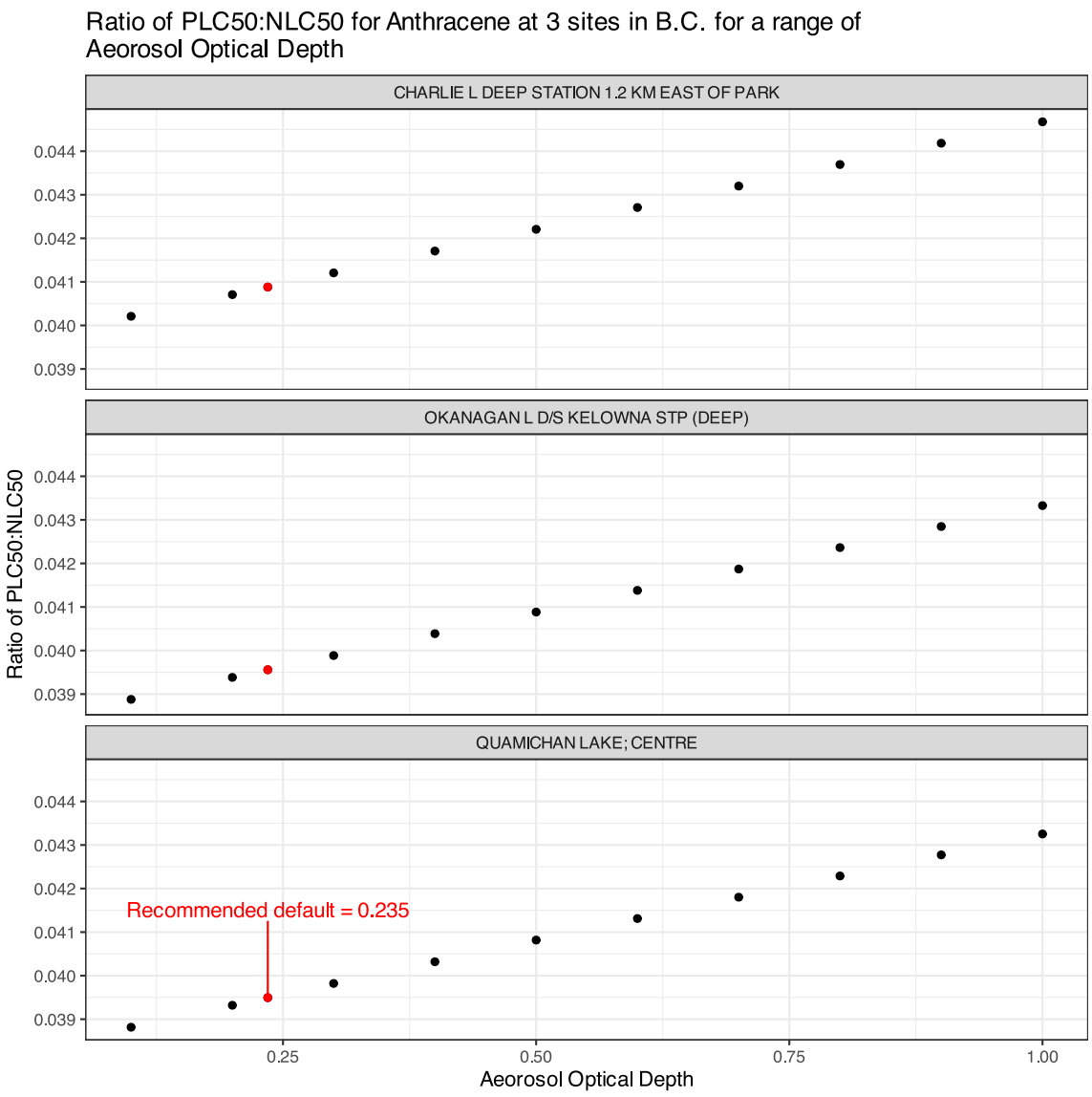
```
aod_test_a <- multi_plc50(sites,
                          pah = "Anthracene",
                          varying = "tauaer",
                          vals = aod_vals,
                          DOC = 5,
                          o3_tc = 300)

ggplot(aod_test_a, aes(x = tauaer, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(aod_test_a, tauaer == 0.235),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(aod_test_a, tauaer == 0.235, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.235",
    nudge_y = 0.1
  ) +
  labs(
      title = "PLC50 for Anthracene at 3 sites in B.C. for a range of
Aeorosol Optical Depth",
    x = "Aeorosol Optical Depth",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(aod_test_a, aes(x = tauaer, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(aod_test_a, tauaer == 0.235),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(aod_test_a, tauaer == 0.235, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.235",
    nudge_y = 0.002
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nAeorosol Optical Depth",
    x = "Aeorosol Optical Depth",
    y = "Ratio of PLC50:NLC50"
  )
```

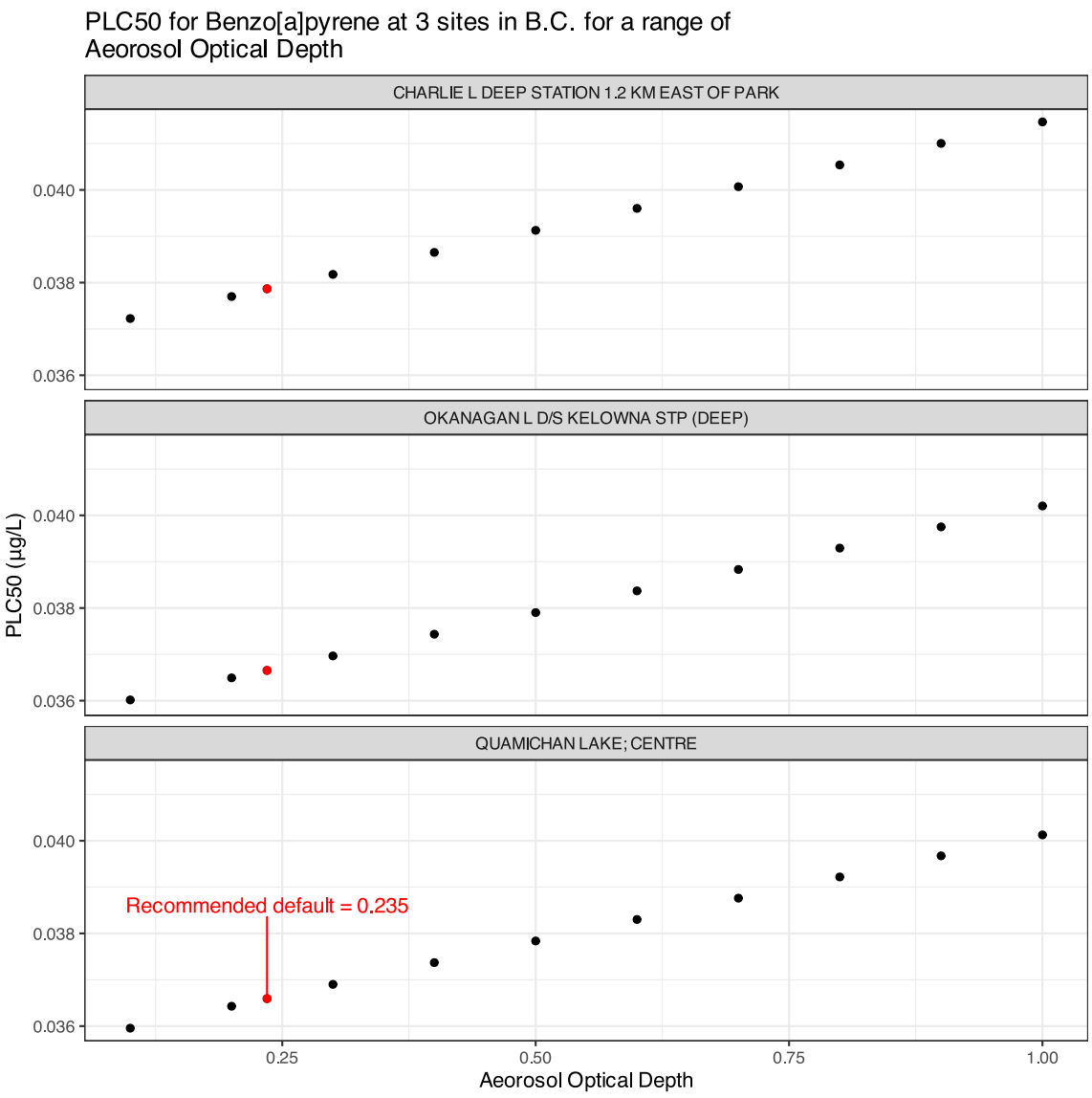


Effect of varying Aerosol Optical Depth (AOD) on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
aod_test_b <- multi_plc50(sites,
                          pah = "Benzo[a]pyrene",
                          varying = "tauaer",
                          vals = aod_vals,
                          DOC = 5,
                          o3_tc = 300)
```

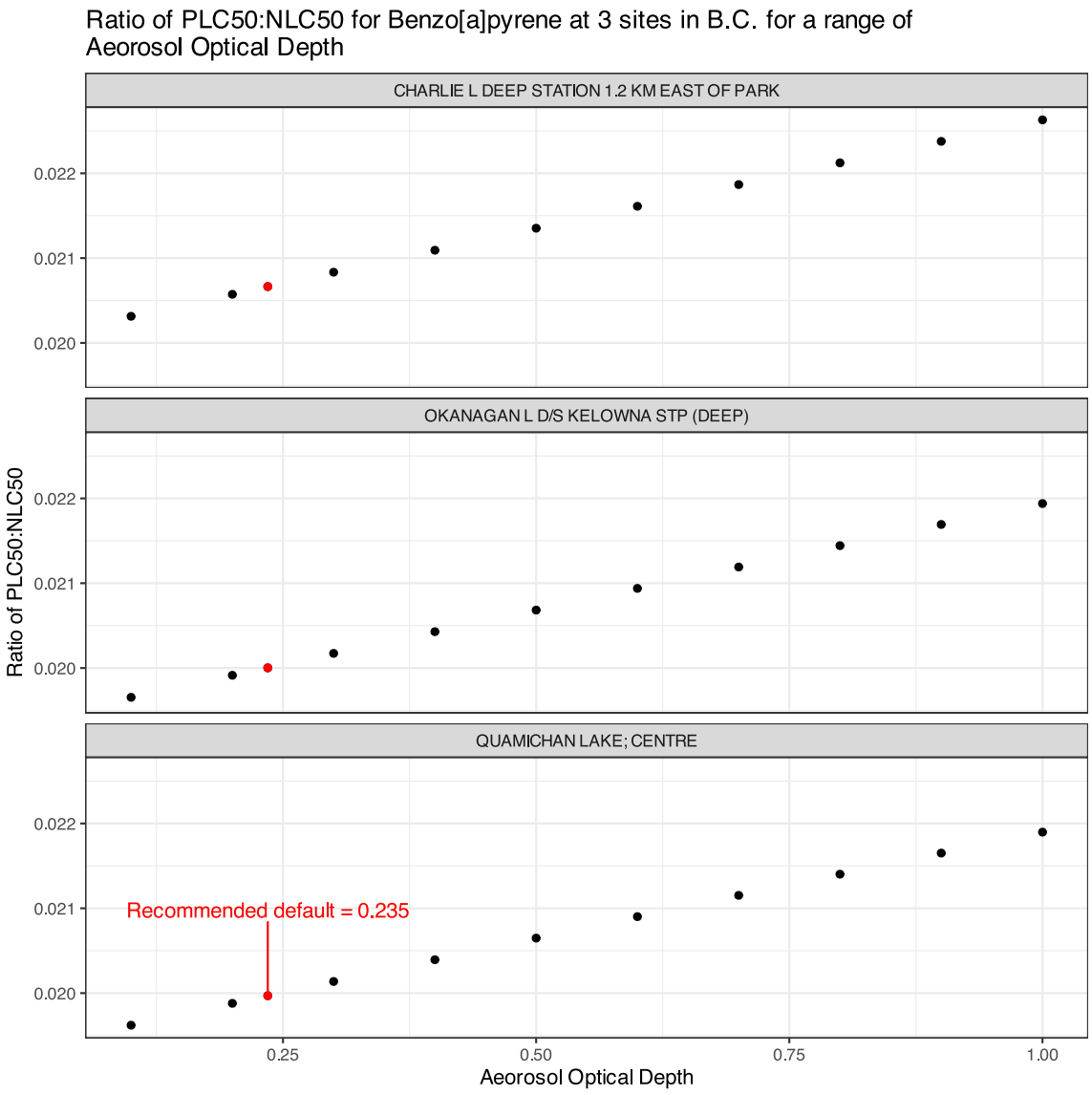
```
ggplot(aod_test_b, aes(x = tauaer, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(aod_test_b, tauaer == 0.235),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(aod_test_b, tauaer == 0.235, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.235",
    nudge_y = 0.002
  ) +
  labs(
     title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range
of\nAeorosol Optical Depth",
    x = "Aeorosol Optical Depth",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(aod_test_b, aes(x = tauaer, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(aod_test_b, tauaer == 0.235),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(aod_test_b, tauaer == 0.235, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.235",
    nudge_y = 0.001
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nAeorosol Optical Depth",
    x = "Aeorosol Optical Depth",
    y = "Ratio of PLC50:NLC50"
  )
```



Aerosol Single Scattering Albedo (`ssaaer`)

Aerosol Single Scattering Albedo is currently set as a default constant value of 0.99. This can be overridden by setting the `ssaaer` parameter of the `set_tuv_aq_params()` function to a different value.

Here we test a range for values from 0.80 to 0.99, including the recommended default of 0.99 (P. Jourabchi [2]).

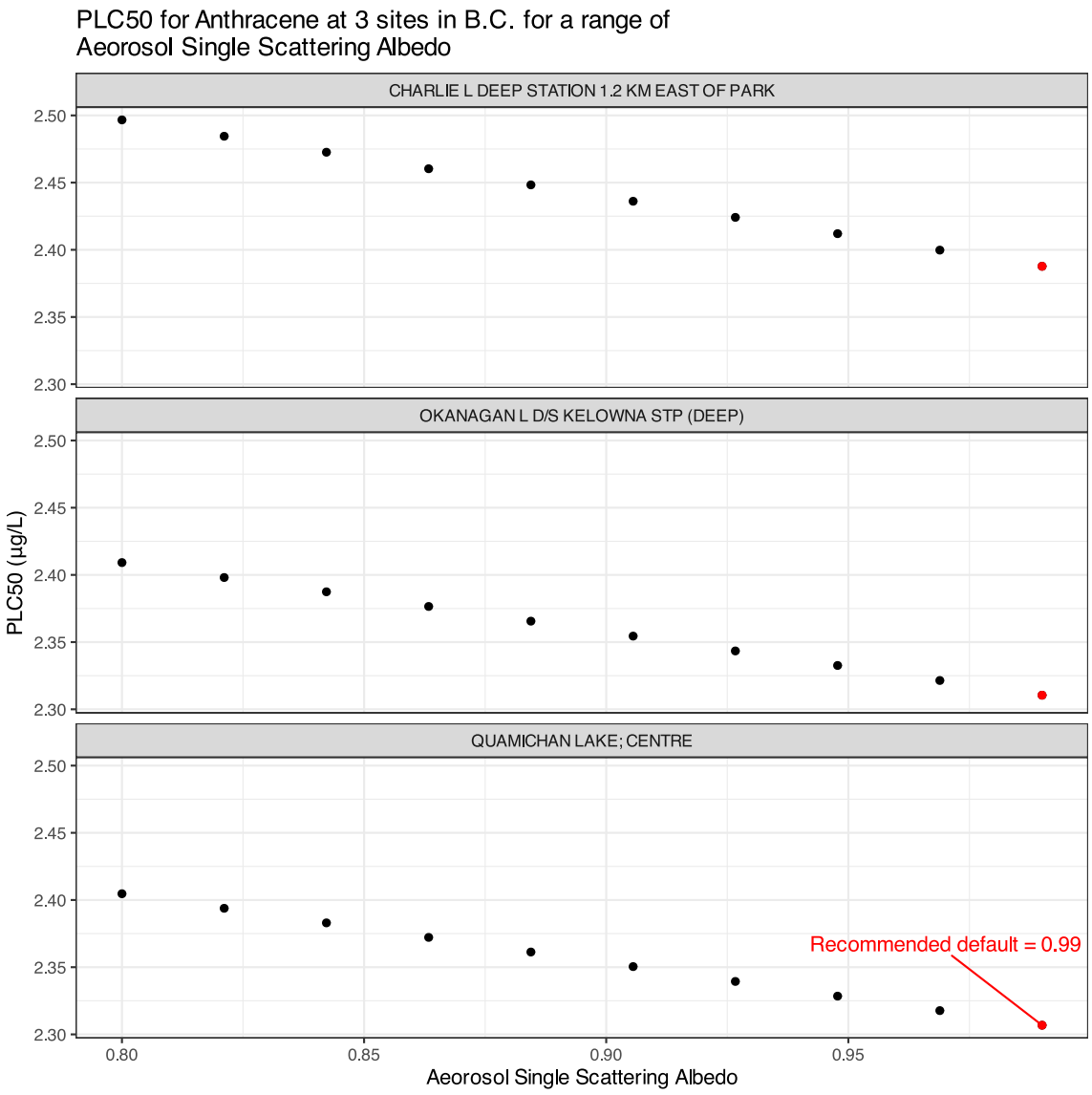
Show/Hide Code

```
ssa_vals <- seq(0.8, 0.99, length.out = 10)
```

Effect of varying Aerosol Single Scattering Albedo on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

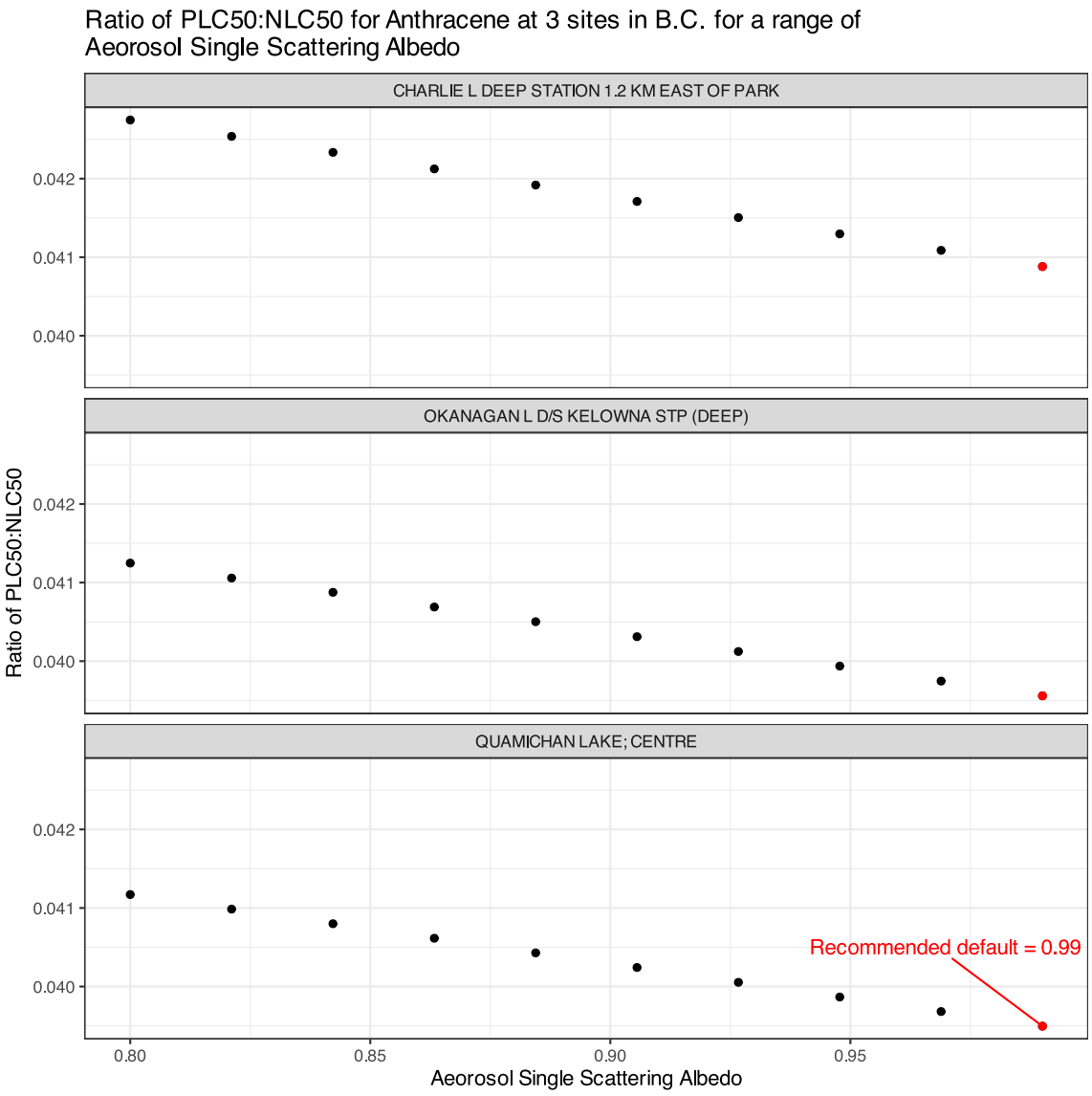
```
ssa_test_a <- multi_plc50(sites,
                          pah = "Anthracene",
                          varying = "ssaaer",
                          vals = ssa_vals,
                          DOC = 5,
                          o3_tc = 300,
                          tauaer = 0.235)

ggplot(ssa_test_a, aes(x = ssaaer, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ssa_test_a, ssaaer == 0.99),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(ssa_test_a, ssaaer == 0.99, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.99",
    nudge_y = .06
  ) +
  labs(
   title = "PLC50 for Anthracene at 3 sites in B.C. for a range of\nAeorosol
Single Scattering Albedo",
    x = "Aeorosol Single Scattering Albedo",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(ssa_test_a, aes(x = ssaaer, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ssa_test_a, ssaaer == 0.99),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(ssa_test_a, ssaaer == 0.99, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.99",
    nudge_y = .001
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nAeorosol Single Scattering Albedo",
    x = "Aeorosol Single Scattering Albedo",
    y = "Ratio of PLC50:NLC50"
  )
```

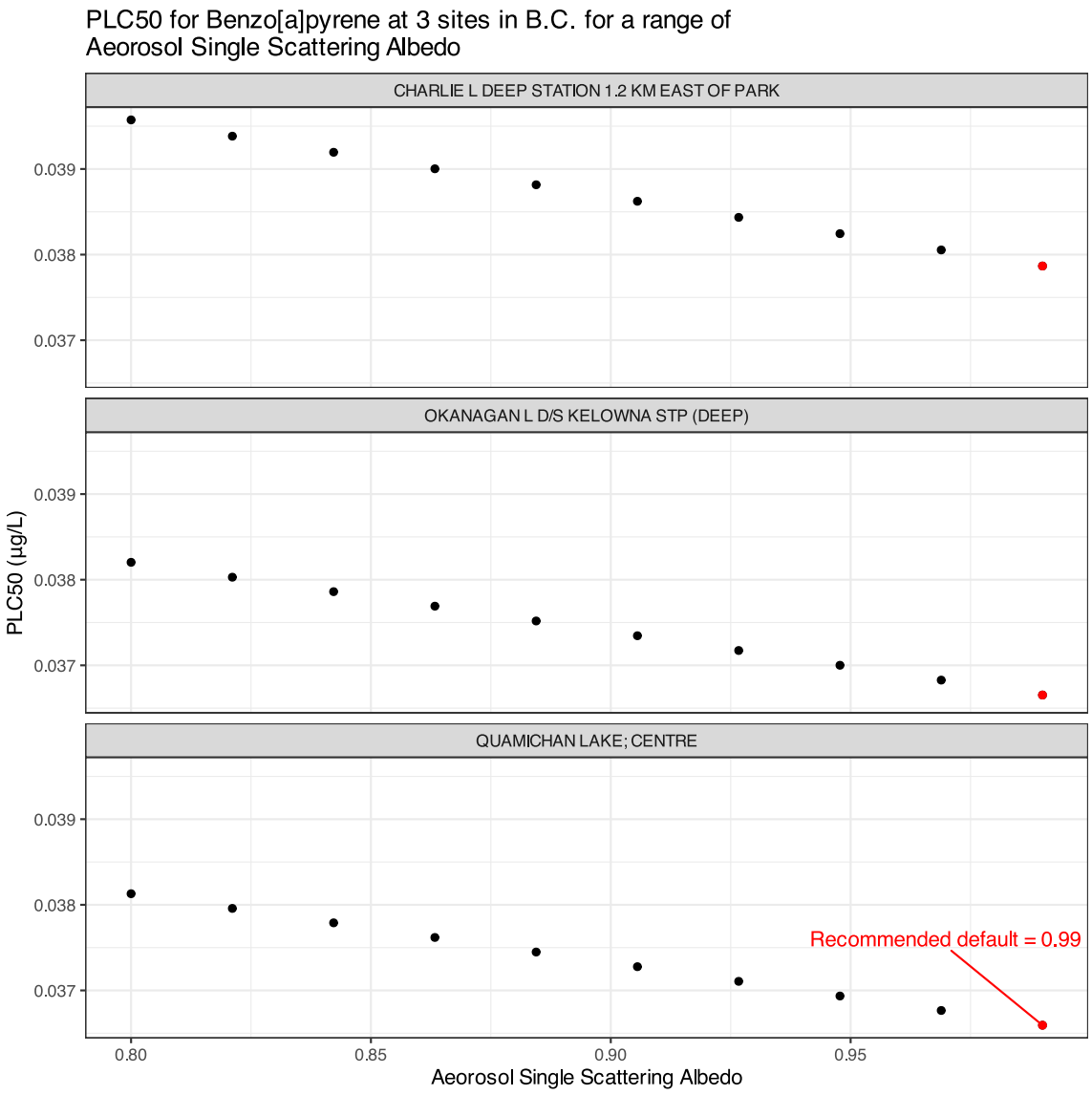


Effect of varying Aerosol Single Scattering Albedo on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
ssa_test_b <- multi_plc50(sites,
                          pah = "Benzo[a]pyrene",
                          varying = "ssaaer",
                          vals = ssa_vals,
                          DOC = 5,
                          o3_tc = 300,
                          tauaer = 0.235)
```

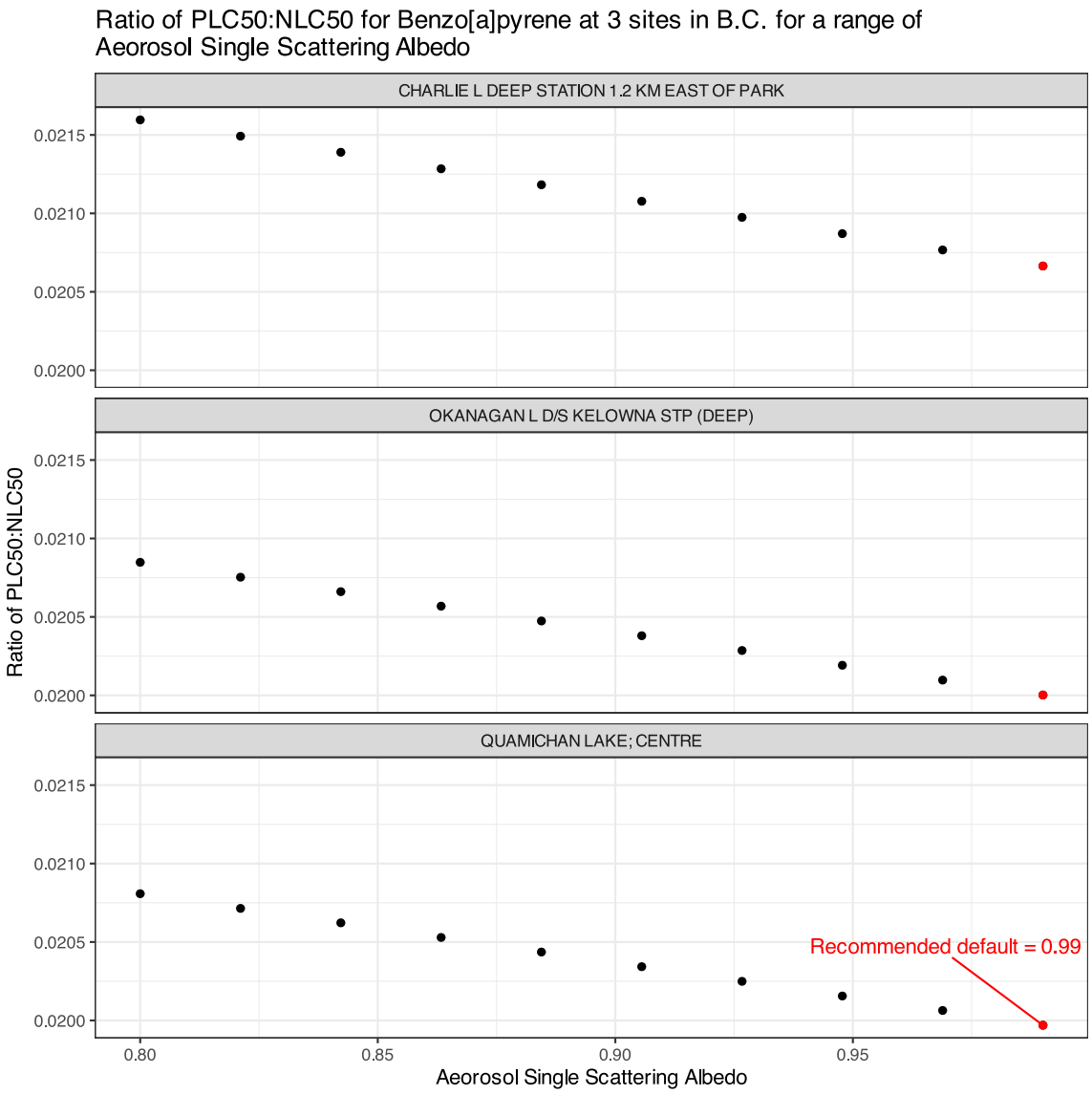
```
ggplot(ssa_test_b, aes(x = ssaaer, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ssa_test_b, ssaaer == 0.99),
    colour = "red"
  ) +
  geom_text_repel(
     data = filter(ssa_test_b, ssaaer == 0.99, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.99",
    nudge_y = .001
  ) +
  labs(
     title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range
of\nAeorosol Single Scattering Albedo",
    x = "Aeorosol Single Scattering Albedo",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(ssa_test_b, aes(x = ssaaer, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  geom_point(
    data = filter(ssa_test_b, ssaaer == 0.99),
    colour = "red"
  ) +
  geom_text_repel(
```

```
    data = filter(ssa_test_b, ssaaer == 0.99, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.99",
    nudge_y = .0005
  ) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nAeorosol Single Scattering Albedo",
    x = "Aeorosol Single Scattering Albedo",
    y = "Ratio of PLC50:NLC50"
  )
```



Latitude (`lat`)

Latitude has a strong effect on the angle of the sun, which will in turn affect the light penetration through water, thus it is important to investigate the sensitivity of the calculation of PLC50 to variation in latitude.

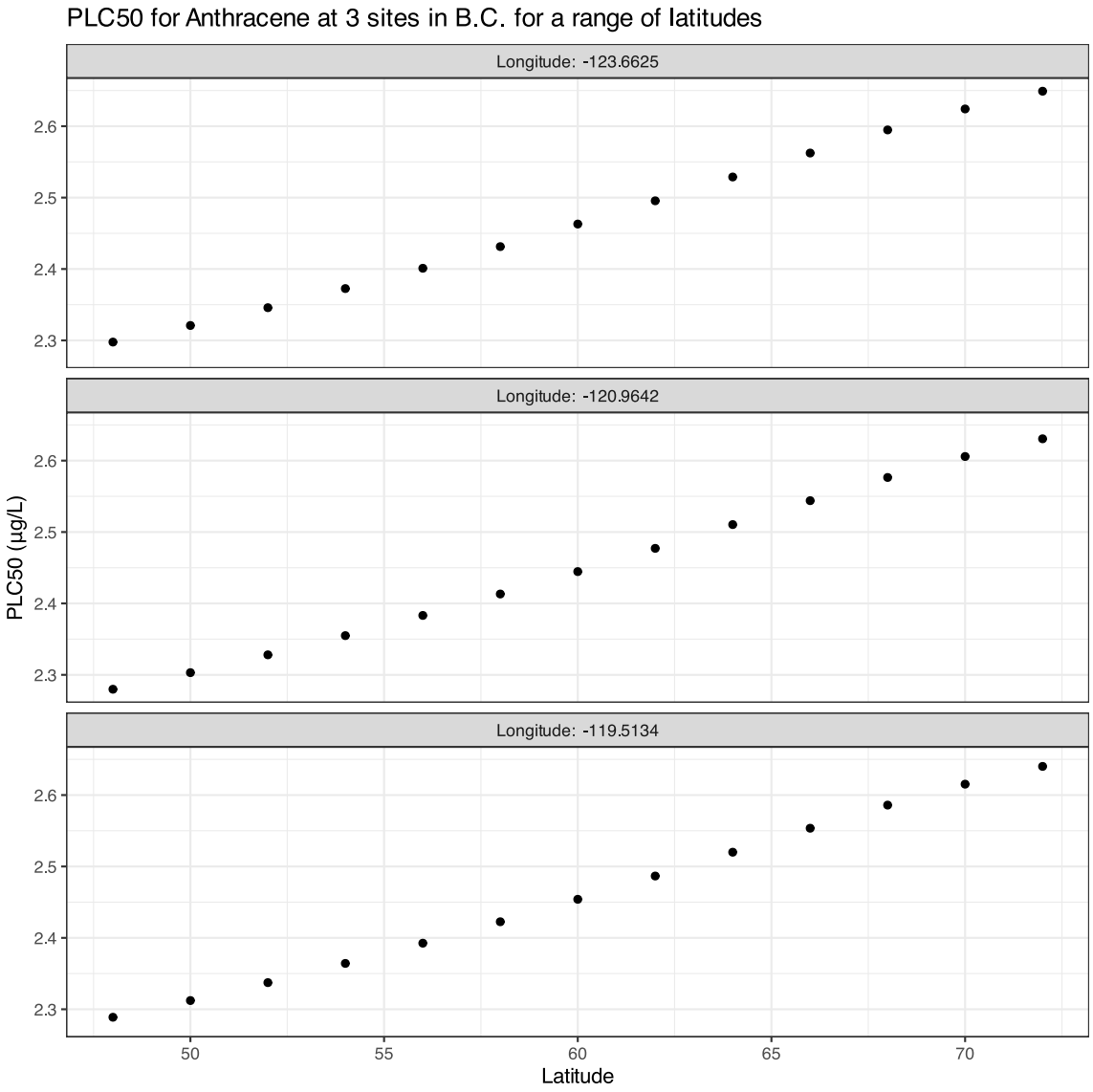
For this analysis, we will maintain the longitudes associated with each site, and make “mock” sites by creating a range of latitudes from 48 to 72 degrees N and pair those with the longitudes of the original sites.

```
lat_vals <- seq(48, 72, by = 2)
```

Effect of varying Latitude on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

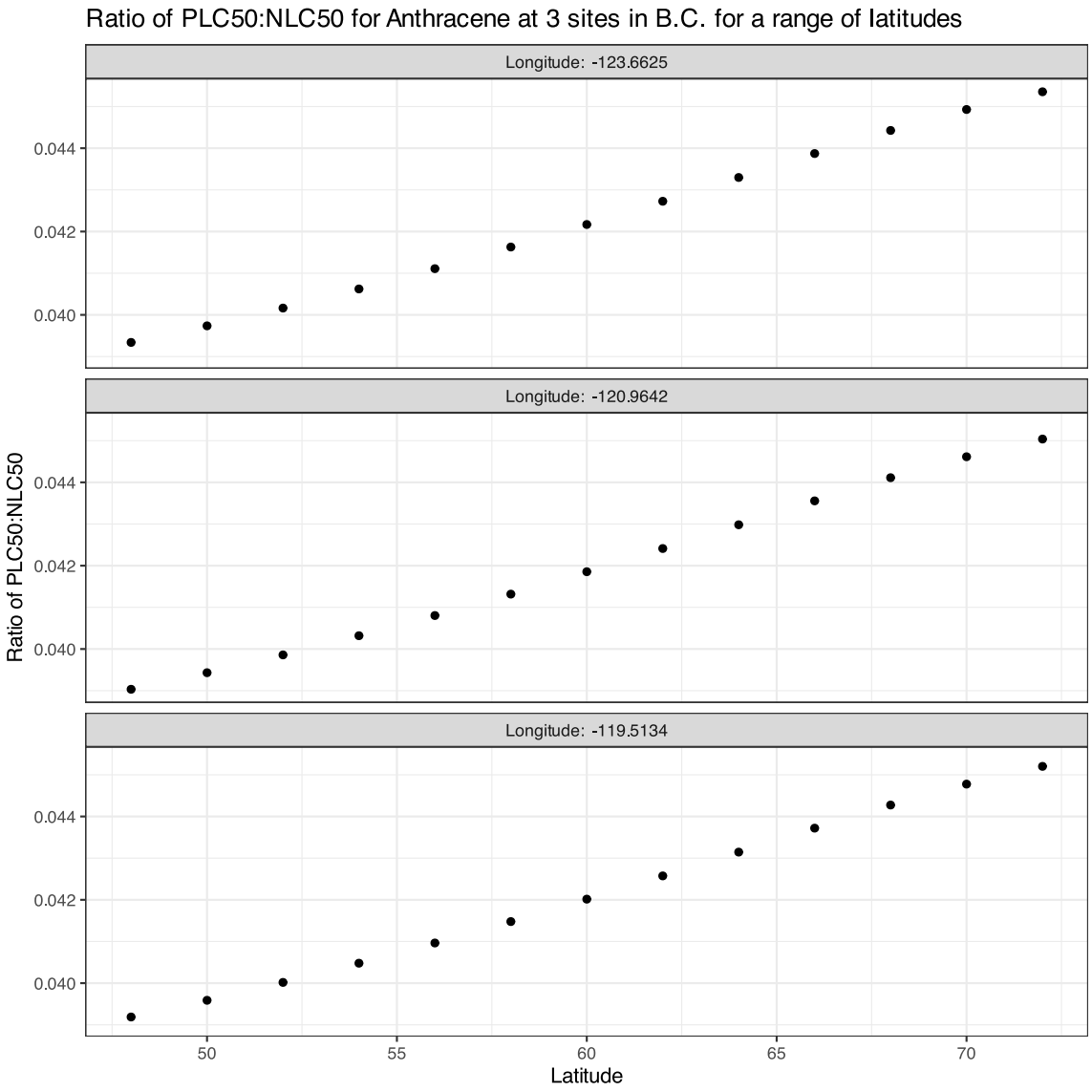
```
lat_test_a <- multi_plc50(sites,
                          pah = "Anthracene",
                          varying = "lat",
                          vals = lat_vals,
                          DOC = 5,
                          o3_tc = 300,
                          tauaer = 0.235)

ggplot(lat_test_a, aes(x = lat, y = plc50)) +
  geom_point() +
     facet_wrap(vars(lon),  ncol  =  1,  labeller  =  as_labeller(\(x)
paste("Longitude: ", x))) +
  labs(
      title = "PLC50 for Anthracene at 3 sites in B.C. for a range of
latitudes",
    x = "Latitude",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(lat_test_a, aes(x = lat, y = plc_nlc_ratio)) +
  geom_point() +
    facet_wrap(vars(lon),  ncol  =  1,  labeller  =  as_labeller(\(x)
paste("Longitude: ", x))) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of latitudes",
    x = "Latitude",
```

```
    y = "Ratio of PLC50:NLC50"
  )
```

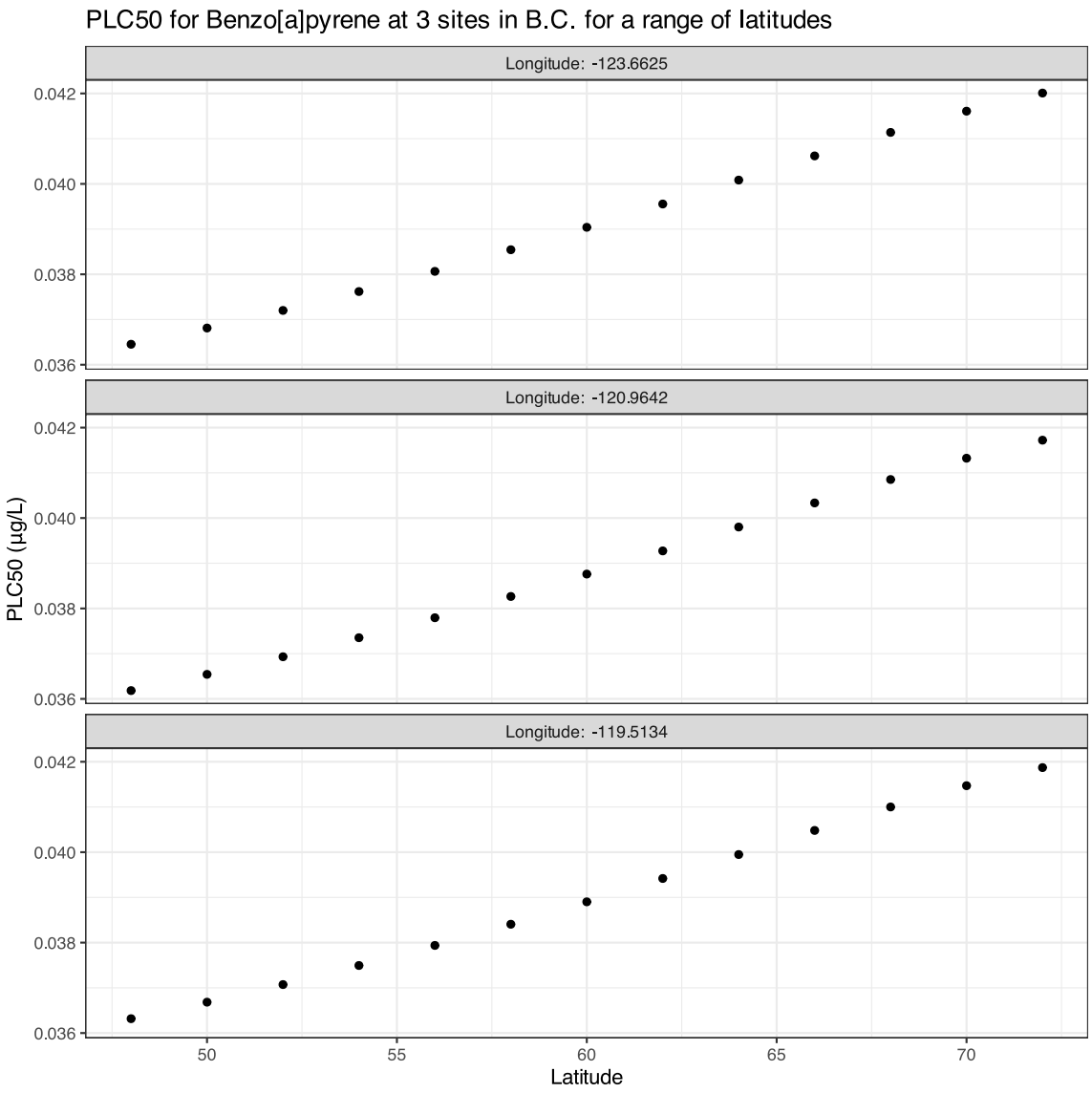


Effect of varying Latitude on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
lat_test_b <- multi_plc50(sites,
                          pah = "Benzo[a]pyrene",
                          varying = "lat",
```

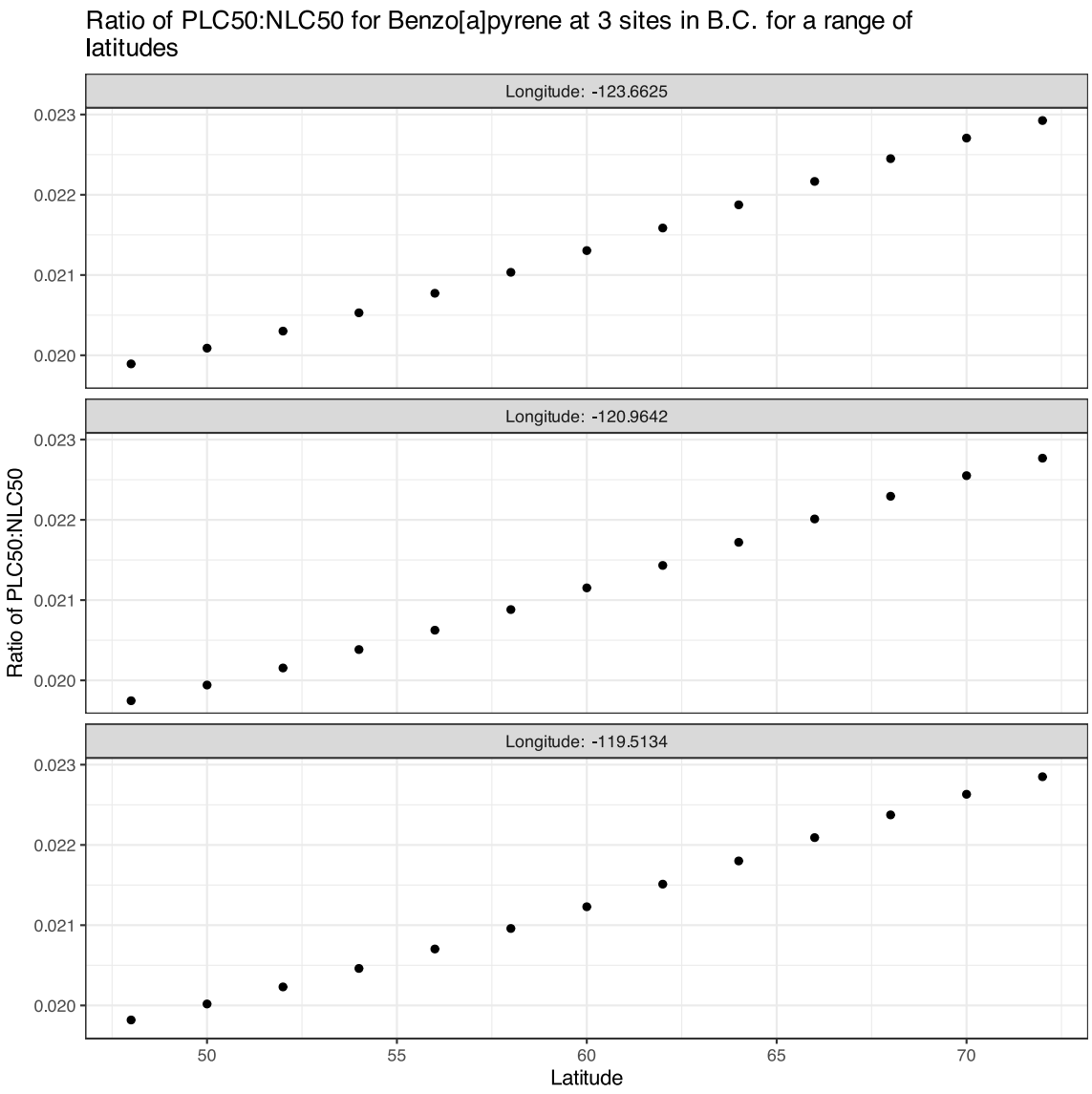
```
                        vals = lat_vals,
                        DOC = 5,
                        o3_tc = 300,
                        tauaer = 0.235)

ggplot(lat_test_b, aes(x = lat, y = plc50)) +
  geom_point() +
     facet_wrap(vars(lon),  ncol  =  1,  labeller  =  as_labeller(\(x)
paste("Longitude: ", x))) +
  labs(
    title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range of
latitudes",
    x = "Latitude",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(lat_test_b, aes(x = lat, y = plc_nlc_ratio)) +
  geom_point() +
    facet_wrap(vars(lon),  ncol  =  1,  labeller  =  as_labeller(\(x)
paste("Longitude: ", x))) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nlatitudes",
    x = "Latitude",
```

```
    y = "Ratio of PLC50:NLC50"
  )
```



Elevation (`elev_m`)

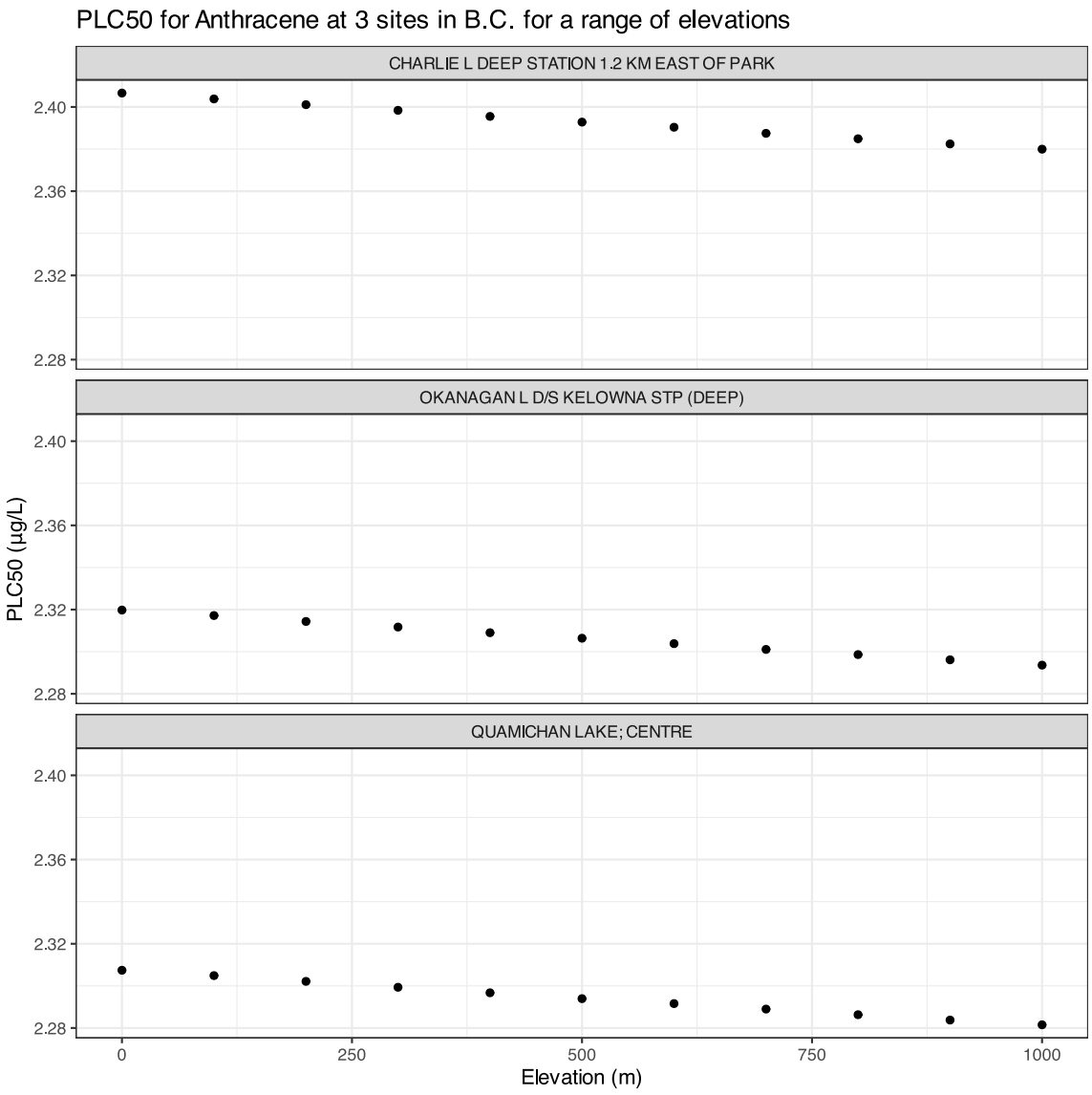
We can test the effect of elevation on PLC50 by varying elevation from sea level to 1000m above sea level. We will keep the latitude and longitude associated with each site.

```
elevation_vals <- seq(0, 1000, by = 100)
```

Effect of varying Elevation on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

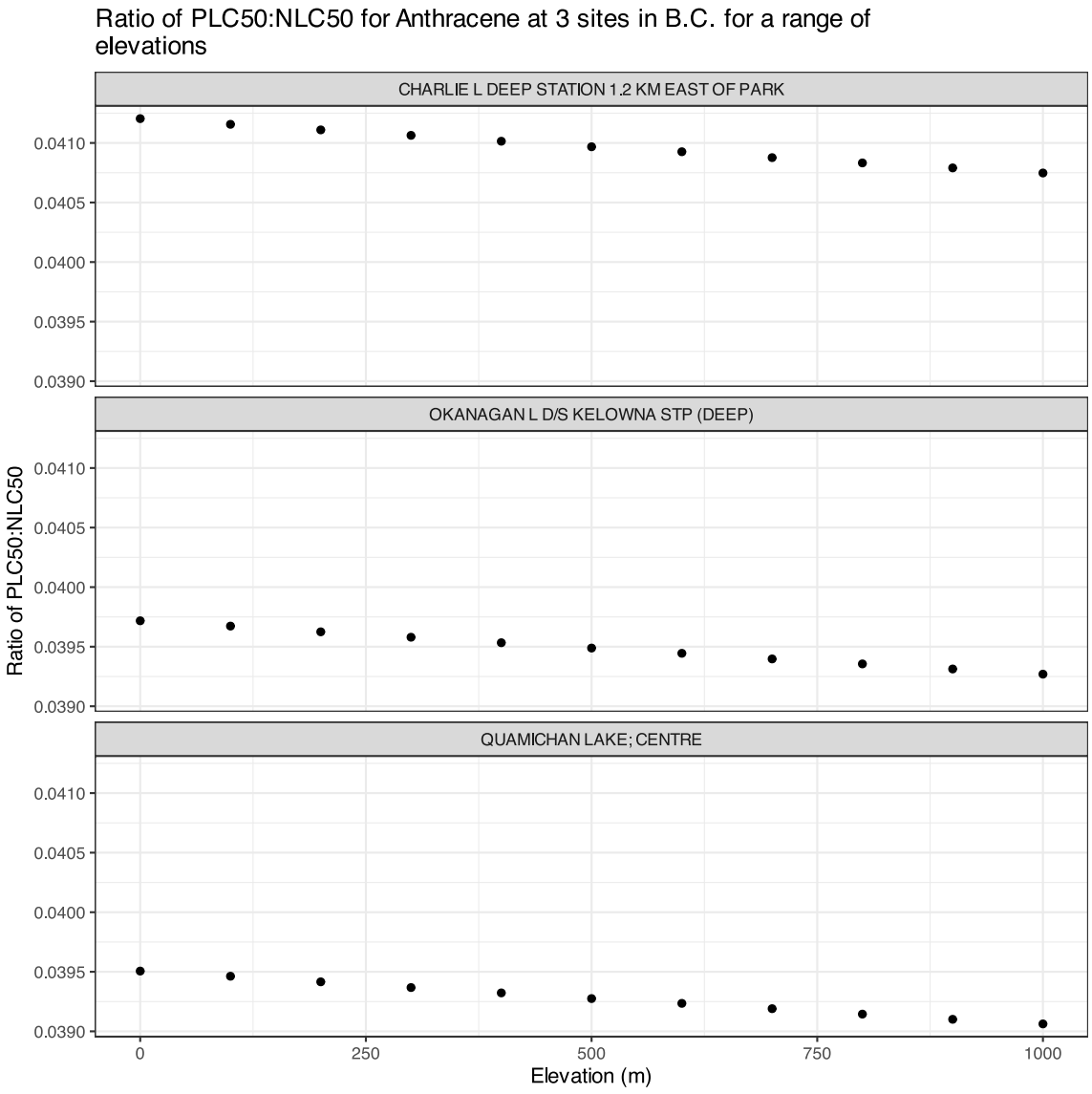
```
elev_test_a <- multi_plc50(sites,
                           pah = "Anthracene",
                           varying = "elev_m",
                           vals = elevation_vals,
                           DOC = 5,
                           o3_tc = 300,
                           tauaer = 0.235)

ggplot(elev_test_a, aes(x = elev_m, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
     title = "PLC50 for Anthracene at 3 sites in B.C. for a range of
elevations",
    x = "Elevation (m)",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(elev_test_a, aes(x = elev_m, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nelevations",
    x = "Elevation (m)",
```

```
    y = "Ratio of PLC50:NLC50"
  )
```

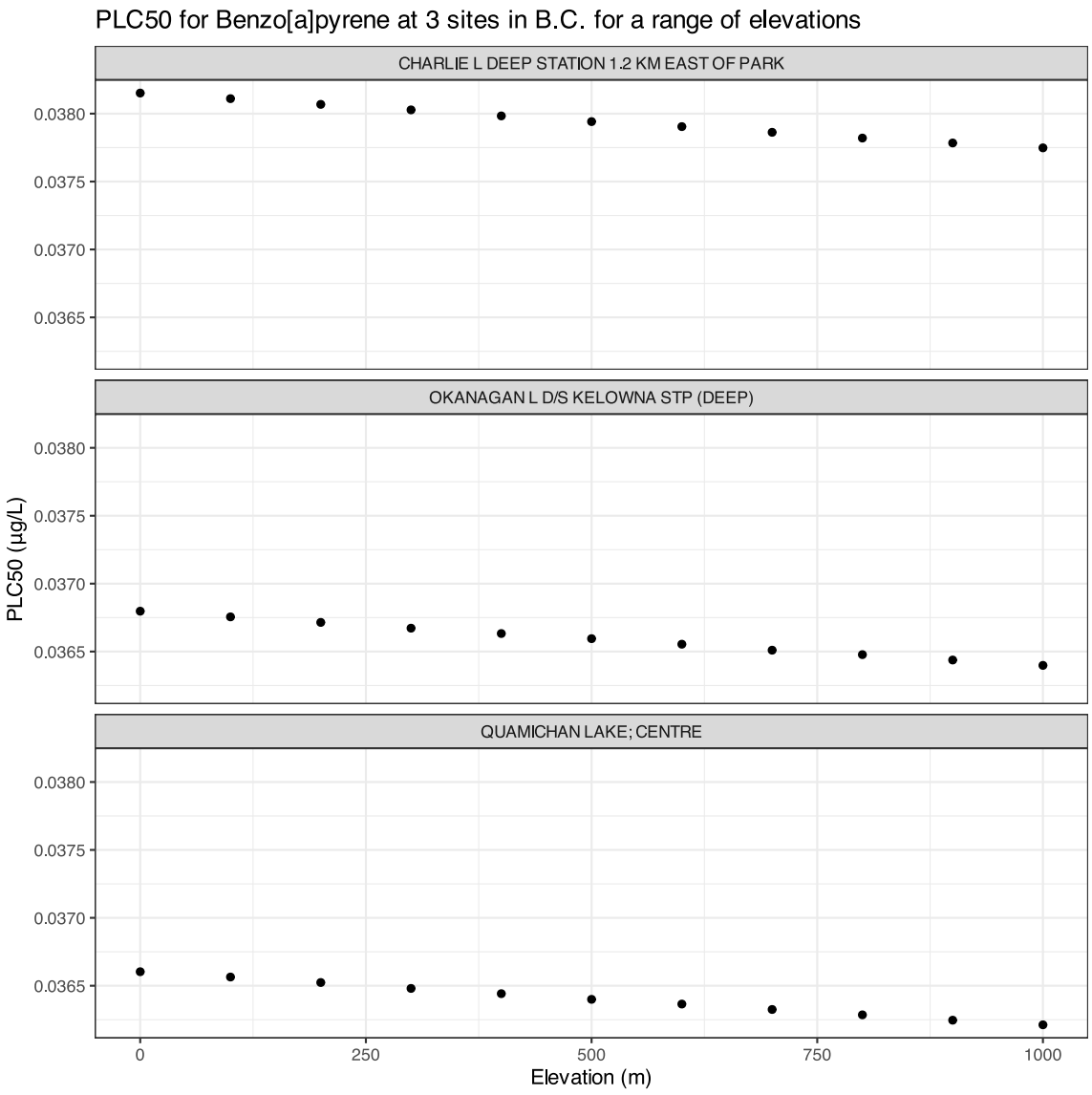


Effect of varying Elevation on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
elev_test_b <- multi_plc50(sites,
                           pah = "Benzo[a]pyrene",
                           varying = "elev_m",
```

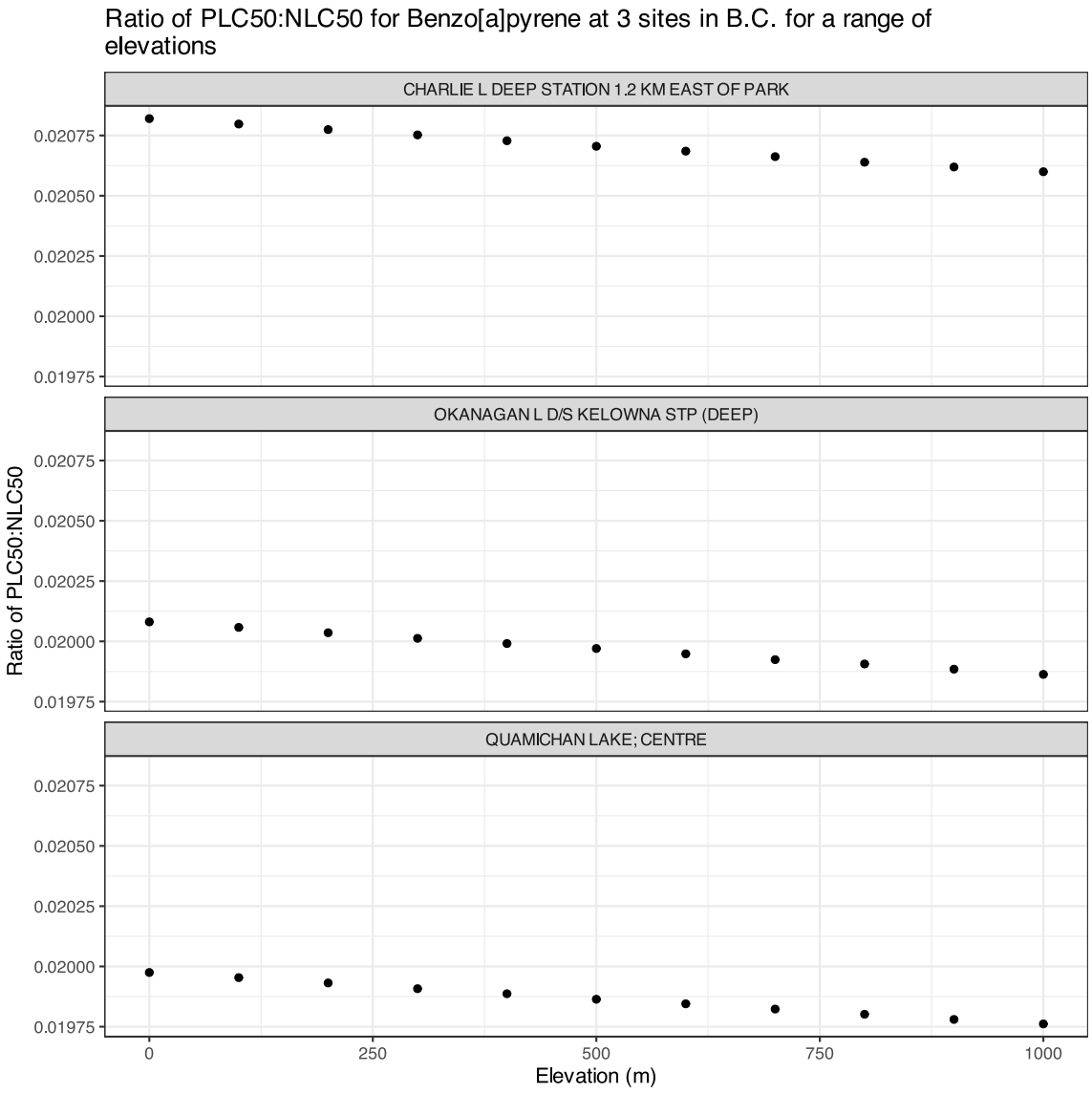
```
                          vals = elevation_vals,
                          DOC = 5,
                          o3_tc = 300,
                          tauaer = 0.235)

ggplot(elev_test_b, aes(x = elev_m, y = plc50)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range of
elevations",
    x = "Elevation (m)",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(elev_test_b, aes(x = elev_m, y = plc_nlc_ratio)) +
  geom_point() +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nelevations",
    x = "Elevation (m)",
```

```
    y = "Ratio of PLC50:NLC50"
  )
```



Water depth (`depth_m`)

The depth at which the photoxicity of a PAH is determined should be a conservative one - i.e., a depth at which sensitive species/life stages exist and thus would be exposed. The default is set at 0.25m.

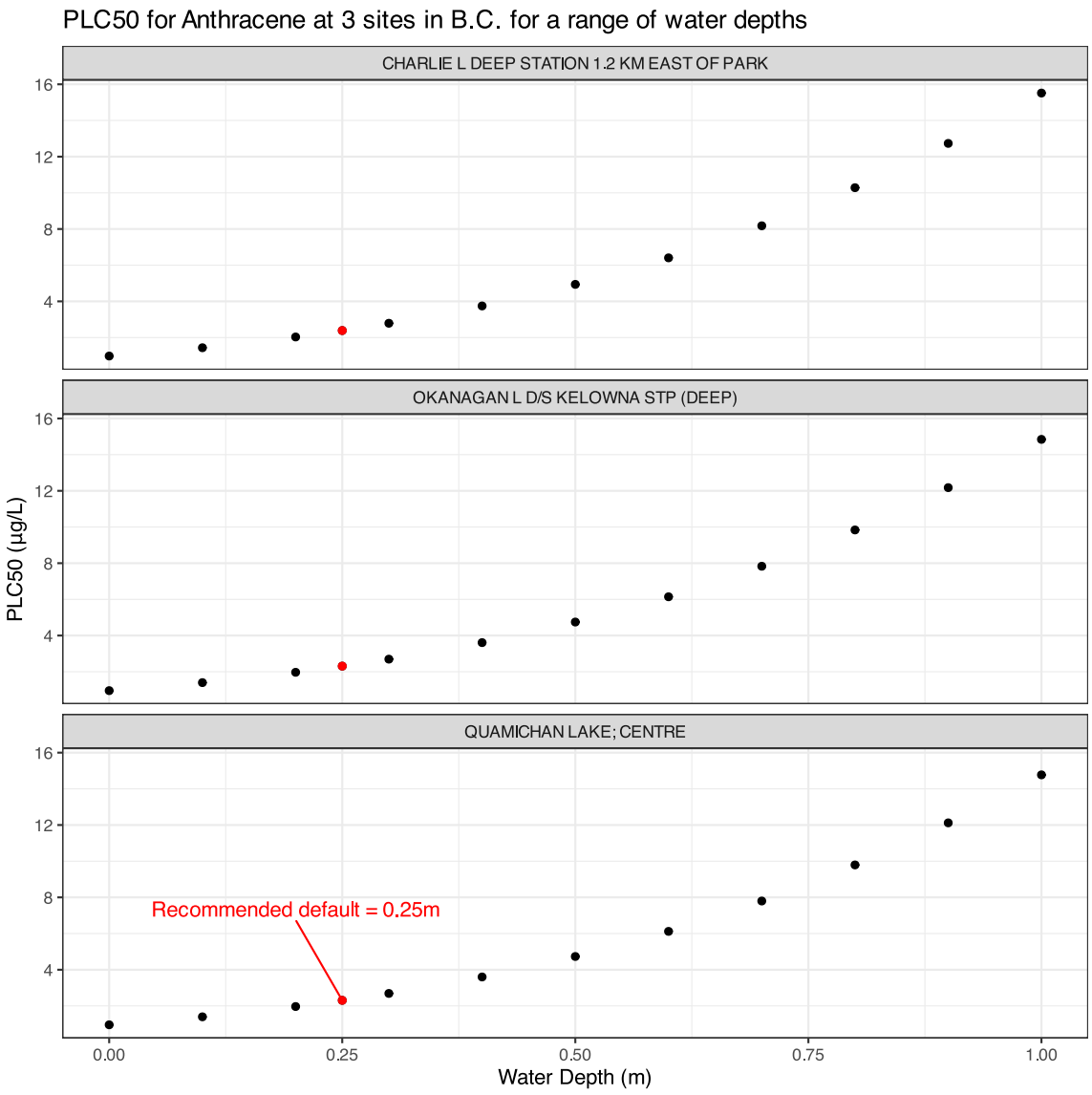
We can test the effect of depth on PLC50 by varying elevation from water level to 1m below the surface:

```
depth_vals <- c(seq(0, 1, by = 0.1), 0.25)
```

Effect of varying Water Depth on PLC50 and ratio of PLC50:NLC50 for Anthracene

Show/Hide Code

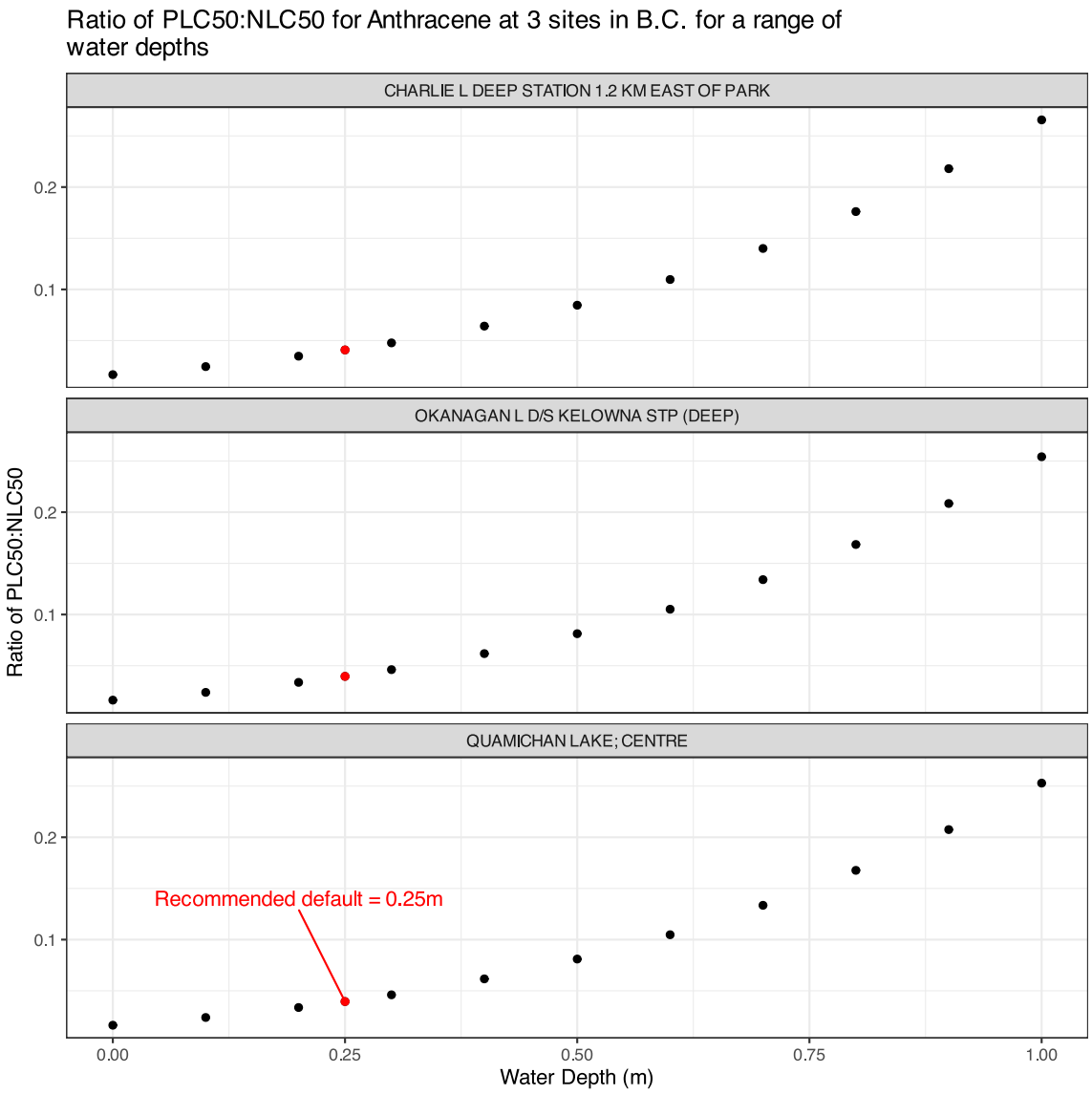
```
depth_test_a <- multi_plc50(sites,
                            pah = "Anthracene",
                            varying = "depth_m",
                            vals = depth_vals,
                            DOC = 5,
                            o3_tc = 300,
                            tauaer = 0.235)

ggplot(depth_test_a, aes(x = depth_m, y = plc50)) +
  geom_point() +
  geom_point(
    data = filter(depth_test_a, depth_m == 0.25),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(depth_test_a, depth_m == 0.25, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.25m",
    nudge_x = -0.05,
    nudge_y = 5
  ) +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "PLC50 for Anthracene at 3 sites in B.C. for a range of water
depths",
    x = "Water Depth (m)",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(depth_test_a, aes(x = depth_m, y = plc_nlc_ratio)) +
  geom_point() +
  geom_point(
    data = filter(depth_test_a, depth_m == 0.25),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(depth_test_a, depth_m == 0.25, name == "QUAMICHAN LAKE;
```

```
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.25m",
    nudge_x = -0.05,
    nudge_y = 0.1
  ) +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "Ratio of PLC50:NLC50 for Anthracene at 3 sites in B.C. for
a range of\nwater depths",
    x = "Water Depth (m)",
    y = "Ratio of PLC50:NLC50"
  )
```

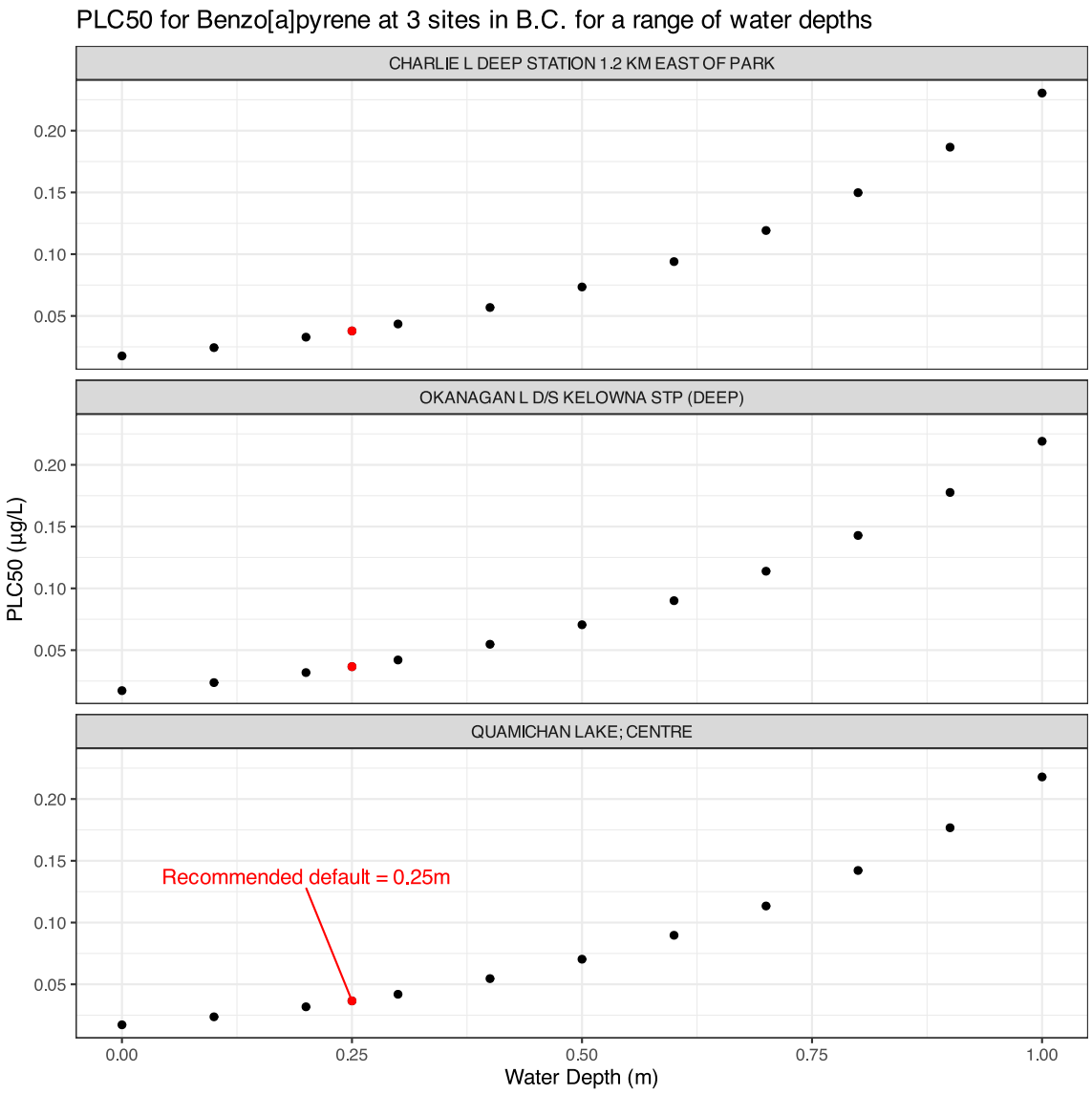


Effect of varying Water Depth on PLC50 and ratio of PLC50:NLC50 for Benzo[a]pyrene

Show/Hide Code

```
depth_test_b <- multi_plc50(sites,
                            pah = "Benzo[a]pyrene",
                            varying = "depth_m",
                            vals = depth_vals,
                            DOC = 5,
                            o3_tc = 300,
                            tauaer = 0.235)
```

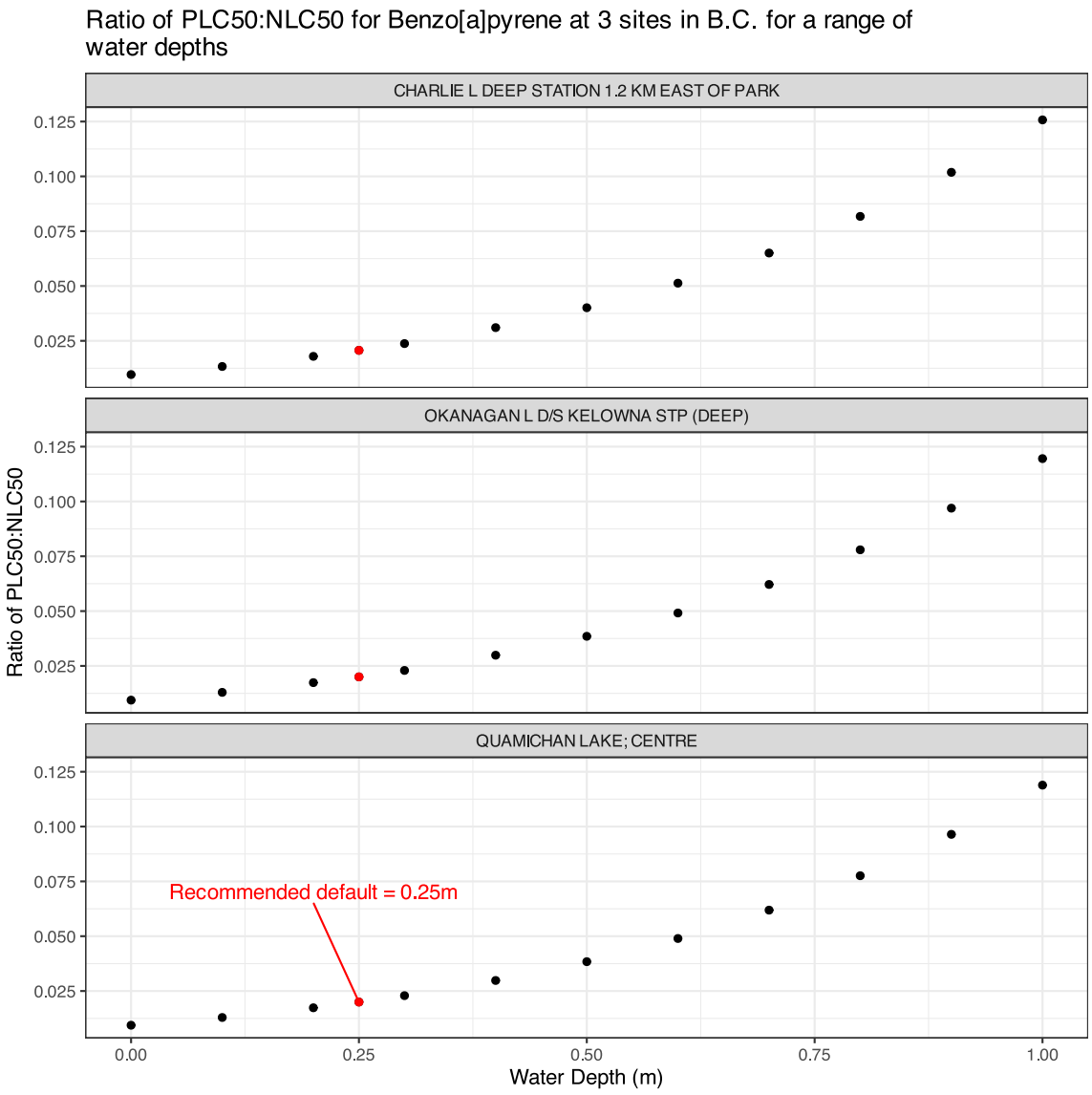
```
ggplot(depth_test_b, aes(x = depth_m, y = plc50)) +
  geom_point() +
  geom_point(
    data = filter(depth_test_b, depth_m == 0.25),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(depth_test_b, depth_m == 0.25, name == "QUAMICHAN LAKE;
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.25m",
    nudge_x = -0.05,
    nudge_y = 0.1
  ) +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "PLC50 for Benzo[a]pyrene at 3 sites in B.C. for a range of
water depths",
    x = "Water Depth (m)",
    y = "PLC50 (µg/L)"
  )
```



Show/Hide Code

```
ggplot(depth_test_b, aes(x = depth_m, y = plc_nlc_ratio)) +
  geom_point() +
  geom_point(
    data = filter(depth_test_b, depth_m == 0.25),
    colour = "red"
  ) +
  geom_text_repel(
    data = filter(depth_test_b, depth_m == 0.25, name == "QUAMICHAN LAKE;
```

```
CENTRE"),
    colour = "red",
    label = "Recommended default = 0.25m",
    nudge_x = -0.05,
    nudge_y = 0.05
  ) +
  facet_wrap(vars(name), ncol = 1) +
  labs(
    title = "Ratio of PLC50:NLC50 for Benzo[a]pyrene at 3 sites in B.C.
for a range of\nwater depths",
    x = "Water Depth (m)",
    y = "Ratio of PLC50:NLC50"
  )
```



Radiative transfer scheme (`nstr`)

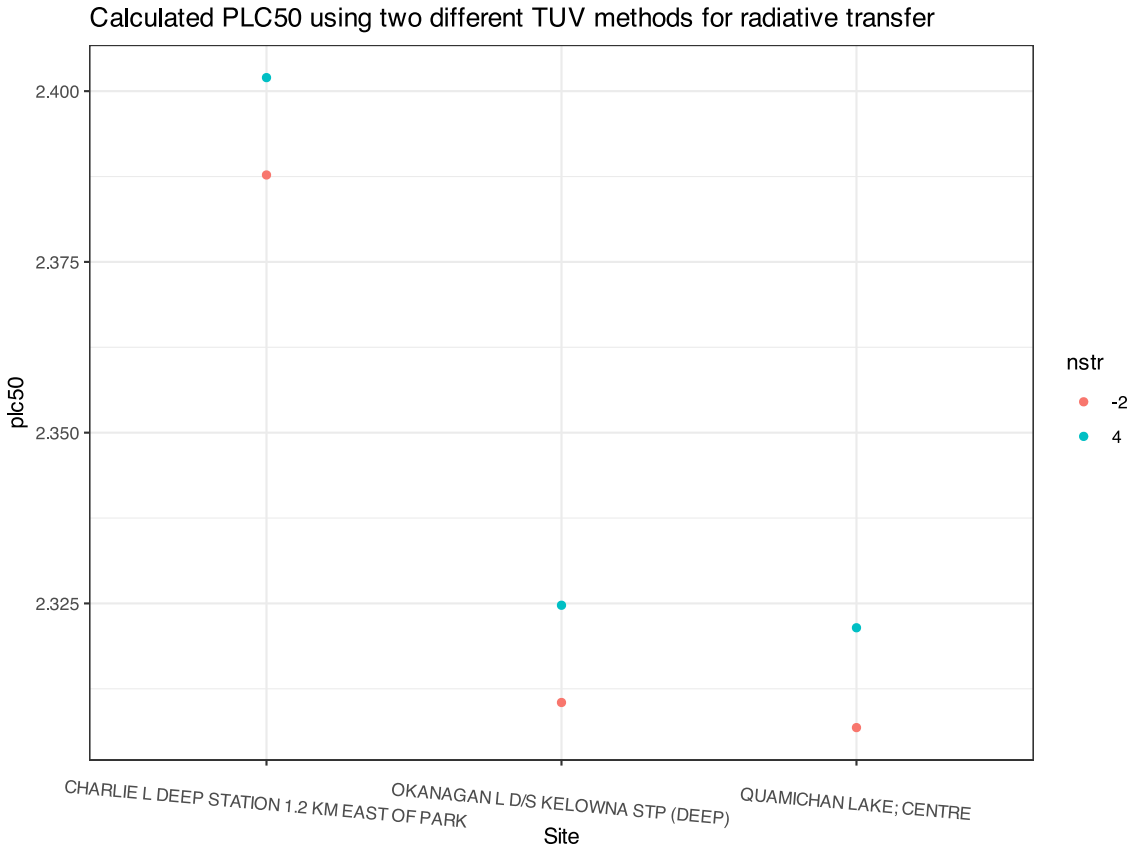
Number of streams for radiative transfer calculations:

- If `nstr` < 2, uses 2-stream delta-Eddington (faster)
- if `nstr` >= 2, uses n-stream discrete ordinates (more accurate: must be even number, maximum = 32)

Show/Hide Code

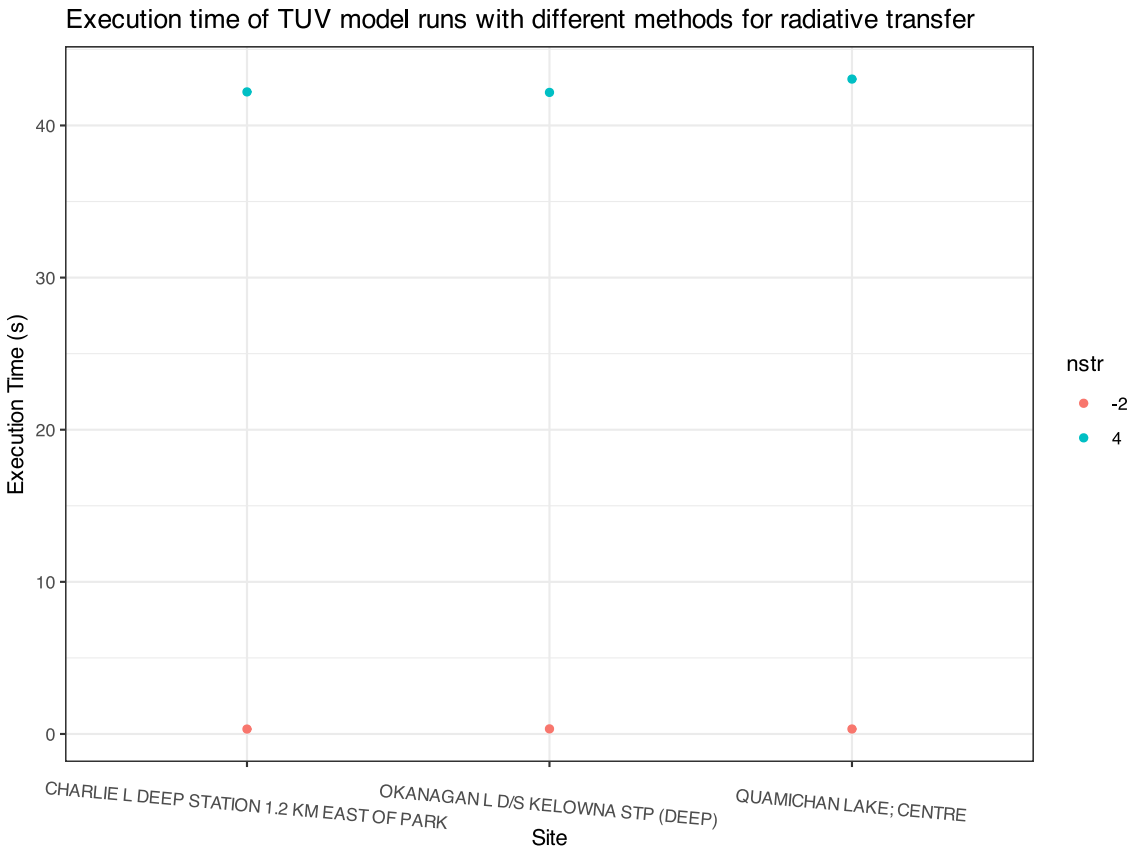
```
out <- multi_plc50(sites,
          pah = "Anthracene",
```

```
          varying = "nstr",
          vals = c(-2, 4),
          DOC = 5,
          o3_tc = 300,
          tauaer = 0.235) |>
  mutate(nstr = factor(nstr))

ggplot(out, aes(x = name, y = plc50, colour = nstr)) +
  geom_point() +
  labs(
   title = "Calculated PLC50 using two different TUV methods for radiative
transfer",
    x = "Site"
  ) +
  theme(axis.text.x = element_text(angle = 355))
```



Show/Hide Code

```r
ggplot(out, aes(x = name, y = timing, colour = nstr)) +
  geom_point() +
  labs(
    title = "Execution time of TUV model runs with different methods for
radiative transfer",
    x = "Site",
    y = "Execution Time (s)"
  ) +
  theme(axis.text.x = element_text(angle = 355))
```



We can see that there are small differences in the calculated PLC50 when using different values of `nstr`, with the values when calculated using `nstr = -2` being on average 0.61% lower than when using `nstr = 4`. Using `nstr = 4` however, is about 129 times slower than using `nstr = -2`. In most cases, unless high precision is required, it is likely that using the much faster `nstr = -2` should be the default.

Methylated Polycyclic Aromatic Hydrocarbons

Absorption spectra for methylated PAHs are not all available from published sources, so it would be beneficial to be able to approximate them for calculating water quality guidelines. In this section we will look at the feasibilty of using the absorbance spectra from a methylated PAH's parent compound as a proxy for the specific spectra. We will do this by calculating the PLC50 for various methylated PAHs for which we have absorbance spectra, and comparing these values to those calculated using the absorbance spectra of the parent PAH.

For these comparisons we will limit it to just one site in the Okanagan.

```
okanagan <- filter(sites, emsid == "0500236")
```

Show/Hide Code

```
# Define some functions:
ma_plot <- function(chemicals) {
  pahwq:::molar_absorption |>
    filter(chemical %in% tolower(chemicals)) |>
    mutate(
      chemical = factor(chemical, levels = tolower(chemicals))
    ) |>
    ggplot(aes(x = wavelength, y = molar_absorption, colour = chemical))
+
    geom_point() +
    labs(
     title = paste0("Molar absorption of ", chemicals[1], " and methylated
derivatives"),
      y = "Molar absorption (L/mol/cm)"
    )
}

nlc50_plot <- function(chemicals) {
  pahwq:::nlc50_lookup |>
    filter(chemical %in% tolower(chemicals)) |>
    mutate(
      nlc50 = vapply(chemical, nlc50, FUN.VALUE = 1),
      chemical = factor(chemical, levels = tolower(chemicals))
    ) |>
    ggplot(aes(x = log_kow, y = nlc50, colour = chemical)) +
    geom_point() +
    labs(
```

```
        title = paste0("NLC50 of ", chemicals[1], " and its methylated
derivatives"),
      y = "NLC50 (ug/L)"
    )
}

plc50_surrogates <- function(chemicals) {
  multi_plc50(
  okanagan,
  site = "name",
  pah = chemicals,
  varying = "Kd_ref",
  vals = c(1, 150),
  depth_m = 0.25
) |>
  group_by(Kd_ref) |>
  rowwise() |>
  mutate(
    Pabs_parent = p_abs(tuv_res, tolower(chemicals[1])),
    plc50_parent = plc50(Pabs_parent, PAH)
  ) |>
  ungroup() |>
  mutate(
    PAH = factor(PAH, levels = chemicals)
  ) |>
  pivot_longer(cols = c(plc50, plc50_parent),
               names_to = "abs_spectra",
               values_to = "plc50") |>
  mutate(
    plc_nlc_ratio = plc50 / nlc50,
    abs_spectra = case_when(
      abs_spectra == "plc50" ~ "specific",
      abs_spectra == "plc50_parent" ~ "parent"
    )
  )
}

plc50_plot <- function(df) {

ggplot(df, aes(x = PAH, y = plc50, colour = abs_spectra)) +
  geom_point() +
  facet_wrap(vars(Kd_ref), ncol = 1, scales = "free_y",
             labeller = as_labeller(function(x) paste0("Kd(305) = ", x)))
+
```

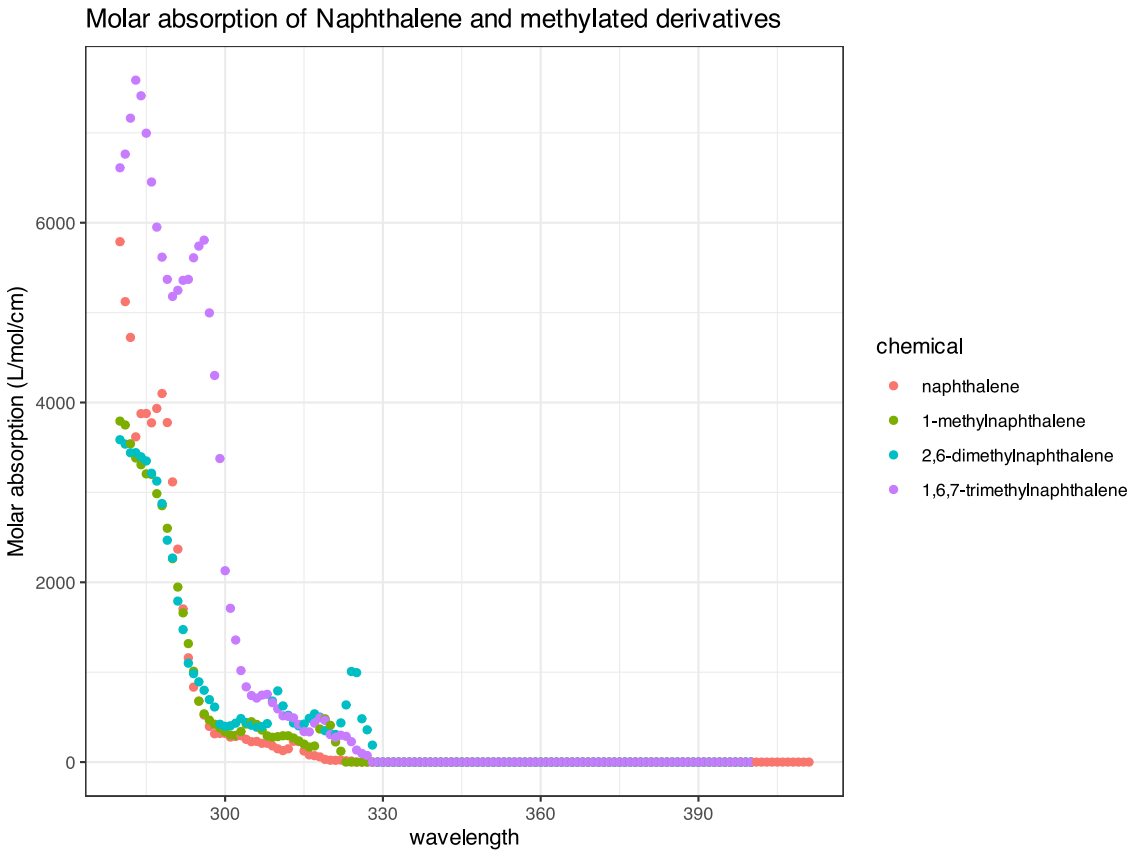
```
  geom_text_repel(
    data = filter(df, PAH != chemicals[1]),
    mapping = aes(label = round(plc_nlc_ratio, 3)),
    show.legend = FALSE
  ) +
  labs(
     title = paste0("Comparison of PLC50 of methylated ", chemicals[1],
", using\nspecific absorption spectra vs absorption spectra of parent
compound"),
    y = "PLC50 (ug/L)",
    colour = "Absorption spectra used",
    caption = "*Text labels indicate the ratio of PLC50:NLC50"
  )
}
```

Napthalene

To start, we can examine the molar absorption specra of three methylated Naphthalene derivatives, as compared to unmethylated Naphthalene:

Show/Hide Code

```
chemicals    <-    c("Naphthalene",    "1-Methylnaphthalene",    "2,6-
Dimethylnaphthalene", "1,6,7-Trimethylnaphthalene")

ma_plot(chemicals)
```

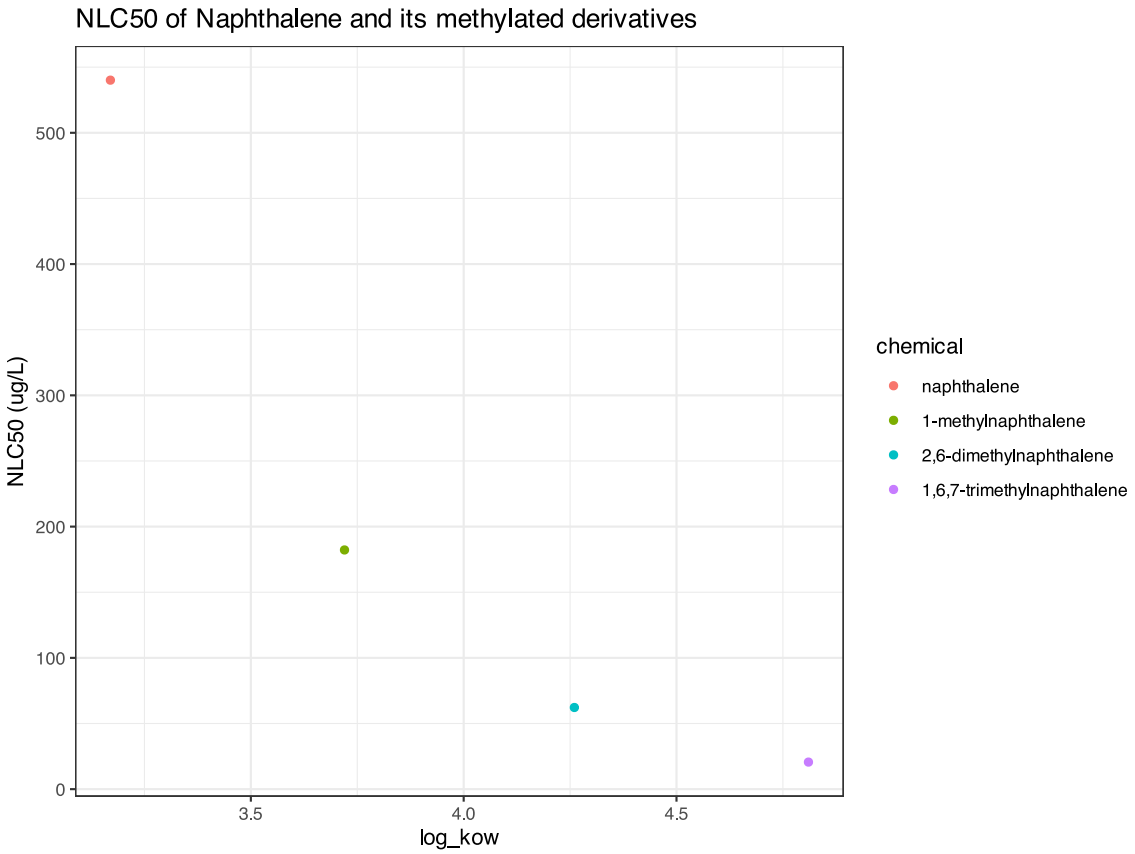


We can see in general that more highly methylated compounds have greater absorption, though it is not consistent across the spectrum.

We can also examine the properties and narcotic toxicity (NLC50) of Naphthalene and its methylated variants:

Show/Hide Code

```
nlc50_plot(chemicals)
```

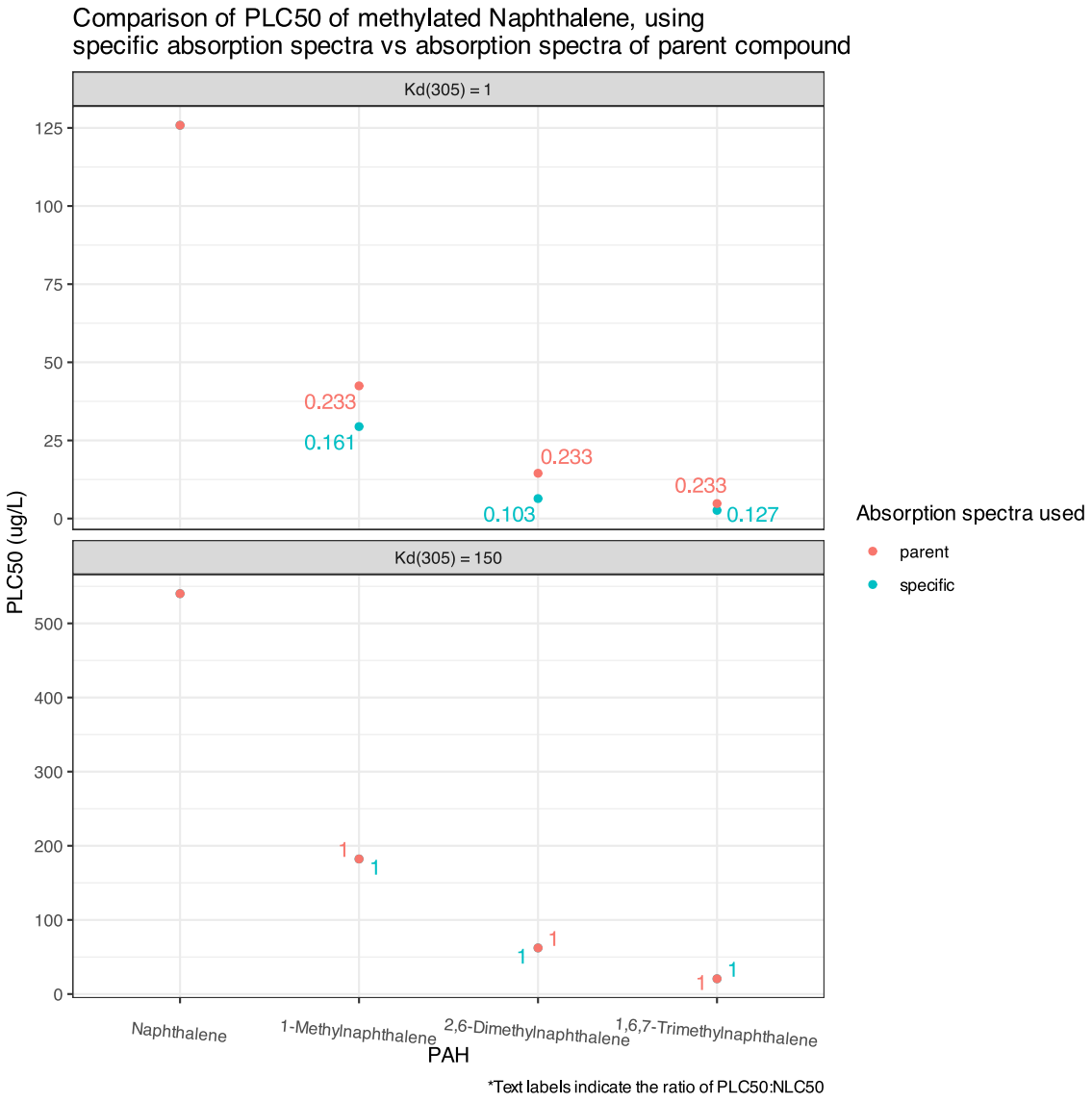


We can see here that 1,6,7-Trimethylnaphthalene has the highest log(KoW) and lowest NLC50.

Finally, we can compare the phototoxicity (PLC50) of Naphthalene and its methylated derivatives at the Okanagan site, at the two values of $k_{d,305}$ (1 and 150).

Show/Hide Code

```
df <- plc50_surrogates(chemicals)
plc50_plot(df) +
  theme(axis.text.x = element_text(angle = 355))
```



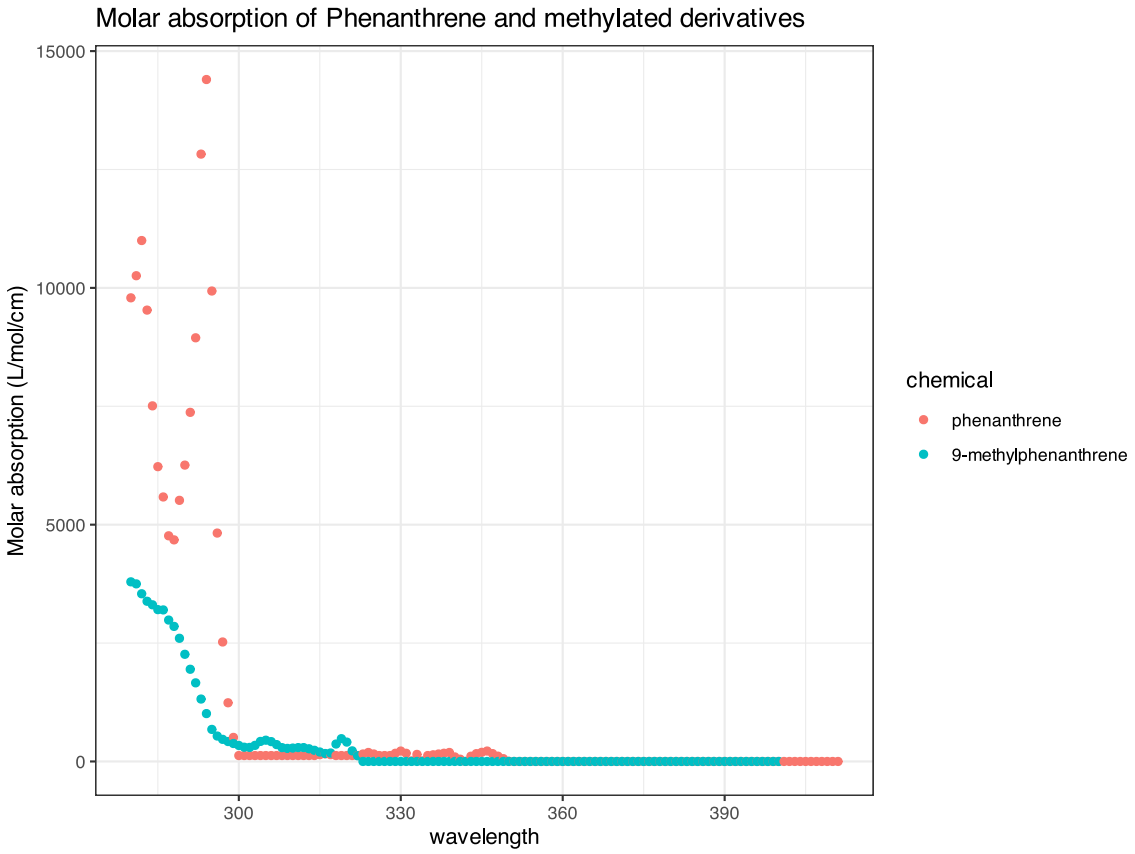
Here we can see that a lower PLC50 (higher phototoxicity) is calculated for all methylated naphthalenes when the absorption spectra of the methylated compound is used, as compared to when that of the parent compound (Naphthalene) is used. This difference is much greater when there is higher light penetration (lower Kd) - which is to be expected, as when there is less light penetration the PLC50 approaches the NLC50 so the absorption spectra of the chemical becomes irrelevant.

Phenanthrene

As above, we can visualize the absorption spectra of Phenanthrene and 9-Methylphenanthrene:

Show/Hide Code

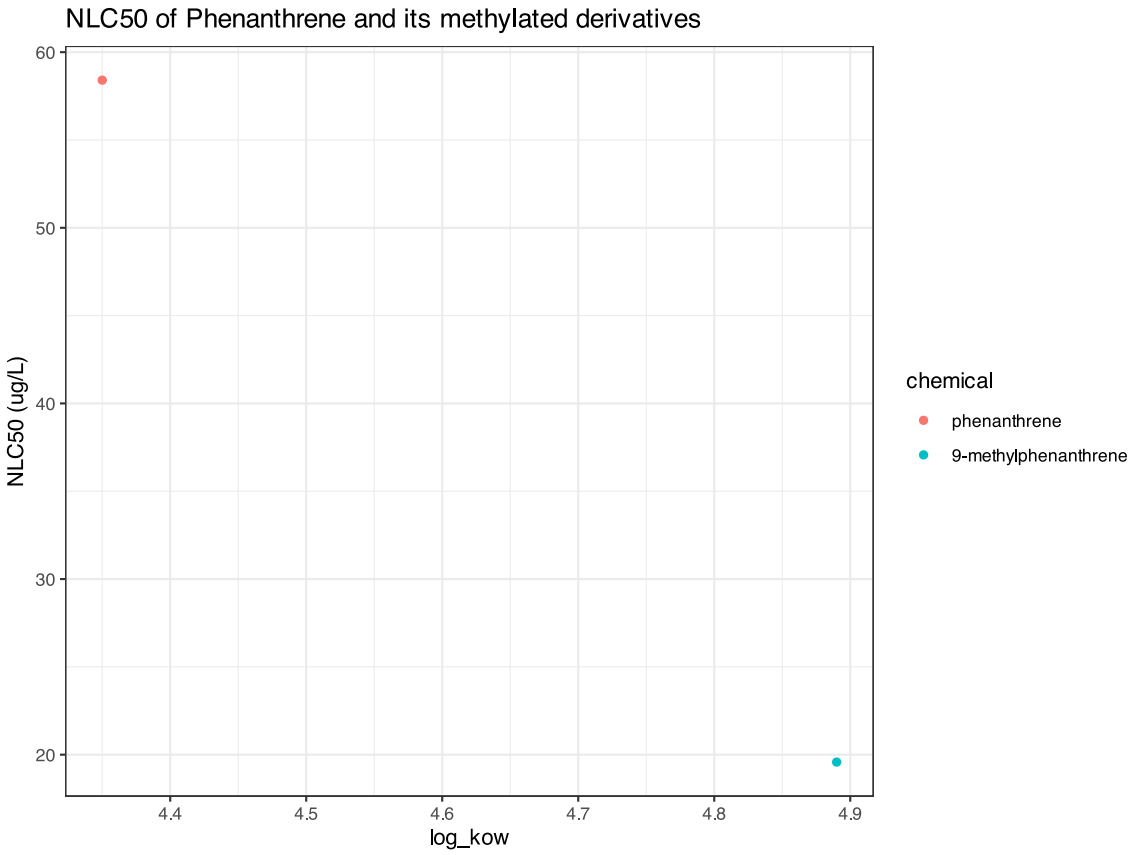
```
chemicals <- c("Phenanthrene", "9-Methylphenanthrene")

ma_plot(chemicals)
```



Here we see that the parent compound Phenanthrene has much higher absorption than 9-Methylphenanthrene at the low end of the light spectrum.

Show/Hide Code

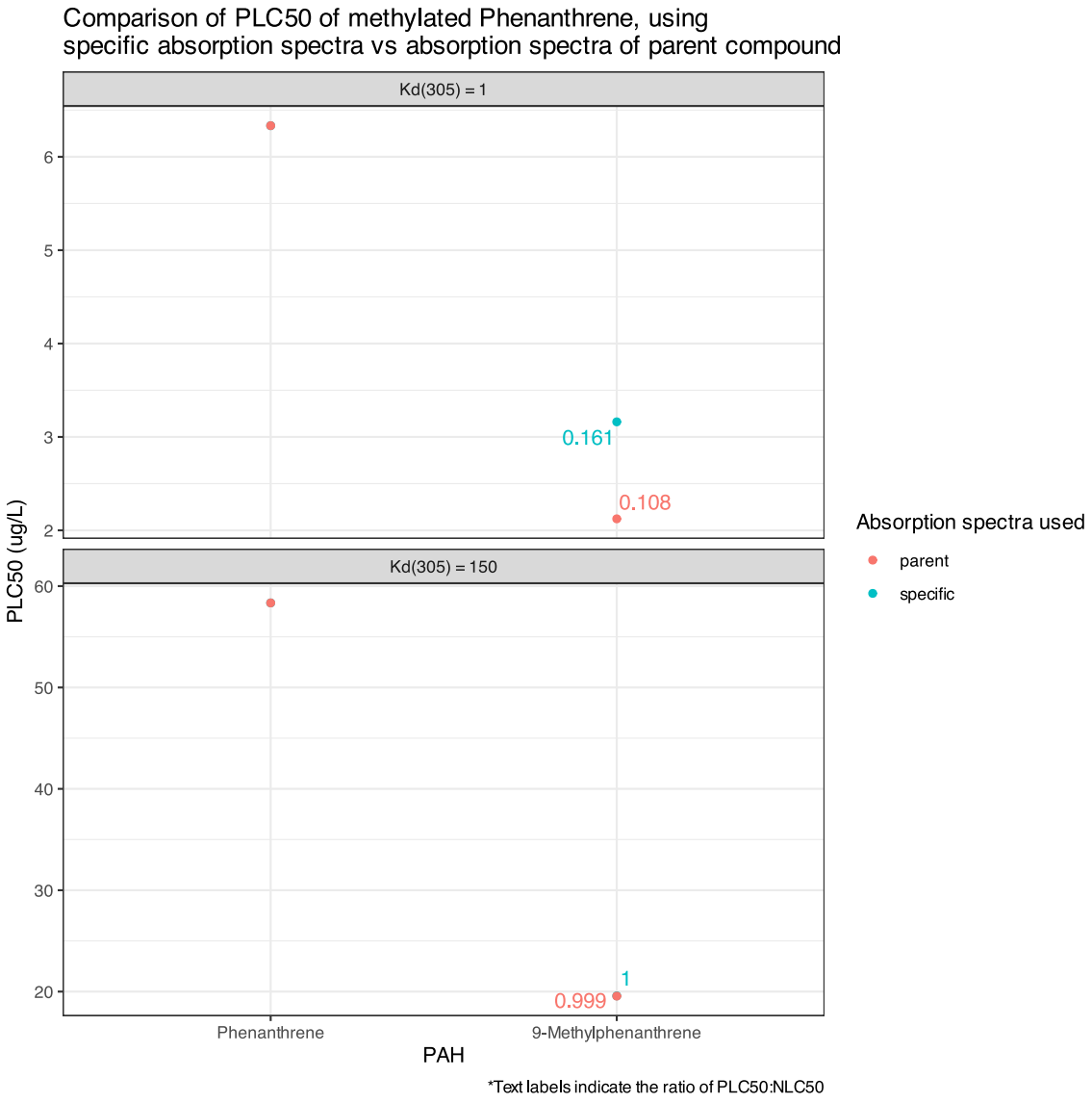
```
nlc50_plot(chemicals)
```



9-Methylphenanthrene has higher narcotic toxicity (lower NLC50) than its parent Phenanthrene.

Show/Hide Code

```
plc50_df_phenanthrene <- plc50_surrogates(chemicals)
plc50_plot(plc50_df_phenanthrene)
```



Using the parent molar absorption spectra for 9-Methylphenanthrene gives a more conservative PLC50 than using the specific spectra for the methylated compound. This is different than the case for Naphthalene.

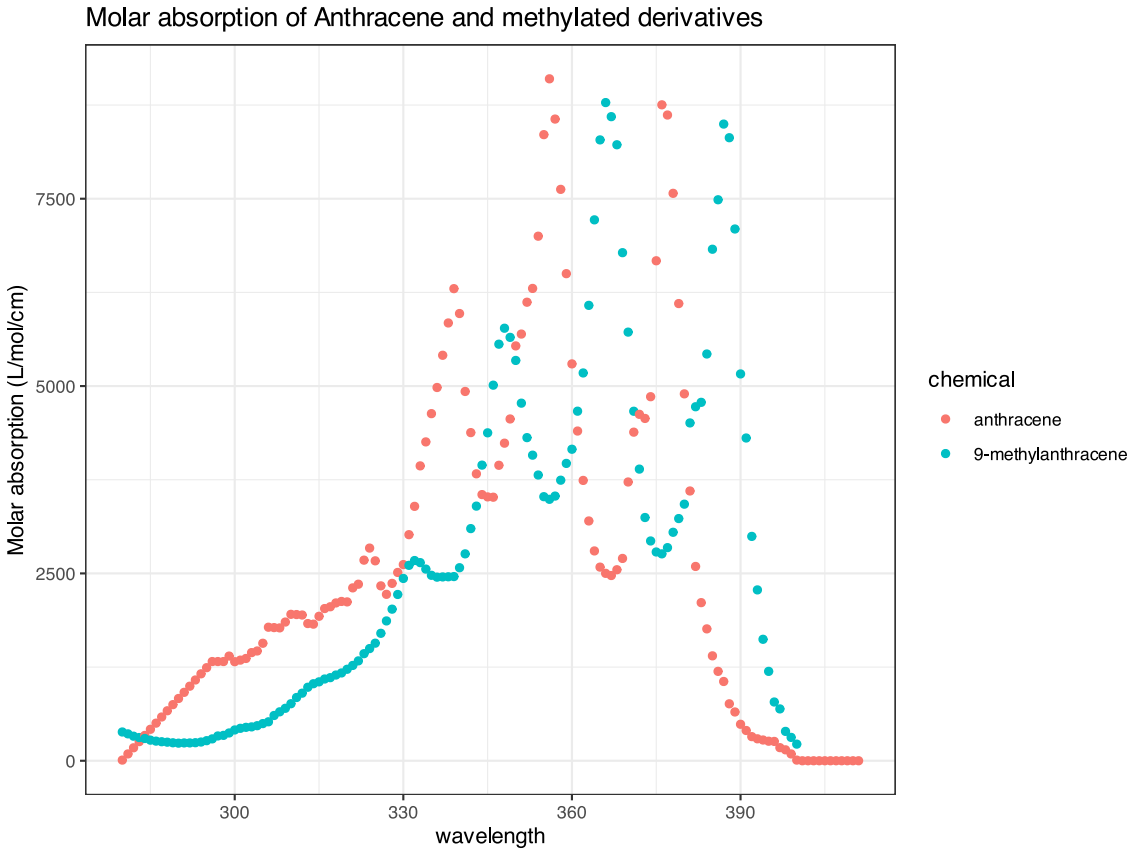
Similar to Naphthalene, this only appears to be substantially different at high light penetration (low Kd(305)).

Anthracene

As above, we can visualize the absorption spectra of Anthracene and 9-Methylanthracene:

Show/Hide Code

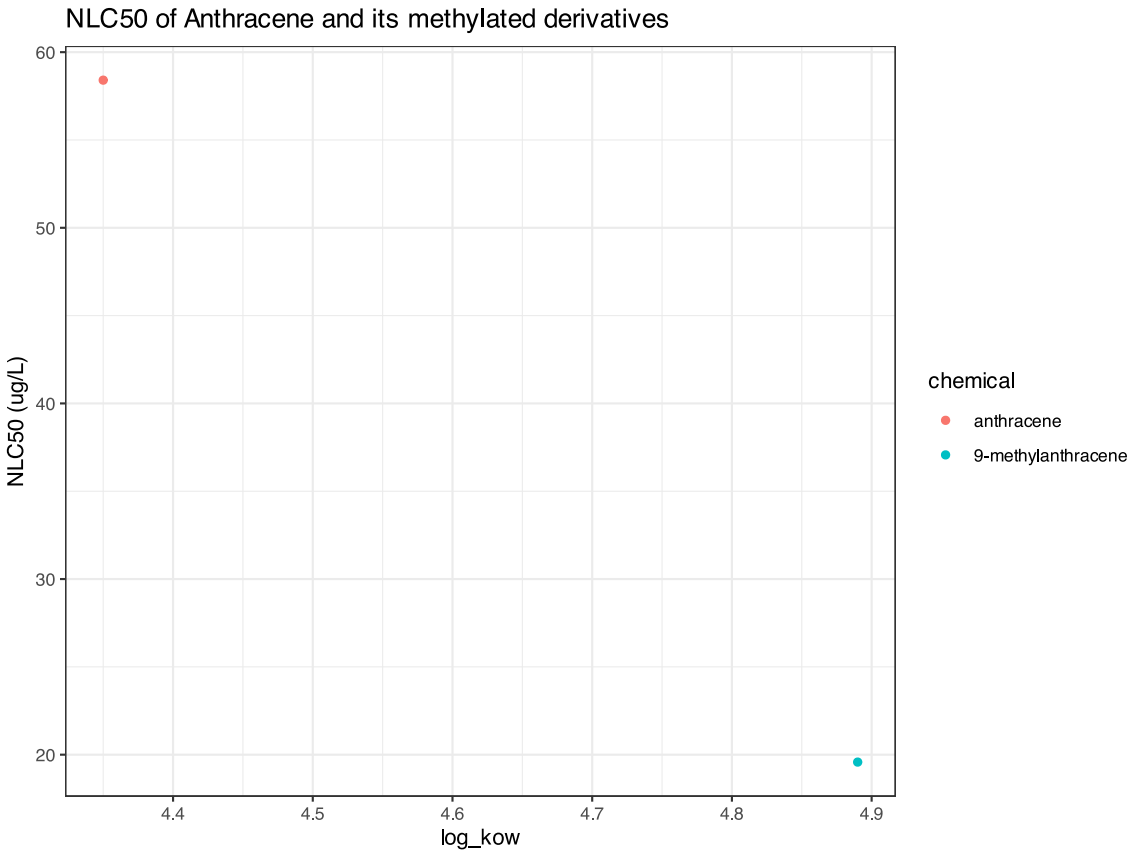
```
chemicals <- c("Anthracene", "9-Methylanthracene")
ma_plot(chemicals)
```



The absorption spectra for both Anthracene and 9-Methylanthracene is very broad compared to that of the other PAH compounds.

Show/Hide Code

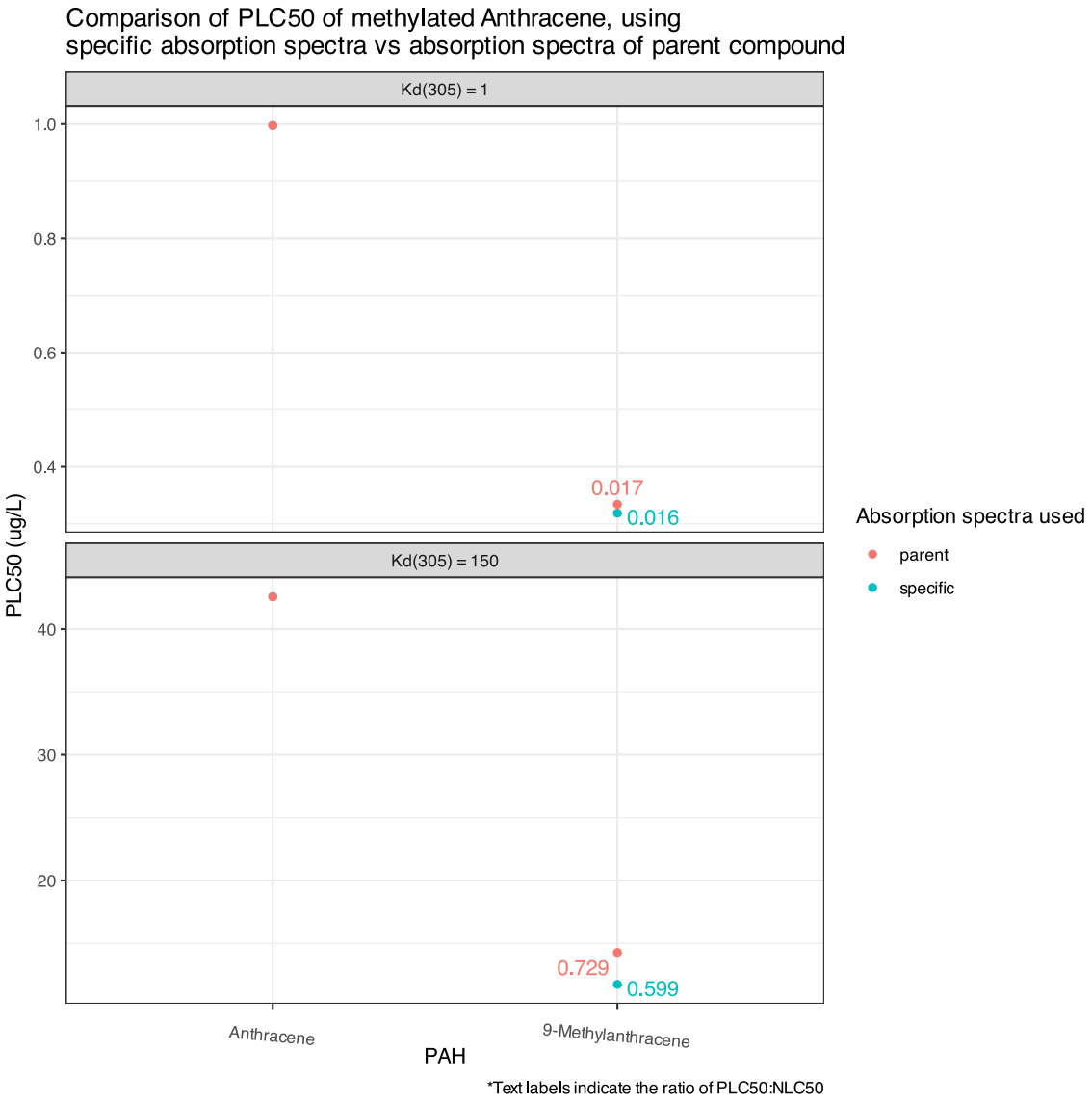
```
nlc50_plot(chemicals)
```



9-Methylanthracene has higher narcotic toxicity (lower NLC50) than its parent Anthracene.

Show/Hide Code

```
plc50_df_anthracene <- plc50_surrogates(chemicals)
plc50_plot(plc50_df_anthracene) +
  theme(axis.text.x = element_text(angle = 355))
```



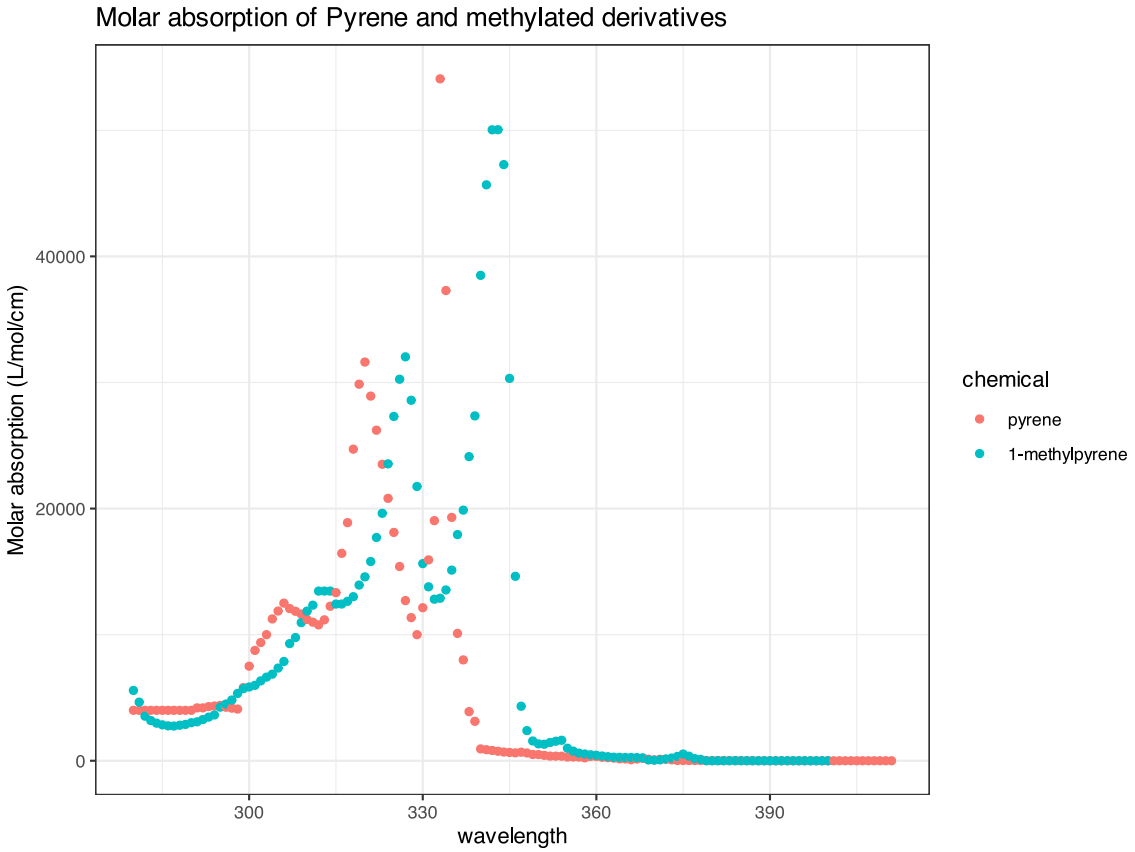
Using the parent absorption spectra for 9-Methylanthracene results in a less conservative PLC50 than if the specific absorption spectra is used. Contrary to that seen in the other PAHs above, this effect is still quite pronounced at high light attenuation (Kd(305) = 150), presumably because of the broad absorption spectra exhibited by both Anthracene and 9-Methylanthracene.

Pyrene

Show/Hide Code

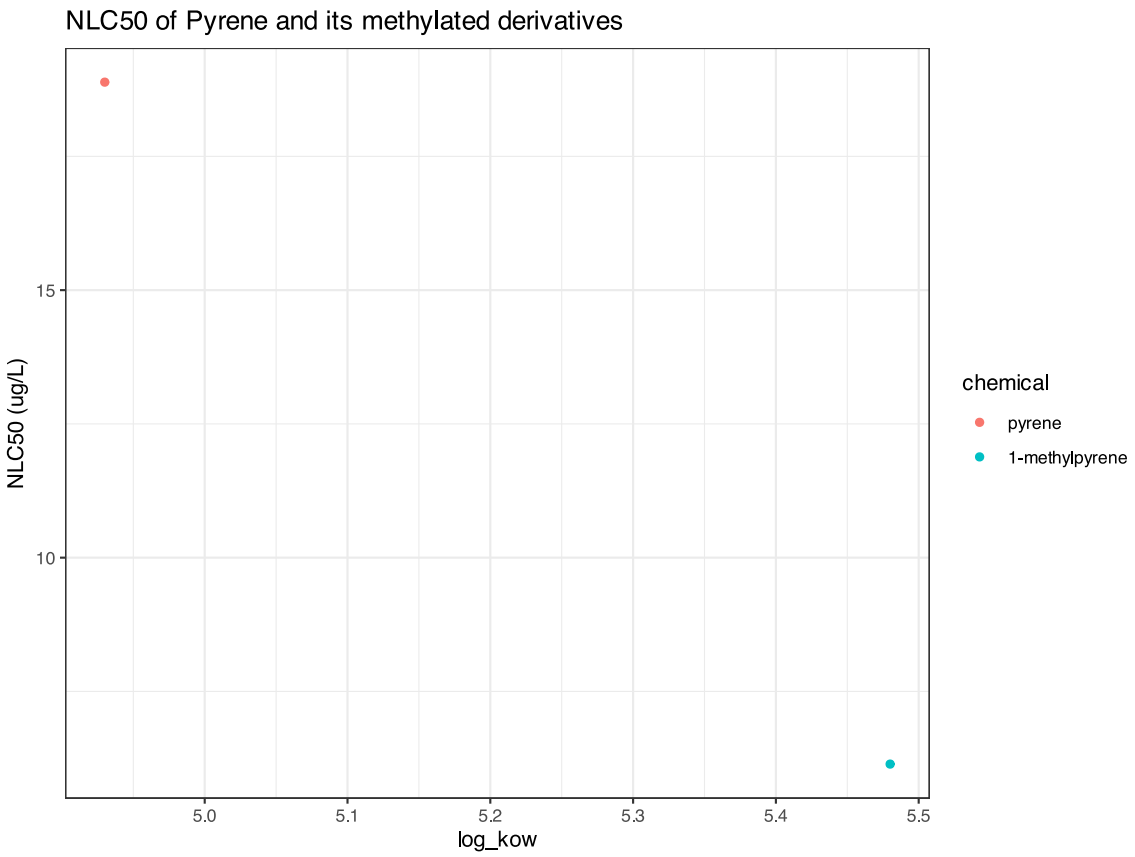
```
chemicals <- c("Pyrene", "1-Methylpyrene")
```

```
ma_plot(chemicals)
```



Show/Hide Code

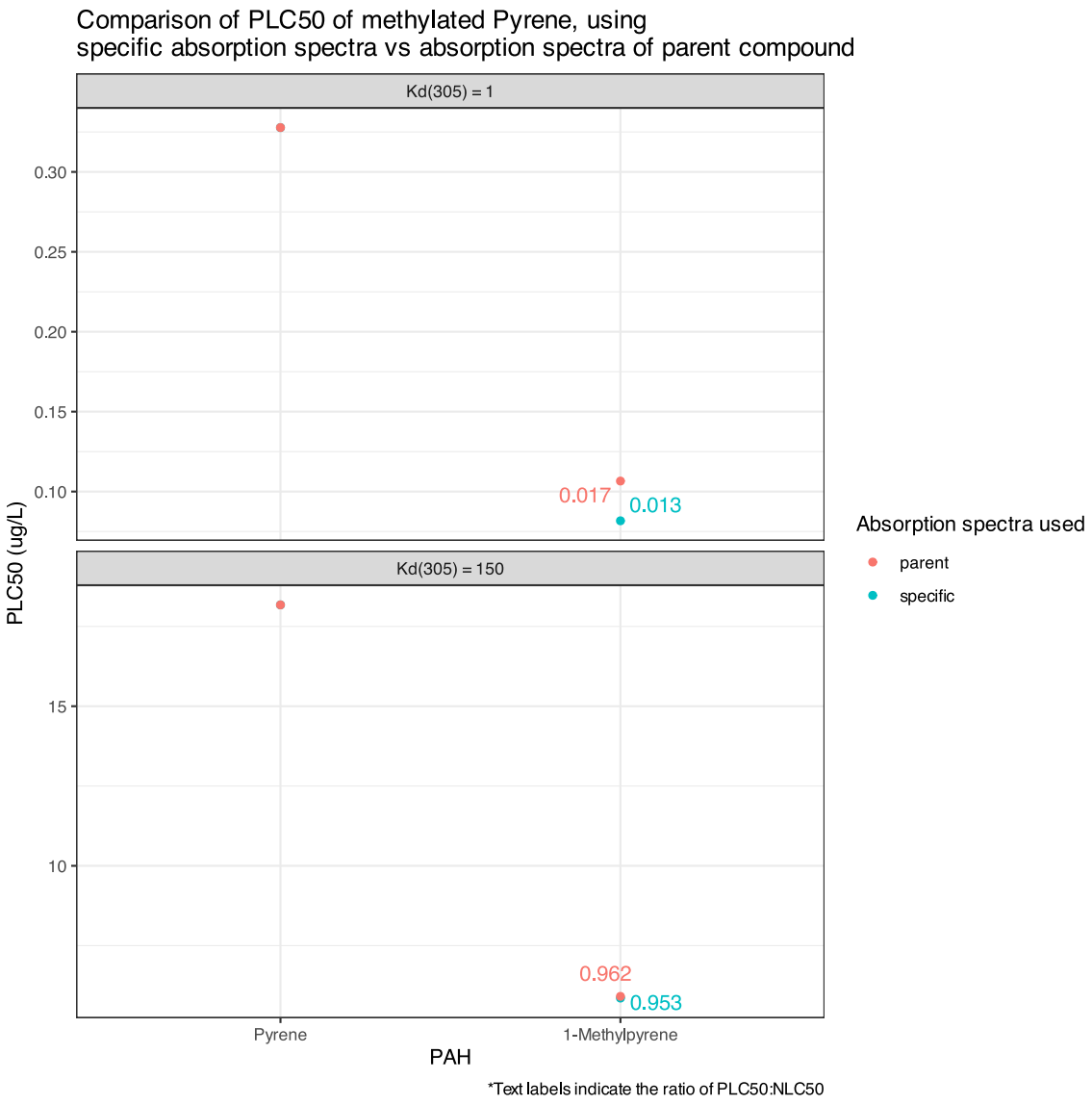
```
nlc50_plot(chemicals)
```



9-Methylpyrene has higher narcotic toxicity (lower NLC50) than its parent Pyrene.

Show/Hide Code

```
plc50_df_pyrene <- plc50_surrogates(chemicals)
plc50_plot(plc50_df_pyrene)
```

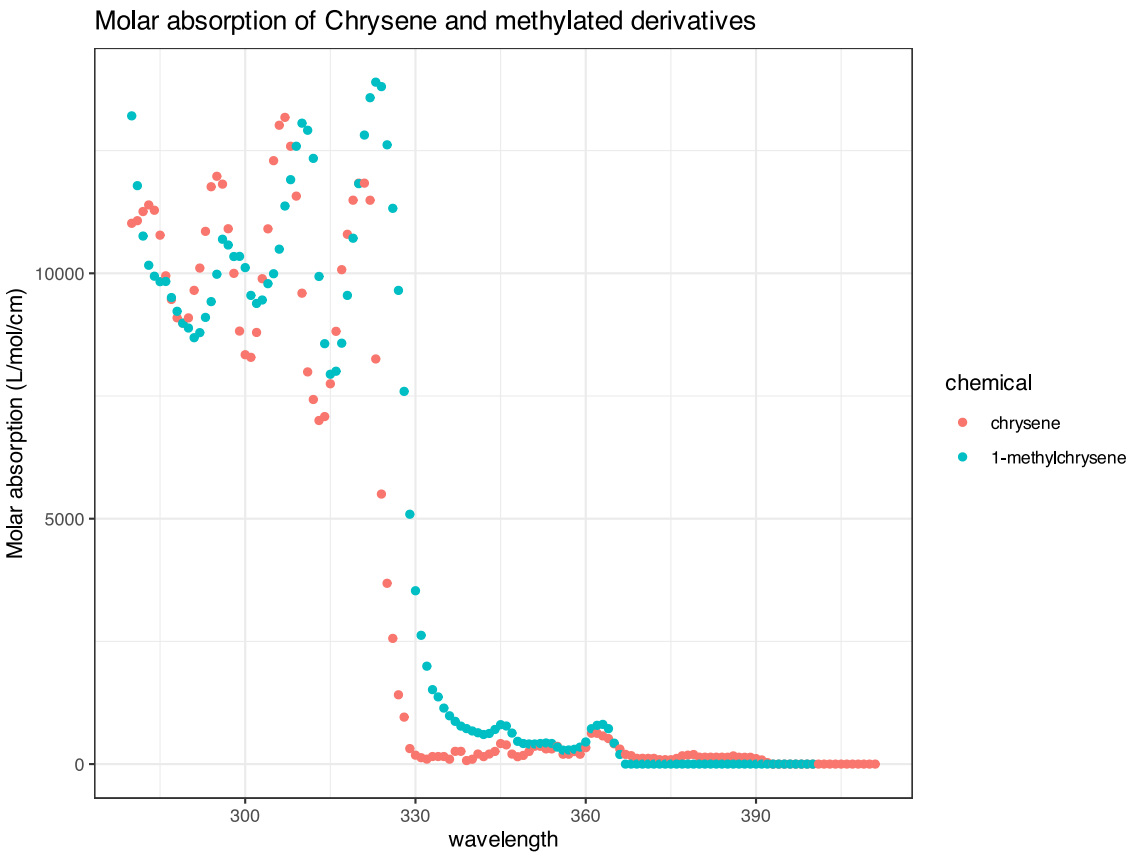


Using the parent absorption spectra for 9-Methylpyrene results in a less conservative PLC50 than if the specific absorption spectra is used.

Chrysene

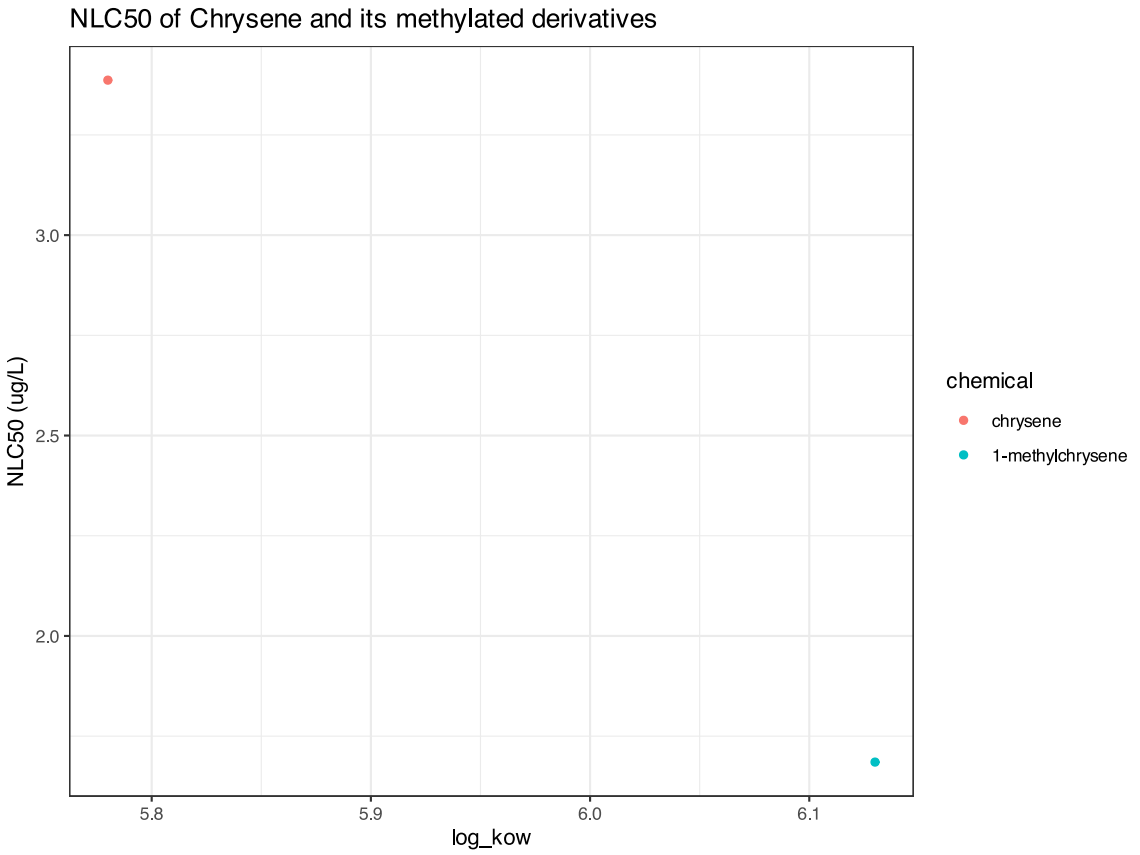
Show/Hide Code

```
chemicals <- c("Chrysene", "1-Methylchrysene")
ma_plot(chemicals)
```



Show/Hide Code

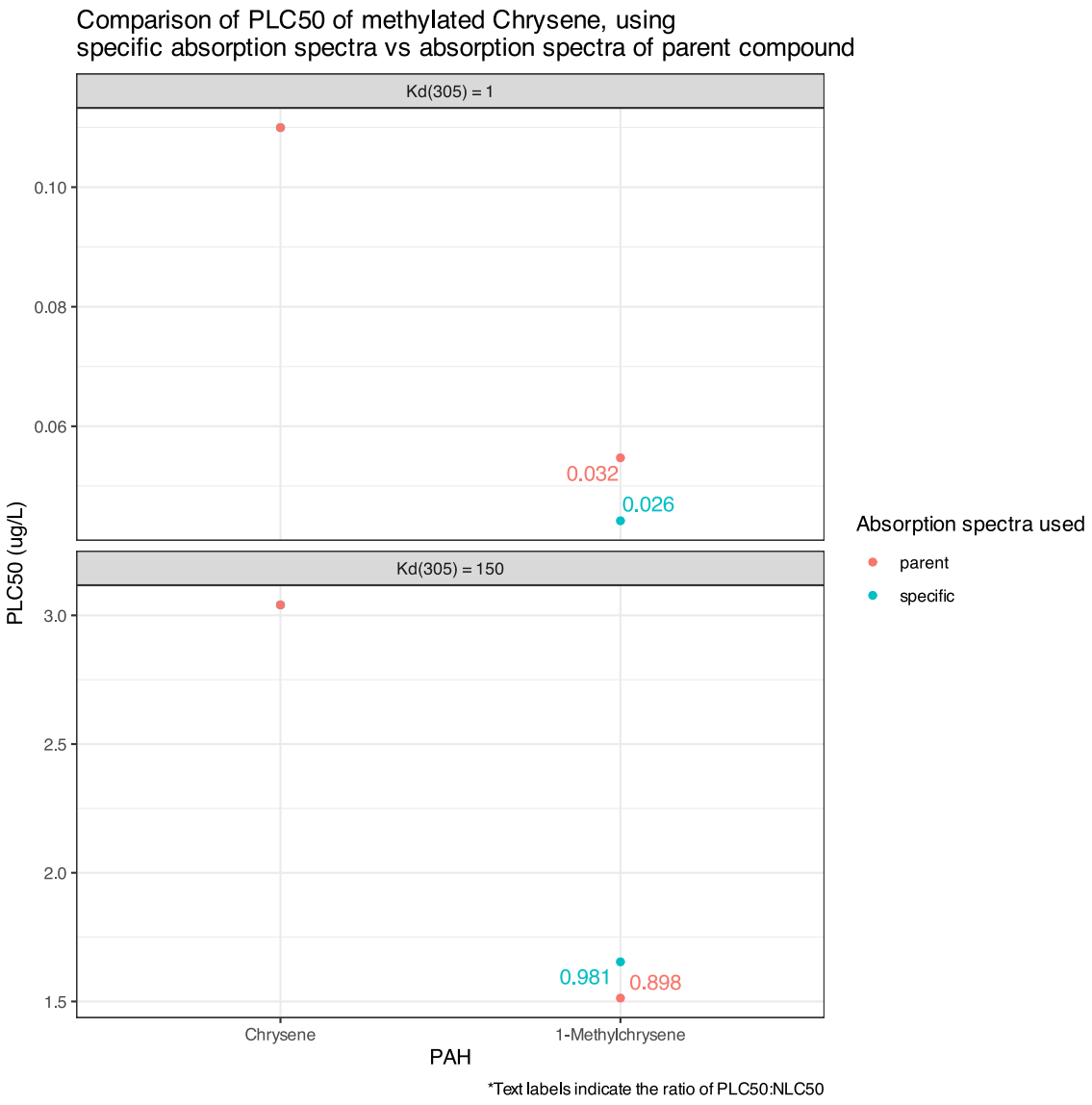
```
nlc50_plot(chemicals)
```



Similar to the other methylated PAHs, 1-Methylchrysene has a lower NLC50 (higher narcotic toxicity) than its parent Chrysene.

Show/Hide Code

```
plc50_df_chrysene <- plc50_surrogates(chemicals)
plc50_plot(plc50_df_chrysene)
```



The results for Chrysene and 1-Methylchrysene show that the effect of using the absorbance spectra of a parent compound can be different depending on the light intensity/attenuation. At low light attenuation (Kd(305) = 1), the specific spectra gives a more conservative PLC50 for 1-Methylchrysene than that obtained using the spectra from Chrysene, while the opposite is true at high light attenuation (Kd(305) = 100).

These results show that substituting the absorption spectra of a parent compound when that of a specific methylated PAH is unknown is possible, but also somewhat complicated. Differences in absorption spectra between methylated PAHs and that of their parent was quite variable across compounds. The difference in the resulting

calculated PLC50 is generally quite small and thus it is likely reasonable to use the absorption spectra of a parent when it is not available for a methylated PAH. However, the magnitude and even the sign of the difference is highly variable. In all cases examined, the NLC50 of the methylated compounds was lower than that of the parent compounds (i.e., they are more toxic), however the final phototoxicity (PLC50) depended on the differences in the absorption spectra and, in some cases, the level of light attenuation.

References

Bibliography

[1] D. P. Morris *et al.*, "The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon," *Limnology and Oceanography*, vol. 40, no. 8, pp. 1381–1391, 1995, doi: https://doi.org/10.4319/lo.1995.40.8.1381.

[2] P. Jourabchi, "Report on estimating light attenuation in support of the B.C. water quality guideline development for phototoxic PAHs," 2023.

[3] J. P. F. Fortuin and H. Kelder, "An ozone climatology based on ozonesonde and satellite measurements," *Journal of Geophysical Research: Atmospheres*, vol. 103, no. D24, pp. 31709–31734, 1998, doi: https://doi.org/10.1029/1998JD200008.