Chapter 2

PHYSICO-CHEMICAL STRATIFICATION OF THE TARGET BASIN OF PEECHI RESERVOIR

Abstract

This chapter gives a brief description of the materials and methods used in the study of physicochemical stratification of the target basin of Peechi Reservoir. Salient climatic and physiographic features affecting reservoir processes are presented. The sampling, preservation and analytical procedures of chemical parameters are also given.

Seasonal variations in water quality observed in an annual cycle are presented. Features of thermal stratification and thermal processes, which lead to thermal stratification, are briefly described. Since the basin has a relatively small shallow area, density currents are not observed. Concomitant with the thermal stratification there is a chemical stratification and details of chemical stratification are given. In the oxycline oxygen dependent species show a decline and anoxic products build up. These are correlated with seasonal variations.

A. MATERIALS & METHODS

1.2.1. Peechi Reservoir - a brief description

The Peechi Irrigation Project, commissioned in 1957 is one of the major irrigation projects in Kerala. The project utilizes water of Manali River, one of the major tributaries of Karuvannur River.
Peechi reservoir is situated in Thrissur district of the state. The geographical location of the reservoir is $10^026'N$ and $76^024'E$ (Figure 1.2.1). Even though it was conceived as an irrigation reservoir, during the course of time it became the only source of drinking water for one million people of Thrissur Corporation and adjoining gramapanchayaths (villages). Kerala Water Authority operates a 50.5 MLD treatment plant drawing raw water from the reservoir. Hence this reservoir plays a crucial role in the socio-economic development of the district.

The Manali River rises in the Vaniampara hills of the Western Ghats. The river flows 48 km before it joins the Kurumali River at Palakkadavu, near Arattupuzha. These two tributaries together form Karuvannur River, which drains into the Laccadives Sea through the backwaters. The terrain in the upper reaches of the Manali river consists of six valleys namely, Plachivakom, Puthumada, Olakara, Thalikuzhi and Pulakkal. Of these Thalikuzhi valley and Pulakkal valley join at about 6 km upstream of Peechi dam (KERI 1983).

1.2.2. *The catchment*

The catchment area of Manali River comprises of a number of hills, adjoining one another. These hills are extension of the Sholayar hill range, which is part of Western Ghats. A major portion of the catchment area is forestland with abundant growth of trees and plants. The forest type is moist deciduous and is notified as reserve forest for forest conservation measures. The thick vegetation and consequent stable soil cover restrict both erosion of soil and weathering of rock, which are the major sources of sediment load coming into the reservoir. Part of the catchment area consists of agricultural
Fig. 1.2.1 Location map of Peechi Reservoir
lands. The catchment area of the reservoir is 107.09 km². The water-spread area of the reservoir is 12.95 km². The presence of many islands of different sizes is unique to the reservoir. These islands effectively divide the reservoir into many small basins (KERI 1983).

The reservoir is formed by erecting a rubble masonry dam across Manali River. The estimated annual runoff to the reservoir is 209.5 Mm³ and the maximum storage capacity of the reservoir is 113.27 Mm³. The silting rate of the reservoir is 0.87 Mm³/year (KERI 1983). This is high when compared to other reservoirs in India (Murthy 1975; KERI 1983). The length of the dam is 213.36 m. Top level of the dam is at an elevation of +80.70 m. The full reservoir level is at +79.25 m.

Two main canals are constructed to deliver water for irrigation purposes. These canal systems draw water during post monsoon period. The basic features of the discharge of dam outlets are given in Table 1.2.1. (KERI 1983). Withdrawal for 50 MLD water treatment plant of KWA is continuous.

The high siltation rate in the reservoir reduces its holding capacity. The accumulation of silt also affects the quality of water and influences the aquatic processes. The reservoir has a labyrinthine shape. This uneven pattern of the reservoir bed divides the reservoir into many basins with different depths. During summer season, when water level recedes the submerged mounts become exposed. The maximum depth of the reservoir is in the basin adjacent to the dam. The mean depth of the reservoir is 8 m and the maximum depth is 34 m. Since the water withdrawal for irrigation is seasonal and varied, it affects the residence time calculation.
Table 1.2.1. Basic features of the discharge outlets of Peechi Reservoir.

(KERI 1983)

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The basin adjoining the dam is considered for this study since its water quality is significant from the treatment point of view. This basin is the deepest one and all the outlets of the reservoir are located in this basin. The sediment carried by the runoff settles in the upstream basins. The lotic and transient sections of the basins have appreciable shallow regions. In the target basin (basin adjacent to the dam) there is a channel, which extends to the dam wall. This channel ensures availability of water to the treatment plant even at the lowest reservoir level. The high siltation rate probably makes the channel a source of fresh unconsolidated silt.

Raw water is drawn for the drinking water treatment plant from the stretch adjoining the dam. This stretch acts as a basin of approximate capacity of 17,00,000 m$^3$ at full reservoir level (KERI 1983). This basin is charged by

(a) runoff from its local catchment area and
(b) from the main stretch which extends to the northeast and southeast directions.

In the absence of major hydraulic disturbances the basin adjoining the dam has its unique identity with regard to heat flux and stratification.

A section of the target basin is shown in Figure 1.2.2.

1.2.3. Sampling and analysis

The study was carried out in two ways

(a) stratification studies in the water column in the target basin and
(b) water quality variations in the intake of Peechi water treatment plant.

Occurrence and pattern of stratification is influenced by meteorological parameters like temperature, wind speed, wind direction, humidity,
Figure 1.2.2. Schematic view of the study basin, Peechi Reservoir
precipitation, solar radiation flux and evaporation. Hence the relevant meteorological parameters were acquired. All the relevant meteorological parameters except evaporation rate data were collected through the automatic weather station maintained by Kerala Forest Research Institute Peechi. Data for the years 1998-2000 were collected. Evaporation data for the study period (1998-2000) was collected from Kerala Engineering Research Institute, Peechi. These include daily data for solar radiation, humidity, maximum and minimum temperatures, and rainfall. Since meteorological data collected were from the immediate vicinity of the target basin, they were used without any further correction.

Evaporation measurements were done by KERI using evaporating pans. Evaporating pans are circular basins with a diameter of 1.2 m and a height of 0.25 m. They were exposed on a wooden platform so that air may freely circulate around the pan.

Stratification studies were carried out during the post monsoon period when the water level in the reservoir was low. For stratification studies depth profiling of various water quality parameters were selected. The task proved to be particularly elusive, since even mild variations in meteorological conditions could affect the intensity and occurrence of stratification.

The following physico-chemical parameters were measured for stratification studies.

i) Temperature

ii) Dissolved oxygen.

iii) Total Iron
iv) Sulfide
v) Phosphorous
vi) Nitrate
vii) Turbidity

1.2.4. Instruments

The instruments and equipments used in the study are described below.

1.2.4a. Water sampler

Water samples were collected using constant volume Krammer water sampler. The sampler has a cylindrical body made up of transparent plexiglass. The sampler volume is 1 L. A gravity messenger was used to activate the lid at desired depth. Provision is provided to siphon the water to container without trapping air.

1.2.4b. Thermometer

For temperature measurements digital thermometer was used. The measurement accuracy of the thermometer is ± 0.1°C.

1.2.4c. pH meter

pH measurements were done using Systronics digital pH meter (model 335). The meter was calibrated before each measurement using standard buffer solutions.

1.2.4d. Turbidity meter

For turbidity measurements Systronics make digital nephelo-turbidity meter was used. The instrument was calibrated as per manufacturer’s directions using standard formazin suspensions of known turbidity.
1.2.4e. Conductivity meter

Conductivity measurements were carried out using calibrated Century make digital conductivity meter (model CC601-P). The measurement unit was $\mu$Scm$^{-1}$

1.2.4f. Hach DREL 2010 Advanced Water Quality Laboratory

Field measurements of chemical parameters were done using Hach DREL - 2010 Advanced Water Quality Laboratory. This field water quality laboratory consists of data logging DR 2010 VIS spectrophotometer, a CO150 conductivity meter (Hach) and pH meter.

1.2.4g. UV-VIS spectrophotometer

For SUVA$_{254}$ measurement Varian UV-VIS spectrophotometer (Model Carey 50) was used.

1.2.5. Analytical Procedures

All chemicals used were of analytical grade unless otherwise specified. For analyses using Hach Advanced water quality laboratory, special reagents were used, which were supplied by the manufacturer.

1.2.5a. Dissolved oxygen.

Dissolved oxygen was measured using Winkler method (APHA 1998). Water samples were collected in BOD bottles of 60 mL volume. Dissolved oxygen was fixed at the sampling site itself. Fixed samples were kept in iceboxes and transported to the laboratory and analysis was conducted within four hours of sampling.
1.2.5b. **Iron**

Iron was measured spectrophotometrically using Hach Advanced Water Quality Laboratory. The proprietary reagent FerroVer Iron reagent (Cat No 21507 – 69) was used for colour development. This reagent is 1,10 phenanthroline based and buffered. The measurement wavelength is 510 nm. The range of measurement was 0-3.0 mg/L. The Estimated Detection Limit for the method is 0.02 mg/L.

1.2.5c. **Nitrate**

Nitrate concentration in the water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data logging spectrophotometer. The proprietary reagent Nitra Ver 5 Nitrate reagent (Cat No 14034 – 99) was used for the analysis. The measurement wavelength is 500 nm. The range of measurement for the method is 0.0-30.0 mg/L.

1.2.5d. **Phosphate**

Phosphate concentration in water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data logging spectrophotometer. The proprietary reagent Phos Ver Phosphate reagent (Cat No 14034 – 99) was used for the analysis. The measurement wavelength is 890 nm. The range of measurement for the method is 0.0-2.5 mg/L. The Estimated Detectable Limit is 0.01 mg/L.

1.2.5e. **Sulfide**

Sulfide concentration in water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data
logging spectrophotometer. Proprietary reagents (Cat No 1816 – 42 & 1817 - 42) were used for the analysis. The principal ingredient was N, N – dimethyl p-phenyldiamine oxalate. The measurement wavelength is 665nm. The range of measurement for the method is 0.0-0.6 mg/L. The Estimated Detectable Limit is 0.01 mg/L.

1.2.6. Sampling and preservation

Sampling was done according to USEPA guidelines (EPA 1983). Sampling of water from the intake of the treatment plant was done using a hand held surface water sampler. Samples were collected in clean rinsed 5L white polyethylene cans from the raw water channel of the water treatment plant. The sampling depth in the channel is 0.2 m. pH of the water samples was measured online using a pre calibrated digital pH meter.

For total iron determination samples were filtered through 0.45-µm filters. This was followed by the addition of 0.2 mL con. HNO₃ as preservative. Analysis was done within 24 hours.

Water quality parameters relevant to drinking water and treatment process were analyzed. The parameters selected included pH, turbidity, electrical conductivity, total alkalinity, total hardness, calcium hardness, magnesium hardness, total iron, specific UV-absorbance at 254 nm and chloride.

1.2.7. Water quality variations at the intake of Peechi Water Treatment Plant

The water quality variations affect the efficiency of the drinking water treatment plant. The variations were studied by regular sampling and analysis.
of various physicochemical parameters of water quality. The study period extended from November 1998 to June 2000. Samples were collected on a fortnightly basis. No sampling was carried out during the monsoon season since the reservoir undergoes total mixing due to large and steady influx. No mobilization of iron was noticed during this period. So the study was confined to post monsoon period (November – May), which also corresponded to low water level in the reservoir.

B: RESULTS AND DISCUSSION

1.2.8. Introduction

The water quality in a reservoir on a long term basis is influenced by:

1. Geomorphology as a barrier to horizontal and vertical currents
2. Dissolved and suspended material budget of the reservoir
3. Water balance, which is influenced by overflow, temperature, seepage and evaporation.

Hence these aspects are presented separately

1.2.9. Geomorphology

Geomorphology of a water body influences the physicochemical processes in the water body. Since the physical processes directly influence the material and energy exchange processes in the reservoir, this leads to water quality variations. The morphological parameters like shape, volume and depth of the reservoir strongly influence and control the various mixing processes and material cycling in the reservoir. From the site map of Peechi reservoir it is evident that the shoreline of the reservoir is labyrinthine. Due to this labyrinthine shape wind influence is minimal. The wind velocity is also
low. Hence the formation of strong surface waves is negligible. The absence of strong surface winds rules out surface mixing. The presence of shoreline vegetation and scattered islets further prevent strong winds.

For the purpose of discussion the reservoir can be envisaged as a number of basins, which are interconnected. When there is no inflow of water from contributing streams (November to May) these basins can be considered as independent water bodies. During this period, the horizontal flow of water from other basins to the first basin (adjacent to the dam) occurs. Hence the water quality variations observed in the first basin is more important from the treatment point of view.

The basin targeted for this study has a triangular cross section and is of maximum depth. The inflow to the first basin enters from the far end passing through other basins. The particles carried over by these inflows settle in the distant shallow basins. So the carry over of materials from other basins to this basin is negligible.

1.2. 10. Water and water borne material balance of the reservoir

Peechi reservoir is in a state of transition from oligotrophic to mesotrophic in character. The euphotic zone depth and phosphate concentration clearly establish this fact (Wetzel 2001). The geochemical nature of formations (granite with interspersed charnakite) supports the low mineral composition (KERI 1983). Since the catchment area consists of reserve forest with agricultural land along its outer edge, they contribute to the nutrient budget of the reservoir. But the overall nutrient concentration is low.
1.2.1 Water balance – influence of temperature, overflow, seepage and evaporation

For any reservoir,

\[ \text{Inflow} = \text{Outflow} + \text{Seepage} + \text{Evaporation} \]

\[ Q_{\text{inflow}} = Q_{\text{outflow}} + Q_{\text{seepage}} + Q_{\text{evaporation}} \]

The residence time of water influences the material exchange processes and energy budget of the water body. Residence time influences the nutrient status of the reservoir. The residence time of water in the Peechi reservoir is estimated as twenty-two months.

Peechi reservoir stands over bedrock of more or less intact granite gneiss located below a few meters of overburden consisting of soil and laterite. No detectable seepage is observed on the exposed edges of the reservoir or down the dam site. Hence it is reasonable to assume that seepage from the reservoir is negligible. The reservoir is fed only through precipitation and subsequent surface runoff. The inflow to the reservoir is confined mainly to the monsoon period and the rainfall pattern affects the water level in the reservoir. The temporal variation in the water level during a typical year and the corresponding rainfall are shown in Figures 1.2.3. and 1.2.4.

Major outputs from the reservoir are the seasonal discharge for irrigation and the continuous supply to the drinking water treatment plants. The crop management in the irrigated areas are so planned that demand for irrigation water is limited to the period from November to March. The only continuous withdrawal is for KWA water treatment plant (50 MLD). This coupled with evaporation and seepage accounts for the fall in water level. The
Figure 1.2.3. Temporal variation in water level for a typical year (1999)
Figure 1.2.4. Temporal variation in rainfall for a typical year (1999)
geological setting excludes any significant seepage from the reservoir. Accounting for the discharge, the daily evaporation rate for a typical year is shown in Figure 1.2.5. The level of water in the reservoir falls rapidly when the irrigation canal is open (10.62 m³/sec). Left bank canal is at an elevation of 67 m and it can be operated only during the months of July to November. During the remaining months withdrawal for irrigation water can be discharged only through the right bank canal, which is at an elevation of 53.3 m. The right bank canal discharges at a rate of 7.08 m³/sec. A total daily discharge of 0.97 Mm³, which is 1.1% of the estimated reservoir capacity, resulted when all the three discharge outlets of the reservoir are operational. But this situation occurs only for a few days in a year. During the problem period (November to May) the water level in the reservoir is below the left bank canal outlet level. Since the water level falls off rapidly and the safety level for the priority water supply has to be retained, irrigation supply is curtailed when the level reaches a critical level. This leads to a conflict of interest between the priority water supply and the originally intended use for irrigation.

Rate of evaporation from a reservoir (mass/unit time) depends on the concentration of dissolved constituents, surface films, wave generation, temperature and wind. As revealed by analysis dissolved constituents in the surface water are low. Visual inspection and analysis of surface water did not show the presence of petroleum films or floating iron oxide. The wind pattern shows that it is weak during the period, November – May. The ambient temperature and humidity variations are shown in Figure 1.2.6. and
Figure 1.2.5. Evaporation pattern for a typical year (1999)
Figure 1.2.6. Variations in daily maximum temperature for a typical year (1999)
1.2.12. **General comments on annual cycle of water quality**

Essential water quality parameters relevant to drinking water were measured periodically to cover all seasons. The results are presented in Table 1.2.2. Corresponding sampling dates are given in Table 1.2.3. In all cases pH is within agreeable range for surface raw water. During rainy season alkalinity shows a lower value from the average. This may be due to dilution of reservoir water by fresh rainwater. However the raw water collected from the water treatment plant intake shows a higher alkalinity, magnitude of the value reaching high at times of stratification. This can be explained in terms of the mobilization of calcium and magnesium phosphate in the sediment and their confinement in the hypolimnion (Stumm and Morgan 1996). The dissolution of calcium carbonate from the sediment is ruled out since the calcium alkalinity concentrations are far below the saturation values (Stumm and Morgan 1996). Calcium concentrations also show correspondingly higher values.

High turbidity values (>5NTU) are showed during times of intense rain, particulates larger than 2μm settle during their passage through the stretch of the reservoir. The low persistent turbidity observed during non-rainy period is mainly due to the particles derived from the sediment circulating in the hypolimnion. All other chemical parameters are well within the prescribed limit for drinking water. Seasonal variations of water quality parameters relevant to drinking water treatment are shown in Figures 1.2.8 to 1.2.12.
Figure 1.2.7. Variation in ambient humidity for a typical year (1999)
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Figure 1.2.8a. Seasonal variation in pH of reservoir water

Figure 1.2.8b. Seasonal variation in electrical conductivity of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)
Figure 1.2.9a. Seasonal variation in TDS of reservoir water

Figure 1.2.9b. Seasonal variation in turbidity of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)
Figure 1.2.10a. Seasonal variation in total iron of reservoir water

Figure 1.2.10b. Seasonal variation in total alkalinity of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)
Figure 1.2.11a. Seasonal variation of chloride of reservoir water

Figure 1.2.11b. Seasonal variation of magnesium of reservoir water
(Sampling dates corresponding to sample number are given in Table 1.2.3.)
Figure 1.2.12a. Seasonal variation of total hardness of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)
1.2.13. Stratification

Stratification studies were carried out in the reservoir during pre-monsoon period when the problem existed at the treatment plant and water level in the reservoir was below 67 m.

Sampling was done at a point 25 m away from the dam. The euphotic zone depth was measured using Secchi disc (Wetzel 1983). The average value of euphotic zone depth was found to be 1.75 m.

1.2.14. Temperature

Ambient temperature at the time of measurement was 32.6°C. Temperature measurements were done at various depths. Temperature variations in the water column are shown in Figure 1.2.13. Temperature decreased with increasing depth. At 0.1 m depth the temperature was 31.8°C. Temperature dropped to 26.9°C at 15 m depth. Thermocline occurs at 7 m. Hence it is expected that corresponding pycnal and chemical stratification can be possible.

Warm climate follows the monsoon. The solar radiation received at 10° N latitude is about 895 cal cm⁻² d⁻¹ during the month of April (Thompson 1999). The average day temperature is fairly high whereas night temperature reaches a minimum during this time. Solar radiation is received for maximum period during this season. This high rate of solar insolation warms up the euphotic zone. The subsurface water is stagnant and does not receive enough solar radiation. This leads to a cooling below the euphotic layer. Since turbulence is minimum, density stratification occurs. This type of temperature transition is fairly sharp with lakes and reservoirs in the temperate region.

With considerable shallow regions a density current is often established in reservoirs due to heat loss (Wells and Sherman 2001). In Peechi reservoir there is no identifiable shallow regions due to the steep slope at the basin edges. Hence any disturbance to a density current is ruled out. The radiation processes (in and out) in the reservoir is schematically represented in Figure 1.2.14.
Figure 1.2.13. Depth profile of temperature in the study basin
Figure 1.2.14. Radiation process in and out of reservoir
1.2.15. Turbidity

Turbidity variations in the water column are shown in Figure 1.2.15. Turbidity varies from 3.8 NTU at 0.1 m to 15.3 NTU at 15 m. Turbidity increases with depth, but around 5 m depth turbidity shows a decrease and then sudden increase. The drop in turbidity at 5 m is probably due to the settling of particulate matter. Corresponding to the continuous increase in turbidity, there is a steady decrease in dissolved oxygen concentration. This pattern of turbidity variations can be explained as follows. The iron(II) mobilized from sediment is soluble. It moves up in the water column by diffusion. As it gets mixed with increased DO, it is oxidized to iron (III). Fe (III) so formed hydrolysates at the pH condition existing in water (pH-6.9-7.8) forming dense ferric hydroxide, which settles down. The colloidal as well as particulate iron hydroxide contributes to the increase in turbidity observed at the section B of the turbidity-depth profile. The process is schematically represented in Figure 1.2.16.

1.2.16. Dissolved oxygen

Surface water analysis did not show any significant presence of algae at the site. Hence the only significant source of dissolved oxygen is partition at the water surface. Oxygen enters the water body through diffusion from atmosphere and this process is temperature dependent. The diffusion coefficient of O$_2$ is about $2.05 \times 10^{-1}$ cm$^2$/s in air and $10^{-3}$ cm$^2$/s in water (Lerman 1979). Hence the diffusion transport in the vertical direction in the water column is slow.

Depth-wise, dissolved oxygen concentration is shown in Figure 1.2.17. The concentration varies from 4.8 mg/L at the surface to zero at 8 m. A value of 4.8 mg/L at the surface at 31.6°C corresponds to a saturation level of 65.7% in water with a chloride concentration range of 0-1000 mg/L (APHA 1998).

Dissolved oxygen concentration decreases with depth. After 8 m the water column becomes depleted of oxygen. Oxygen from the atmosphere diffuses to the water column. Diffused oxygen moves vertically as well as
Figure 1.2.15. Depth profile of turbidity in the study basin
Figure 1.2.16. Redox processes of iron in a water column

(Stumm and Morgan 1997)
Figure 1.2.17. Depth profile of Dissolved Oxygen in the study basin
horizontally. Wind action generates different kinds of surface waves, though weak, these facilitate the surface dissolution of oxygen. In the case of Peechi reservoir wind influence is negligible and only weak surface winds are prevalent. During monsoon period wind velocity is appreciable. During this period the wind velocity is above 3 ms\(^{-1}\). Only when the wind velocity exceeds 3 ms\(^{-1}\) Langmuir circulation develops (Imboden and Wuest 1995). Hence during the period of stratification the vertical diffusion of dissolved oxygen is greater than horizontal diffusion. As DO diffuse down the column it oxidizes the reduced species present in the water column.

During stratification events build up of mobilized constituents from the underlying sediment occurs at the stratum. As these constituents move upwards, the increasing concentration of dissolved oxygen on the way oxidizes easily oxidisable constituents. The presence of natural organic matter and hydrogen sulfide also affects the downward distribution of oxygen.

### 1.2.17. Specific absorbance at 254 nm (SUVA\(_{254}\))

It has been established that there is a good correlation between SUVA\(_{254}\) and dissolved organic carbon (DOC) (Patterson and Bishop 1996; Vuorio et. al. 1998; Abbt-Braun and Frimmel 1999). Hence it is reasonable to assume that in the absence of specific organic pollutants SUVA\(_{254}\) represents DOC derived from NOM. Specific UV absorbance at 254 nm (SUVA\(_{254}\)) is an indicator of natural organic matter (NOM) in a water body. For routine monitoring of the water body this is recommended as a convenient parameter (APHA 2000; Exall and vanLoon 2000).

Biomass production occurs mainly in the euphotic zone where light penetration is high. Part of this biomass sinks and part of it is used up by the organisms. Natural organic matter is also derived from leaching of plant residues from the water shed. All these contribute to the value of SUVA\(_{254}\). The depth wise variation of SUVA\(_{254}\) is given in Figure 1.2.18. SUVA\(_{254}\) corrected for turbidity increases with depth. Absorbance varies from 0.051 at the surface to 0.162 at 15 m depth. It shows a sharp increase at around 7 m.
Figure 1.2.18. Depth profile of SUVA$_{254}$ in the study basin
The gradual increase corresponds to a slow diffusion from the sediment layer. This also matches with iron, which is also mobilized from the sediment layer.

1.2.18. Iron

Iron concentration in the reservoir shows variations in the water column. The depth profile of iron is given in Figure 1.2.19. Iron concentration varies from 0.05 mg/L at the surface to 5.0 mg/L in the lowest sampled depth i.e. at 15 m. It has been reported that the occurrence of anoxic conditions causes a significant cycling especially of iron and manganese at the oxic–anoxic interface, due to changes in solubility related to the changes in the oxidation state (Davison et al. 1982; Yagi 1986; De Vetre et al. 1988; Egeberg et al. 1988; Landing and Westerlund 1988). The classic work of Mortimer (1941) on Esthwaite Water provided the basic features of iron cycling in a seasonally anoxic lake as well as an interpretation of those observations in terms of the redox condition of the lake and fluxes across the sediment-water interface. During summer, when water column in the reservoir is stratified, the hypolimnion of the water body becomes anoxic and upward mobilization of mineral constituents occurs. When the water column is anoxic, Fe$_2$O$_3$ reduction occurs in the strongly reducing sediment stratum (Stumm and Morgan 1996).

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3 \text{H}^+ + 2e^- & \rightarrow 2 \text{Fe}^{2+} + 3 \text{OH}^- \\
\text{Fe}^{3+} + 3\text{OH}^- & \rightarrow \text{Fe(OH)}_3(s) \\
\text{Fe(OH)}_3(\text{amorphous}, s) + e^- & \rightarrow \text{Fe}^{2+} + 3\text{OH}^- \\
\text{Fe(OH)}_3(\text{amorphous}, s) + 2\text{H}^+ + \text{HCO}_3^- & \rightarrow \text{FeCO}_3 + 3\text{H}_2\text{O}
\end{align*}
\]

Reduced Fe (II) diffuses to the sediment-water interface where it is gradually oxidized to Fe$^{3+}$ and hydrolyzed to insoluble Fe (OH)$_3$. As a result there is no build up of dissolved iron in the water column.

When stratification develops, biological processes consume oxygen and the bottom waters become anoxic. Reductive dissolution of iron oxide continues to occur in the sediments. Fe (II) diffuses in to the anoxic bottom water and is oxidized at the oxycline forming a peak in particulate iron hydroxide in the water column. Below the oxycline, where the water is
Figure 1.2.19. Depth profile of Iron in the study basin
strongly reducing, dissolved Fe (II) is stabilized and its concentration increases with time. pE of the hypolimnion is lowered far below what is required to remove essentially all of the oxygen. After virtually all of the O2 is gone, the pE can go sufficiently low for the sequential reduction of nitrate, ferric and sulfate (Stumm and Morgan 1985, Pankow 1991).

\[
\frac{1}{2} O_2(g) + H^+ + e^- \rightarrow \frac{1}{2} H_2O \quad pE^0 = + 13.75
\]

\[
\frac{1}{2} NO_3^- + H^+ + e^- \rightarrow \frac{1}{2} NO_2^- + \frac{1}{2} H_2O \quad pE^0 = + 7.15
\]

\[
\frac{1}{6}NO_2^- + \frac{4}{3} H^+ + e^- \rightarrow \frac{1}{6}NH_4^+ \quad pE^0 = + 5.82
\]

\[
\text{FeOOH}_{(s)} + HCO_3^-(10^{-3}) + e^- \rightarrow \text{FeCO}_3(5) + 2H_2O \quad pE^0 = - 0.8
\]

\[
\frac{1}{6} SO_4^{2-} + \frac{4}{3} H^+ + e^- \rightarrow \frac{1}{6}S_{(s)} + \frac{2}{3} H_2O \quad pE^0 = - 3.30
\]

\[
\frac{1}{8} SO_4^{2-} + \frac{5}{4} H^+ + e^- \rightarrow \frac{1}{8} H_2S_{(g)} + \frac{1}{2} H_2O \quad pE^0 = - 3.50
\]

This colloidal iron (III) hydroxide particles agglomerate into larger particles and settles to the bottom. Thus the concentration of iron increases towards the bottom layers. Other mineral constituents like phosphate bind with iron species and become immobile.

1.2.19. **Sulfide**

The presence of sulfide in an environment is closely related to the redox condition of the environment. Under oxidizing conditions sulfur exists exclusively as sulfate. But under reducing condition it can be converted to S\(^0\) or S\(^2-\). In Peechi reservoir, during stratification, sulfide concentration varies from 0.0 mg/L to 0.075 mg/L at 15.0 m depth. At a sampling depth of 0.5 m the concentration of sulfide is below detectable level (BDL). On further going down the concentration increases. The depth wise variation of sulfide concentration is shown in Figure 1.2.20. Sulfur undergoes cyclic transformations. In deoxygenated hypolimnitic conditions the simultaneous presence of iron (II) and sulfide is possible because these are the preferred oxidation states at low redox potentials. Measurements have shown that iron (II) and sulfide can coexist in solution at values in excess of the theoretical solubility product, and the possibility of organic complexation and the formation of kinetically inert metastable states have been suggested (Hutchinson 1957; Hem 1960). The reduction of sulfate in biosynthesis is
Figure 1.2.20. Depth profile of sulfide in the study basin
termed assimilatory sulfate reduction and can take place in aerobic and anaerobic environments. Under reducing conditions (pC < -2) various microorganisms mediate the reduction of SO$_4^{2-}$ by natural organic matter. Metal sulfides, especially amorphous ferrous sulfide may be formed which gradually crystallizes to FeS. Sulfate reducing bacteria *Desulfovibrio desulfuricans* prefers a pH between 6 and 8 but can function between pH 4.2 and 9.9 (Baas Becking et al. 1960; Karamenko 1969; Zehnder 1988). At the anoxic boundary in the reservoir redox cycling of sulfur compounds occur (Davison and Heany 1978; Davison et.al. 1982; Jacob and Emerson 1982; Stumm and Morgan 1996; Langmuir 1997).

$$\text{SO}_4^{2-} + 9\text{H}^+ + 8e^- \rightarrow \text{HS}^- + 4\text{H}_2\text{O}$$

$$\frac{1}{8} \text{SO}_4^{2-} + \frac{5}{4} \text{H}^+ + e^- \rightarrow \frac{1}{8} \text{H}_2\text{S} \text{(g)} + \frac{1}{2} \text{H}_2\text{O} \quad \text{pE}^0 = -3.50$$

1.2.20. Nitrate

Nitrate shows increasing trend in the water column as depth increases. Nitrate concentration in the water column varies from 0.1 mg/L at the topmost sampling depth (0.1 m) to 0.7 mg/L in the lowermost sampling point (15 m). The variation of nitrate concentration with respect to depth of the water column is given in Figure 1.2.21. The trend indicates that nitrate reduction is not efficient in the anoxic layer.
Figure 1.2.21. Depth profile of nitrate in the study basin