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**STUDIES ON WATER AND SEDIMENT QUALITY FROM
MUSSOORIE PHOSPHATE MINING AREA**

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C E R T I F I C A T E

This dissertation entitled "Studies on Water and Sediment Quality from Mussoorie Phosphate Mining Area" embodies the work carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work has not been submitted in part or in full for any degree or diploma of any university.

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INTRODUCTION

INTRODUCTION

Water is considered polluted when it is altered in composition or condition, directly or indirectly, as a result of the activities of man, so that it becomes unavailable or less suitable for any or all of the functions or purposes for which it would more be suitable in its natural state.

In the developed countries even though waste discharges are high most of the population is supplied with piped water treated and disinfected so as to be safe for the common man. In developing countries the vast majority of the population have to use sources that are quite unprotected from pollution. In many countries water-borne diseases are still endemic and the prevailing insanitary conditions often result in epidemic outbreaks.

Environmental Impact of Mining

Down and Stocks (1977) have defined mining as the removal of minerals from the earth's crust for use in the service of man. These mining activities effect some changes in the natural environment. Due to mining activities, water, sediments and soil, and thus, the human civilization is being affected. This work is concerned with the impact of phosphorite mine on water quality; hence the impact of mining on water is described below in great detail.

Water Pollution Due to Mining:

Certain types of mining release toxic substances like metal ions and chemical reagents, which pollute sources of water.

Water is utilised in many stages of mining and mineral processing. These water pollutes the receiving water in various ways. Down and Stocks (1977) have classified the environmental impact of mining. They have described that the use of water in the mining pollutes the ground or surface water in the following ways:-

- (i) The discarded water after collecting the valuable minerals;
- (ii) process water used for beneficiation;
- (iii) water used to cool down pumps, compressors etc.;
- (iv) water used to control the dust, vehicle washing, drilling fluids etc;
- (v) polluted water stored in mine dumps;

may contaminate the ground or surface water. Apart from it rain fall erodes different pollutants from the mining area and pollute the water. In many urbanized regions and in areas where there has been considerable disruption of natural materials through excavations, strip mining and road building, the exposed and loose material undoubtedly weathers at an accelerated rate, which accelerates the mobilization of trace metals into aquatic systems (Rubin, 1974). Fallout of

aerial pollutants is likely to affect surface waters. According to Rubin (1974) airborne particulates and gaseous species can be significant sources of trace elements for natural waters when deposited as fallout or rainout.

Individual Pollutants:

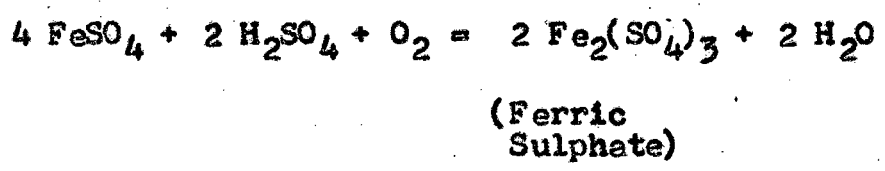
According to Down and Stocks (1977) there are following individual pollutants which pollute the water:-

- (i) Organic pollutants: mainly comprise the proteins, fats, carbohydrates etc. in sewage from mines. Coal, oil and certain organic reagents used in mineral processing also pollute the water. Detergents from vehicle washing etc., may contaminate the water. A major source of lead contamination of soil from atmospheric pollution is undoubtedly the exhausts of motor vehicles using petrol to which tetra-ethyl lead has been added, Purves (1977).
- (ii) Cyanides: This is common in gold mill waste and its concentration affect the aquatic animals. Krenkel (1974) describes that combination of CN^- with H^+ forms deadly HCN.

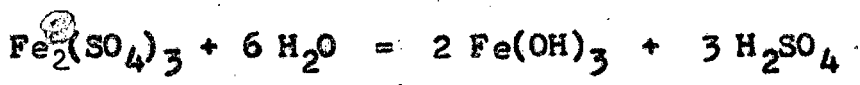
- (iii) **Acidity and alkalinity:** Some of the aquatic animals can survive if the pH is between 4-9. Acid water is common in the mine which can change the pH of water and thus can contaminate the water. If the acidity is very high, corrosion can take place. Forstner and Wittmann (1979) describe that exposure of sulfide minerals to atmospheric oxygen and moisture results in most acidic weathering reactions. Oxidation of sulfide components in pyrite gives sulphate whereby acidity (H^+) is generated and Fe^{+2} ions are released.
- (iv) **Base metals:** High concentration of base metals contaminate the water. There is possibility that water sources nearby the base metal mines is having higher concentration of base metals.
- (v) **Fluorides:** Fluoride pollution is mainly found in the waste waters from fluorspar mining. According to Purves (1977) due to disposal of fluorine damage to plants occurs and there is a hazard to man and farmstock. Gaseous fluorides are readily adsorbed by leaves which bring metabolic changes in the plants. Fluorosis in farm animals resulting from high intakes of fluoride is characterized by dental and skeletal defects.

- (vi) **Dissolved Solids:** Generally mine effluents have high concentrations of dissolved solids. Bicarbonates, sulphates and chlorides of calcium and magnesium cause hardness of water. Soluble salts of iron and aluminium can react in bicarbonate alkaline conditions to give precipitates of insoluble hydroxides. Krenkel (1974) has found evidences which indicate that water hardness may be a factor in heart disease.
- (vii) **Colour:** Colour can be both unsightly and damaging, the reddish deposits of precipitated ferric hydroxide in some mine streams is an example. If deoxygenation of such water occurs, black ferrous sulphide may be formed.
- (viii) **Suspended Solids:** Suspended solids interfere with self-purification of water by diminishing light penetration and hence photosynthetic activity, and damage fisheries by silting over of food organisms. If the solids are at all abrasive damage to fish, plants and pumps, etc., can be caused while silting may cause flooding or interference with navigation. Suspended solids increases the turbidity which affects the life of the aquatic animals.

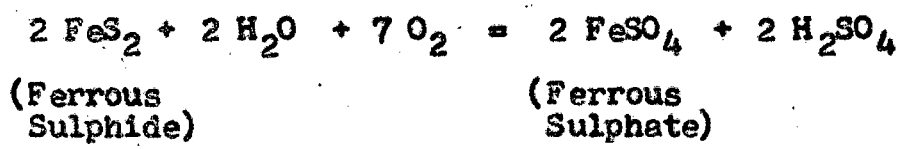
In the presence of the SO₄ and Oxygen ferric sulphate forms which is soluble in water -



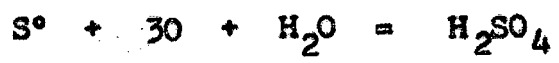
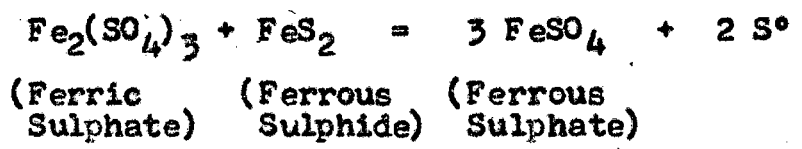
In the presence of water sulphuric acid is formed -



(b) In the presence of water following reactions take place -



(c) Ferric iron directly reacts with ferrous sulphide to produce H₂SO₄ -



AMD causes low pH, which restricts most organisms in the water, high total acidity and sulphate levels, high iron, high total solids but low suspended solids.

High ferrous iron decreases the oxygen content because it is being utilised to form ferric iron. The acidic water dissolve heavy metals and makes the water toxic.

- (ii) Heavy metals pollution: The sources of heavy metals vary, but are largely restricted to discharges and drainage from coal and metal mines. Heavy metals are lethal if concentration is high for aquatic animals as well as for the human beings. Luckey (1975) agrees that at lower doses or in trace quantities some minerals are essential to life and others are used with no hint of toxicity exhibited. But Groot and Allersma (1975) describes that the heavy metals can occur in relatively high concentrations and influence the fluvial ecosystem and, after their transport to the sea, also influence the food chains in the marine environment. The harmful effects are linked to the accumulation in biological systems, even in their lowest forms of development.
- (iii) Deoxygenation: Aquatic organisms and plants can survive in the aerobic conditions. Certain mining activities causes deoxygenation which is dangerous for aquatic life.

(iv) **Eutrophication:** Eutrophication is the chief problem leads by the concentration of phosphorus in the water, there is a tremendous growth of the aquatic plant; and the result is algal bloom. The algae needs oxygen for its growth. It takes dissolved oxygen, which cause deoxygenation. Deoxygenation kills aquatic animals and the lakes become unsuitable for the aquatic life.

Large algal bloom increases the decay of the algal plant with the same speed. This produces noxious decay products which aggravate the pollution.

Phosphorus concentration that limit the growth of algae vary considerably from one alga to another.

A general value for the concentration of phosphorus likely to limit the growth rate of natural algal populations is approximately $10 \mu\text{g l}^{-1}$ although for significant growth rate considerably more than this concentration is required. Algae common to eutrophic waters are reportedly growth limited at phosphate concentrations in excess of $10 \mu\text{g l}^{-1}$ (Jenkins and Ives, 1973).

The mining of phosphate and its application in agriculture, industry and household have increased nearly exponentially over the last few decades. The daily per capita

excretion of P is 1.5 g. (Stumm, 1973). Fertilizers and the resulting food by products account for the largest single source of man-induced phosphorus in the environment. Of the total phosphorus mined in the U.S. for domestic use a minimum of 12% finds its way into the aquatic environment via fertilizers (Stumm, 1973).

Thus mining of phosphorites and its use as fertilizer is having its implications on the environment. The study of water and sediment quality in the stream near phosphorite mine, Mussoorie, is an attempt to find out the impact of phosphorite mine on the nearby stream. Due to mining of phosphorite both at Durmala and Maldeota, it is expected that the concentration of phosphate in the nearby Bandal river, in which mine water joins, should be higher. Underground water also may get higher concentration of phosphate. Underground water is being used for the drinking purposes in the nearby villages. The same water is being supplied to Dehradun for domestic purposes. Bandal river joins Song river, which finally joins the Ganges in Haridwar. This water is being used for irrigation purposes. Under these circumstances it is worthwhile to study the environmental impact of phosphorite mine, Mussoorie.

Review of the Literature

By mining, man restores incipiently marine phosphorus in increasing quantities to the land. Because the rate of mining exceeds the rate of transport to the sea, ecological unbalance results causing pronounced pollution in inland and coastal waters. Eutrophication is the result of phosphorite mining. Garrels et al (1975) have described the global cycle of phosphorus in a simplified way and have shown that in the balance state 20 million metric tonnes of phosphorus per year is being transferred to the soil out of 4×10^9 million metric tonnes in the sediments. 18.3 million metric tonnes of the phosphorus from the soil again comes back to the sediments. Only 1.7 million metric tonnes of the phosphorus from the soil is being carried to the ocean by the streams. There is 10 thousand million metric tonnes of mineable phosphorus. The mining of phosphorus further adds 12 million metric tonnes of phosphorus in the soil. Rate of mining exceeds the rate of transport of phosphorus to the soil and finally to the ocean, and thus, ecological unbalance results.

Numerous literatures are available on the distribution of phosphorus in the fresh and marine waters. Talling and Talling (1965) have shown relative high total phosphate concentration in African lakes. They have observed that the river Rhine carries approximately 300 mg m^{-3} of $\text{PO}_4 - \text{P}$ and about an equal amount of particulate P. Now a days, when water from

surrounding peat areas come into such a lake, it may add considerable amounts of phosphate to the lake water. During autumn, the incoming peat rich water containing 1 mg l^{-1} of P is mixed with the lake water. Due to the high rates of water renewed a large part of this phosphate is watered out leaving in the lake a value of about 2 gm^{-2} of $\text{PO}_4 - \text{P}$.

Verderin (1967) and Stumm and Morgan (1970) have reported for USA and Europe respectively that the phosphorus concentration generally exceeds 200 mg l^{-1} in the river waters. Stumm and Morgan (1970) have reported average 20 mg P l^{-1} concentration of phosphate phosphorus by weathering. He has reported equal amount of phosphorus to be present in the form of organic phosphorus. Stumm (1973) has reported that at present there is no problem due to phosphorus in the aqueous environment in the U.K.

Phosphorus is one of the major nutrients. Golterman (1980) has tried to give the mathematical models to establish the relation between nutrient input and nutrient concentration and the relation between nutrient concentration and algal growth. He concludes that in eutrophic situations recycling of nutrients from the algae may become relatively much more important. Sedimentation lead to keep concentration low during the period of increasing loading of the lake. He has suggested that phosphate removal is the only cure for the devastating effects of lake algal blooms.

Literature survey indicates that in India only few work has been done on 'P' in the fresh water systems. Literatures on the distribution and mineralisation of phosphorus in the marine environment are available. Most of the literatures deal about the geology, origin and petrology of the phosphorite rocks. Patwardhan and Ahluwalia (1967, 73, 74), Raha (1970), Banerjee and Naraiian (1976) have reported about the geology, origin, mineralogy and petrology of phosphorite rocks. It is not relevant to discuss it here about geology and origin since they are covered in the geology section. However, a brief description of the distribution of phosphorus in the marine water, mineralogy and chemical analysis of phosphorite can be reviewed.

Rao and Rao (1968) have reported about the distribution of phosphorus in the Bay of Bengal and have found seasonal variation. Surface average values of total phosphorus exhibit a seasonal variation from high values of 3.4 $\mu\text{g. at/l}$ (July, 1961) and 3.02 $\mu\text{g at/l}$ (July, 1962) to low values of 0.99 $\mu\text{g at l}$ (April, 1961) and 1.66 $\mu\text{g. at/l}$ (April, 1962). From October to December also they have found low values of phosphorus. They have observed increase of phosphorus with depth upto 500 meters.

Viswanathan and Ganguly (1968) have observed in the North Indian ocean that between 100 meters and 500 meters

below sea surface phosphate-phosphorus increase with depth. The average value of phosphate-phosphorus varies between 0.2 to 3.34 $\mu\text{g. at/l}$ with the depth upto 500 meters, they have reported that mixing and upwelling of deep water control the concentration of nutrient in the sea.

Readdy and Sankaranarayanan (1968) have reported that in the Western North Indian Ocean the nutrients indicates low concentration at the surface layer upto 50 or 75 m. they have observed different concentrations of phosphate in different latitude and longitude. Generally upto 75 meters the phosphate concentration varies from 0.2 to 0.6 $\mu\text{g at/l}$. Between 75 to 200 meters it varies from 0.5 to 2.5 $\mu\text{g at/l}$. The meridional and zonal variations are due to variable intensities of the current velocities and consequent vertical movements of waters.

Subramanian (1980) about the mineralisation of phosphate minerals in the marine environment has reported that the calcite and apatite precipitates with the increase of pH. For the precipitation of apatite he has reported the pH range of 7 to 7.6. The enrichment of individual minerals take place within a narrow pH range.

Extensive studies have been done about the mineralogy and chemical composition of phosphorite deposits in Rajasthan, Mussoorie, Himachal Pradesh, Andhra Pradesh etc. by various

workers. Choudhuri and Banerji (1976) describe the geology, origin, mineralogy and chemical composition of Kasipatnam apatite deposits (Andhra Pradesh). They find a complex mineralogy with zonal assemblages, which is not relevant to mention it here. Among the phosphate minerals fluorapatite dominates, though chemical analysis reveals appreciable amount of chlorine (0.49%). In the chemical analysis of apatite 42.52% of P_2O_5 , 52.60% of CaO has been reported. SiO_2 and Al_2O_3 is not present in the apatite rocks.

Pareek (1978) have reported the geology, petrography and origin of phosphorite in the Himalaya of Himachal Pradesh. By the X-ray analysis of phosphorite he has found apatite and quartz as the major constituents, while dolomite is in trace amount. He has discussed about the chemical analysis done by Katiyar and Singh and has reported that P_2O_5 varies from 4 to 35%. The fluoride content varies from 1 to 4% and the CO_2 content varies from 0.3 to 33.4%.

Banerjee (1971) has described the geology petrography, chemical composition and origin of Precambrian stromatolitic phosphorites of Udaipur (Rajasthan). He has reported that collophane, quartz dolomite, calcite, dolomicrite and clays are the principal mineral constituents. The most important phosphate mineral is carbonate fluorapatite. Calcite and dolomite constitute the chief gangue in the

stromatolitic phosphorites. Secondary limonite and limonitized pyrite occur sporadically. Among the heavy minerals tourmaline, zircon and garnet are present. The chemical analysis done in the different laboratories by different workers, shows low F:P₂O₅ ratio. It varies from 0.04 to 0.19%. Chlorine content is insignificant. Carbonate and oxides of manganese occur sporadically in brecciated limonitized quartzite, phyllite and phosphorite.

Banerjee et al (1980) have also reported about the petrology, mineralogy, geochemistry and origin of Udaipur and Jhabua phosphorite. They have observed similarity in mineral composition of Jhabua and Jhamarkotra but the carbonate substitution is more in Jhabua. They have given the same mineralogical composition, given by Banerjee (1971). The chemical composition given by them is also similar to the value given by Banerjee (1971). They have compared the chemical composition of Jhabua and Jhamarkotra and have found higher P₂O₅ : F ratio in Jhabua phosphorite (0.13 - 0.14%) in comparison to Jhamarkotra phosphorite (0.05 - 0.09%). CaO and P₂O₅ values are quite high. CaO varies from 39 to 57% whereas, P₂O₅ varies, from 18 to 37% in both the regions. SiO₂ and MgO values are low. SiO₂ varies from 2 to 22%, whereas MgO varies from 0.1% to 16%. Generally, sodium is absent in Jhamarkotra. Sulphate content is negligible. Partial substitution for PO₄ to CO₃ is more

distinguished in Jhabua phosphorites than Jhamarkotra phosphorites.

Saraswat et al (1970) after the chemical analysis of phosphorite rocks of Mussoorie have reported high contents of Mo, Ni & Ba in these rocks, which confirm the environment of deposits, shallow to deep marine condition. They have observed higher uranium content in Mussoorie phosphorite in comparison to other phosphorite deposits.

Rao and Rao (1971) after the petrographic analysis of Maldeota and Mussoorie have found that both are similar in their mineralogical composition, but the calcite content is higher in Maldeota. The surface sample of phosphorite shows higher collophane content while in the underground sample calcite predominates. Pyrite is present upto 10%. Carbonaceous matter is found to occur frequently as fine inclusion in collophane. Secondary veins of calcite and quartz passes through most of the compact rock samples, while a fibrom mineral, probably wavellite, extensively replaces part of the phosphorite.

Dubey and Parthasarthy (1975) after the observation of mineralogical composition of Durmala have reported collophane, calcite, quartz, pyrite, felspar and clayey matter as essential constituents. The phosphate minerals identified by X-rays are carbonate apatite and carbonate substituted variety of apatite-francolite.

Ravi Shanker (1976) has reported about the chemical composition of Maldeota phosphorite that the P_2O_5 content of the phosphate zone varies between 17% to 20%, averaging 19.2%. The corresponding grade in the surface trenches, being richer due to leaching out of carbonate, varies between 20% to 30% P_2O_5 , depending on the extent of weathering. Average silica content is 7%. Fluorine content ranges from 0.18% to 0.22% and the chlorine from 0.18% to 0.22%. By the spectrochemical analysis of phosphorite rocks he has found 1000 ppm Ba and 300 to 800 ppm Sr. Vanadium concentration generally ranges between 100 to 300 ppm. The selenium content in the same zone varies from 17 to 35 ppm. Phosphorite rock is found to be mildly radioactive.

Mehrotra et al (1981) have observed petrography, chemistry and mineralogy of Mussoorie phosphorites. The mineralogical studies reveal hydroxyl-fluoroapatite i.e. francolite as the main phosphate mineral, but some dahllite, brushite and uraninite are also present. Pyrite is generally associated with phosphates and sometimes replaces it. The phosphate have detrital particles of quartz, dolomite, chert, clayey matrix and iron minerals within them. The chief carbonate impurity in phosphorites is dolomite and not calcite.

However, literature about the impact of phosphorite mining on the water is rare. Shukla (1981) has made an

attempt to observe the environmental impact of phosphorite mining (Mussoorie), which has not been published so far. The study of water and sediment quality in the stream near phosphorite mine, Mussoorie, is a step further to find out the impact of phosphorite mine on the nearby stream.

MUSSOORIE PHOSPHORITE

GEOLOGY

The geological studies of Mussoorie has been done in great details by Ravi Shanker (1971,1975). Sant (1979) has described the geology of the Indian platforms & its occurrences (phosphate). The phosphorite deposit of Dehradun-Mussoorie area has been found associated with Lower Tal Formation. The deposition took place in the shallow water reducing environment. According to Ravi Shanker (1971) the Tal Formation is folded in a doubly plunging synclinal structure; which is known as the Mussoorie syncline. Fig - 2:1 shows the geological map.

Classification and lithology:

The generalised geological succession of the Dehradun-Mussoorie area based on G.S.I. & PPCL, 1981 is as follows:

Group/Formation	Age
Alluvium	Recent
Dun Gravel/Old Terraces	Pliestocene to sub-recent
Siwalic Group	Middle Miocene to Early Pliestocene
Subathu Group	Upper Palaeocene to Upper Eocene
Tal Formation	Jurassic to Cretaceous
Krol Formation	Permian to Jurassic*
Infra-Krol	Permian
Blaini Formation	Permo-Carboniferous
Nagthat Formation	Devonian-Silurian*
Chandpur Formation	Devonian-Silurian*
Simla Formation	Early Palaeozoic to Precambrian*

(* = tentative age)

Statigraphically it has been divided by well marked break indicated by "Blaini Boulder Bed" into two (GSI & PPCL, 1981)-

- (1) Pre-Blaini Formations - which includes:
 - (i) Simla Formation;
 - (ii) Chandpur Formation; and
 - (iii) Nagthat Formation;
- (2) Post-Blaini Formations - which includes:
 - (i) Blaini Formation;
 - (ii) Infra-Krol Formation;
 - (iii) Krol Formation;
 - (iv) Tal Formation;
 - (v) Subathu Group; and
 - (vi) Siwalik Group.

Out of all these formations only Chert Member of Lower Tal Formation is important, because it consists of valuable phosphorite deposits; and hence only Chert Member of Lower Tal Formation has been described in detail:

Tal formation:

Recently after Medlicott (1864), Middlemiss (1887) & Auden (1934-35) the Tal Formation of the Mussoorie Syncline, in Dehradun and Tehri Districts, was re-mapped and re-classified by Ravi Shanker (1967) as follows:



7H-1308

Garhwal Thrust Unit	Schistose phyllites Limestone and quartzite Volcanic tuff		Older Palaeozoic
----- Garhwal Thrust -----			
Sabathu Formation	Olive shale, Shell marl and Limestone		Lower to Middle Eocene
----- Unconformity -----			
Upper Tal Formation	(ii) Limestone member (Shelly Calcareous) Grits	15-20 m.	Lower and/or Middle Cretaceous
	(i) Quartzite member (sequence of quartzite are-koses grits to pebbly quartzite and thin grey, to green shales, red silt-stones often mud cracked)		
----- Disconformity -----			
Lower Tal Formation	(iv) Calcareous member-Ferruginous, Siliceous or sandy limestone	5 m.	
	(iii) Arenaceous member massive and banded siltstone/subgrawackes	300-500 m.	
	(ii) Argillaceous member (c) Silty shale and siltstone.	150 m	Middle Jurassic
	(b) Calcareous splintery banded shales, buff coloured on weathering		
	(c) Black micaceous shale, with pyrite, often carbonaceous.		Lower Cretaceous

contd....

-
- (i) Chert member
 - (b) Phosphate Unit
Phosphate rock with thin intercalations of shales and chert
 - (a) Chert Unit 150 m
Bedded black with subordinate layers of black shale and thin streaks of phosphate rock.

----- Disconformity (?) / Submarine diastem / Transitional locally -----

Transition Zone
(developed locally)

Argillaceous limestone (often phosphatised) interlayered with thin streaks of phosphate rocks (also brecciated at places) and chert.

Upper Krol Formation

- (ii) Light grey, argillaceous limestone and purple grey shale.
 - (i) Grey to bluish grey dolomitic limestone and dolomite.
-

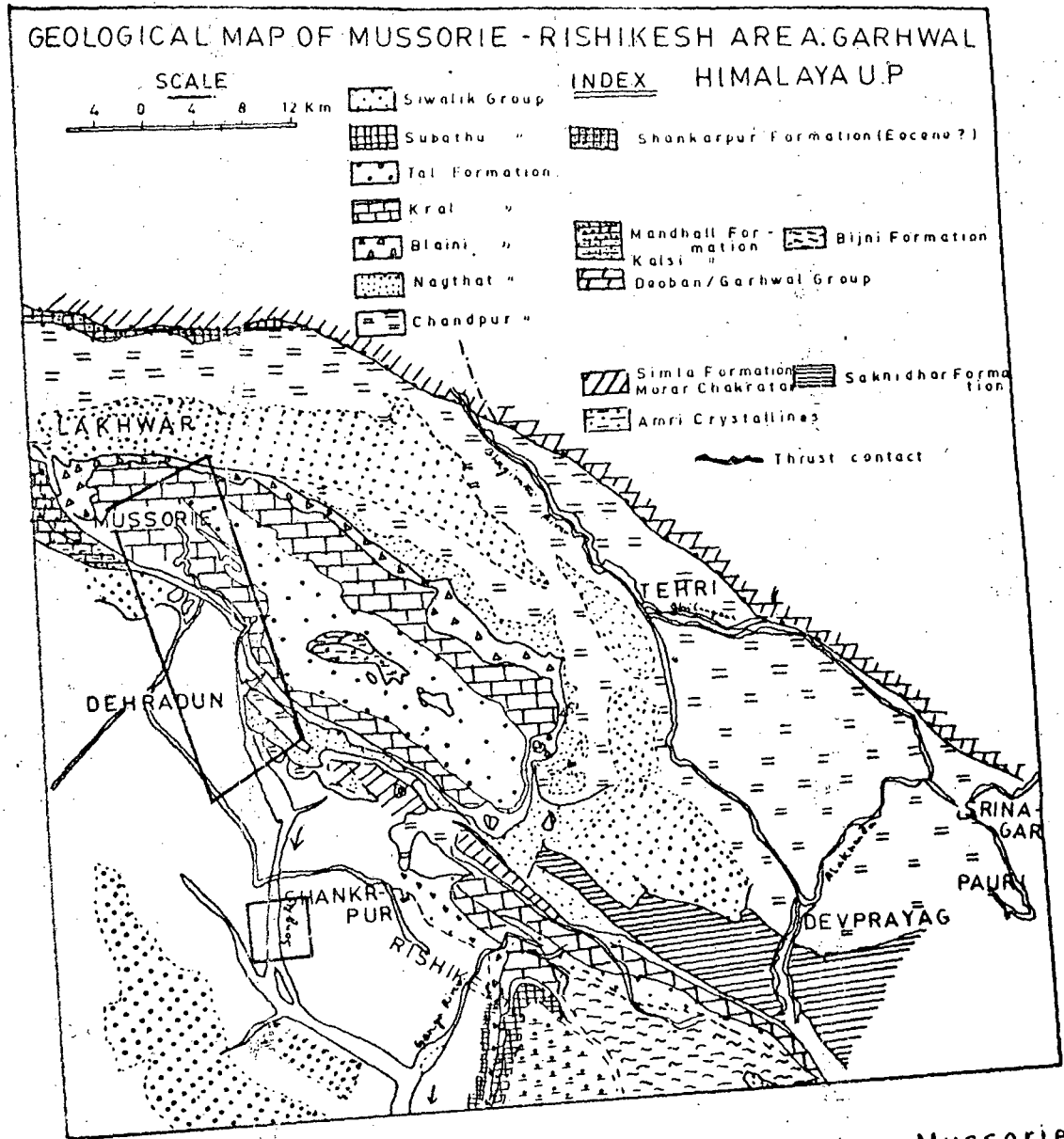


Fig.2.1. Map taken from excursion guide of Dehradun-Mussorie area (October 1981)

SAMPLING AREA

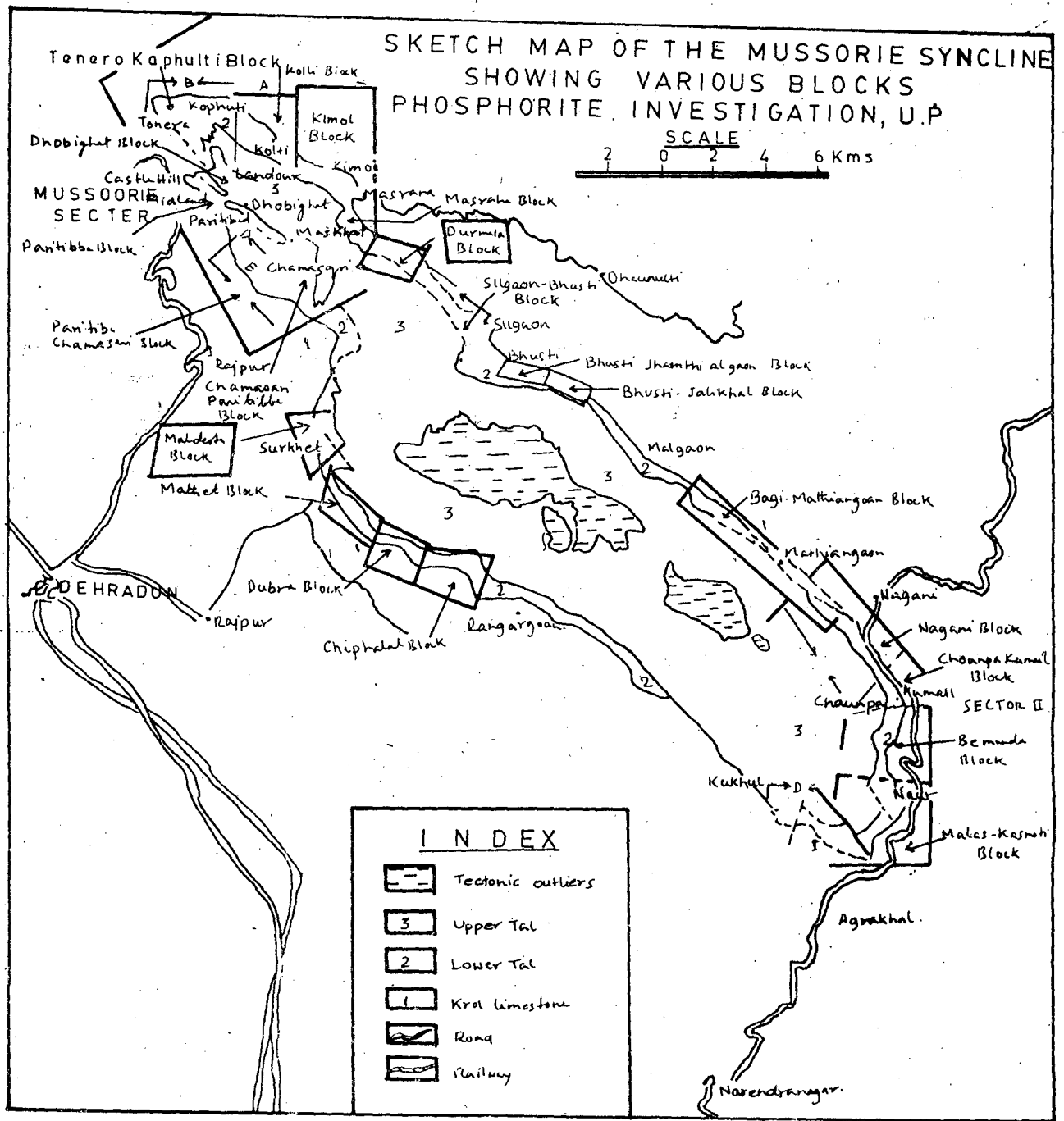


Fig.2.2. Map taken from the excursion guide of Dehradun-Mussorie area (Oct, 81)

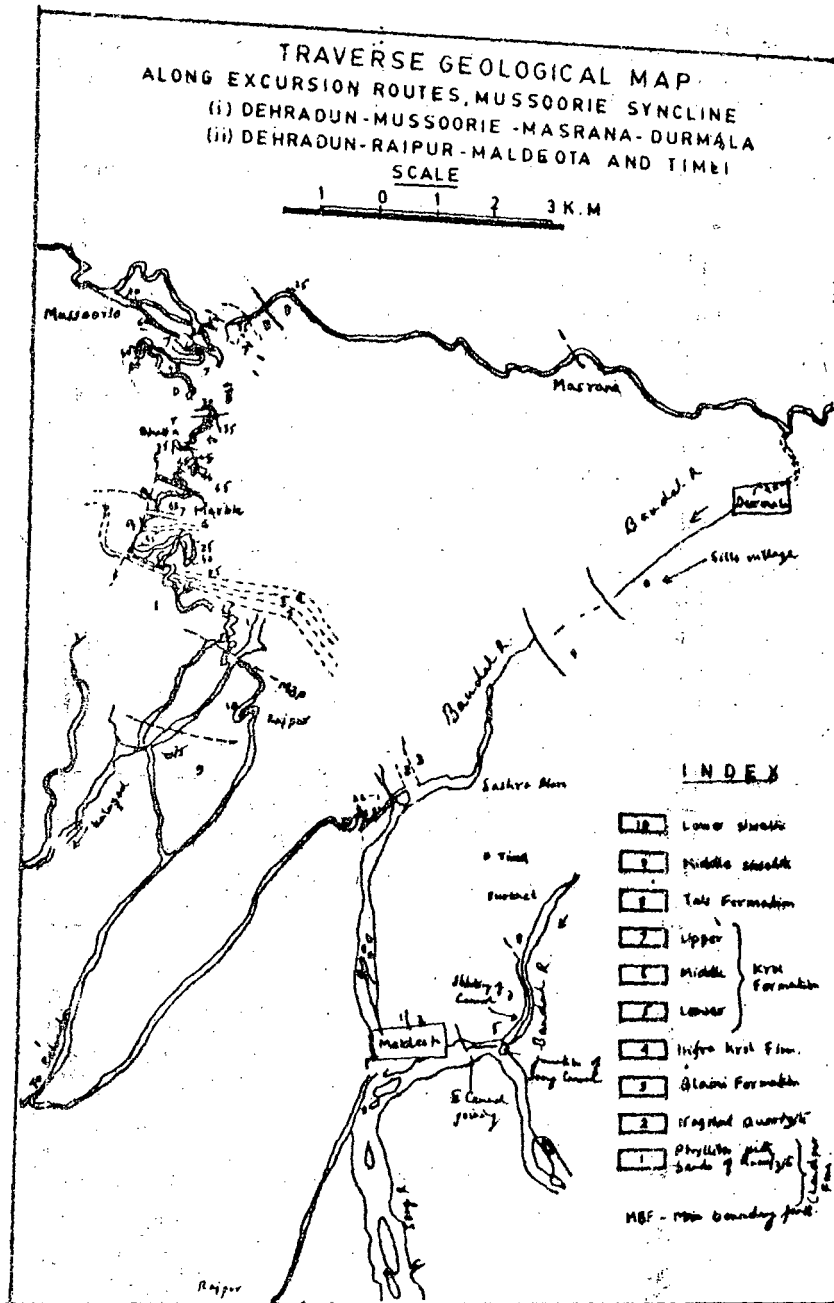


Fig. 2.3 Map taken from the excursion guide of Dehradun - Mussoorie area (Oct. 81)

H Course of river flow is not known

The Tal Formation has been divided into two formations by Ravi Shanker (1971-75) viz.,

- (a) Lower Tal Formation; and
- (b) Upper Tal Formation.

Ravi Shanker has found a sharp change in the environment of deposition from essentially marine in Lower Tal to sub-aqueous or sub-aerial (non-marine), in Upper Tal Formation. However, Patwardhan & Ahluwalia (1973) did not found unconformable contact between the rocks grouped as Lower & Upper Tal series or between the underlying Krol sediments and the base of the Lower Tal series.

Ravi Shanker (1971,75) has divided Lower Tal Formation into four numbers viz.,

- (i) chert;
- (ii) argillaceous;
- (iii) arenaceous; and
- (iv) calcareous,

depending upon the dominance of chert, shale, sand/silt or carbonate in the sediments. The Upper Tal Formation is sub-divided into a lower quartzite member and upper limestone member.

The Krol-Tal contact and Chert Member of Lower Tal Formation bears potential deposits of rock phosphate and it extends upto 120 Kms.

Lower Tal Formation

Chert member

The mineralisation of rock phosphate is localised to chert member. Based on distinct lithology Ravi Shanker has classified the chert member into (a) chert unit; and (b) phosphate unit.

(a) Chert unit:

According to Ravi Shanker (1971) the chert unit consist of a sequence of bedded chert, chert-shale alternations and phosphate rock with thin alternations of black shale. It overlies the argillaceous limestone or dolomitic limestone of the Krol Formation. The black chert is often thickly bedded and is generally nodular towards its upper portion but below the main phosphatic zone. These nodules are usually highly phosphatic whereas the cherty matrix in which they are embedded is generally non-phosphatic or only mildly so. Tiny phosphatic nodules also occur in the shaly intercalations. Thin bands of black carbonaceous algal limestone are also sometimes found

in the chert member. Pyrite is occasionally associated in the rocks of the chert member.

(b) Phosphate unit:

According to Ravi Shanker (1971) it consists of phosphate rock with or without chert and/or shale intercalation. Phosphate rock in this area is generally dull grey to brownish black in colour, nodular, granular to massive ophanitic in texture, occasionally bedded, brittle and friable. Pareek (1978) has reported a number of varieties of phosphate rocks. Ravi Shanker (1971) has classified it as:

- (i) Friable platy and laminated;
- (ii) Grenular;
- (iii) Variegated lenticular and pelletal variety; and
- (iv) Nodular variety.

According to Ravi Shanker (1971) isotropic collophane (carbonate hydroxyl fluorapatite), with some fibrous an-isotropic francolite and dahllite is the major mineral constituent. Phosphate unit varies in thickness from streaks to about 18 meters.

Upper Tal Formation

Ravi Shanker (1971,75) has divided it into -

- (1) Lower quartzitic member; and
- (2) Upper limestone member.

It is dominantly a quartzitic sequence with a thin calcareous capping and therefore, has been divided into a lower quartzitic member and an upper limestone member (Ravi Shanker, 1971).

Genesis

Origin and environmental condition of deposition of chert and phosphrite is very controversial. Some consider the chert to be consolidated or indurated siliceous bioliths, some consider it to be of metasomatic origin by replacement of host limestone whereas others reject both the biochemical and the metasomatic origins for these deposits and regard them as primary precipitates of silica gel (Pettijohn, 1957). Sea water is supposed to be the source of silica. Some consider some local sources as volcanic ash to be the reason for enriched silica (Gosh, 1968); whereas others (Terr and Twenhofel, 1932), believe the silica to be derived from chemical weathering of constituents.

About phosphorite presence of more particles of definite skeletal and faecal origin support the biochemical origin (Patwardhan and Ahluwalia, 1973; 1974; 1975). According to them association of carbonaceous and organic matter with the pelletal as well as the laminated variety of these phosphorites support biogenic origin. But they agree that inorganic influx of phosphorus to the sea water, volcanic emanations or terrestrial reworking of an older phosphatic rock cannot be ruled out.

Ravi Shanker (1971,75) has described the mode of formation of Mussoorie phosphorite in shallow water reducing environment. Saraswat et al (1970) after observing the presence of high contents of Mo, Ni & Ba in these rocks confirm the deposit under shallow water marine condition. According to Banerjee & Narain (1976) association of oncolites and stromatolitic structure in the related sediments gives the evidence in favour of shallow water marine condition of phosphorite deposits. The phosphate rock is formed by the biochemical process; the soluble phosphate in the mud, derived partly from the decay of phytoplanktons and algae, and partly from the river and sea water, reacts with the precipitating calcium carbonate giving

rise to the insoluble calcium phosphate, which after concentration during diagenesis consolidates as beds of phosphate rock Ravi Shanker (1975). He further describes that phosphate concentration increases by the removal of non-phosphatic material by waves. Replacement does not take place in the concentration of phosphours. It is directly precipitated from the water.

GENERAL DESCRIPTION OF THE AREA

Location

Location and brief description of Durmala and Maldeota area and the phospharites given by Dubey and Parthasarathy (1975) and Ravi Shanker (1976) respectively are summarised below:

Durmala:

At Durmala ($78^{\circ} 10' 10'' - 30^{\circ} 26' 12''$) (Mussoorie) the phosphorite bearing horizons are situated on the northern limbs of Mussoorie synform between the village Durmala ($78^{\circ} 10' 10'' - 30^{\circ} 26' 12''$) and Rudrwara ($78^{\circ} 9' 31'' - 30^{\circ} 26' 18''$). They are about 10 kms. S 70° E of Mussoorie at the contact of Krol and Tal Formations associated with black shale and cherts and are having an approximate thickness of five meters.

Maldeota:

Maldeota phosphorite prospect is situated about 20 kms. from Dehradun and extends between the villages Tamotwala ($30^{\circ} 21' 30''$ - $78^{\circ} 08' 30''$) and Timli ($30^{\circ} 22' 30''$ - $78^{\circ} 08' 15''$) in Dehradun district, U.P.

Sample locations for Maldeota - Durmala has been given in figure - 2.1 to 2.3. Physiography, vegetation and climate for Mussoorie - Dehradun given by Atkinson (1973) has been described below:

Physiography

The phosphate deposit of Maldeota-Durmala is in the mountainous area of the lesser Himalaya. It rises abruptly and without any intermediate undulating slope from the apparently level surface of the flat country below to height varying from a few hundred to three or four thousand feet. They are composed of sandstones and conglomerates, and the dip of the strata is usually towards the general mass of the mountains at a low angle. The form of disturbance of the strata is very regular, producing broad normal anti-climate flexures, the axis-plane sloping towards the mountains. Towards the plains the slope has

been weathered out, so that plainwards the Siwaliks exhibit a steep face from which rise the highest summits of the range, while a long gentle undulating slope inwards and forms a longitudinal shallow valley known as Dun by meeting the foot of the next line of hills. The latter, run on a line parallel to the Siwaliks, but at a distance of five to ten miles from them.

The bottom of Dun valley is by no means continuous. In some places it is cut through by the passage of the streams that drain the interior of the mountains; in others, it is quite obliterated by the near approach to each other of the two ranges that flank it, and which usually form distinct lines.

This is moreover, a structural feature and not due simply to denudation. In the country between the Sutlej and the Kali, these valleys are called Duns. The lower part of the Duns generally appears to be covered with a deposit of boulders and gravel that slope somewhat steeply from the Himalaya towards the Siwaliks, so that the whole bottom of the valley is considerably raised above the level of the plain.

In consequence of this elevation, the outer hills when viewed from the interior of the valley, as from Mussoorie, present a very insignificant outline. The drainage of these valley usually collects along their longitudinal axis and either falls into some of the larger streams that cross them, or less frequently finds an independent exist for itself into the plains by a sudden bend to the south through a break in the outer range. Owing to the considerable elevation of the Dun above the plains down to the level of which the drainage finds its way in a very short distance, the unconsolidated strata that form the floor of these valleys are constantly cut through to a great depth by water courses. Consequently, the surface, though often presenting an apparent flat for several miles together, is frequently broken up into steps which on the whole, are tolerably level, but at different heights, the one above the others. This phenomenon is not uncommon, and is constantly observed along rivers that are eroding their banks. To the same causes also are to be attributed the practical impossibility of procuring water by means of wells in the Duns, a difficulty which mainly arises from the thorough dessication of the gravelly soil by the deep drainage.

Vegetation

In Maldeota-Durmala there are well-grown specimens of Himalayan conifers, deodars, spruce, cypress, pine, fir, yew, and juniper, besides house-chestnut, poplar, oaks, box, birch, and maple. There are European fruitrees, apples, pears, plums, peaches, quinces, and edible chestnuts.

Climate

The climate and health aspects of Mussoorie are, as a whole, very favourable. The average rainfall, give an annual average of 92.08 inches.

The rains begin almost invariably about the middle of June, preceded by a new showers and continue until near the end of September. This is the most unpleasant and least invigorating period of the year. From the end of March until the beginning of the rains, the climate is delightful, though the sun's rays are oppressive for a few hours of the middle of the day, the mornings and evenings are always cool. The period of the year from which the greatest benefit to health is derived is from the cessation of the rains until the end of December.

The temperature varies considerably with deviation and aspect the thermometer seldom records above 70°C whilst as low as 10°C is occasionally registered during the winter.

General Description of
Mining & Drainage

Maldeota:

In Maldeota phosphorite is distributed in both the eastern and western region. Generally phosphorite is associated with chert but sometimes it directly overlies Krol limestone and dolomite.

The informations collected from PPCL, Dehradun (1983) reveal that average thickness of the phosphate unit in outcrop varies from 0.45 m to 7.8 m. and the grade varies from 15% to 40% P_2O_5 . The total reserves is 10.64 million tonnes out of which probable reserves is 4.98 million tonnes and possible reserves is 5.66 million tonnes.

The tonnage of phosphorite from Maldeota mine is 45300 tonnes out of which 20000 tonnes is from open cast mine. The quality of underground mine is 17-18% P_2O_5 ; Quality of open cast mine is 20% P_2O_5 .

Table 2.1 Table showing thickness, reserve, production and grade in Maldeota-Durmala region

	Maldeota	Durmala	
		(Thickband)	(Thinband)
Strike length of phosphate band (meter)	1300	1520	550
Thickness of the phosphate unit (meter)	0.45-7.8	3-9	0.6-1.5
Reserves (Millian tonnes)			
(a) Probable	4.98	3.69	
(b) Possible	5.66	5.45	
(c) Total	10.64	9.14	
Tonnage			
(a) Underground mine	25300	7100	
(b) Open cast mine	20000	15600	
(c) Total	45300	22700	
Grade P ₂ O ₅ (%)			12-27
(a) Underground mine	17-18	19-20	
(b) Open cast mine	20	25-30	

Source: PPCL, Dehradun (March, 1983)

In Maldeota there are two underground mine audit 1 and 2 where phosphorites are being mined. Apart from underground mines phosphorites are being mined from quarry.

For underground mining different drills are being made at different levels and finally it is being blasted. The phosphorites are transported to Harrawala, which is about 10-15 kms. from Dehradun. Phosphorites are grinded and packed into the bag to sell it in the market. The details about the production, reserves etc. have been given in Table- 2.1.

Nearby the mine Bandal river flows, generally north to south. Though with the use of boulders protection has been made so that dumped phosphorite should not go to the Bandal river, drizzling water from mine goes to the river and thus adding phosphate to the water. Apart from that people use phosphate fertilizers for healthy crops. This also goes to the river when the shower falls.

Bandal river is not always full of water. Only during the rainy season the whole course of river is full of water. Bandal river finally joins Song river, which goes to the Ganges in Haridwar. Water from Bandal and Song rivers is being used for drinking as well as irrigation purposes. Thus it is interesting to study the quality of water.

Durmala:

In Durmala two phosphorite bands have been found associated with chert unit. One of the two bands extend upto a distance of 1.5 kms. The thickness varies from 3 to 9 m; and P_2O_5 content varies from 24 to 33%. The phosphorite occur in bedded and platy forms. The other band extends upto 550 m. The thickness is 0.6 to 1.5 m and P_2O_5 content varies from 12 to 27%. The phosphorite occurs in granular form.

The PPCL, Dehradun (1983) reports that total reserves in Durmala block is 9.14 million tonnes whereas probable reserves is 3.69 million tonnes and possible reserves is 5.45 million tonnes. The tonnage in Durmala is 22700 tonnes, out of it open cast is having tonnage of 15600 tonnes. Quality of the underground mining is 19-20% P_2O_5 . Quality of open cast mine is 25-30% P_2O_5 .

In Durmala only two mines are operational audit-1 and audit-3. A new mine audit-2 B is under construction. Rest of the mines audit-1 A, audit-2 and 2 A are closed. Apart from underground mine there is an open cast mine.

The Bandal river in Durmala flows NE to SW. The dumped phosphorite goes to the river when rain falls and carries with it the dumped material. Mine water also goes to the river and disturbs the normal chemical composition of the fresh water.

METHODOLOGY

METHODOLOGY

Sampling Procedure

Sampling of water and sediments was done from Durmala (Mussoorie District) via, Maldeota (Dehradun District) to Doiwala (Dehradun District) near Rishikesh (35 kms.) along the Bandal River, one of the tributary of Song River, which (Song River) finally goes to Ganga River near Haridwar. The sampling was done in June, 1982 and again it was done in March, 1983 to complete the rest of the course of Song River where it joins the Ganges River in Haridwar. Water samples were kept in Plastic bottles and sediments were kept in polythene bag and were sent to the Laboratory for analysis, where it was kept in the cold room (Temperature 3° C) in order to avoid organic decay. During sampling of sediments care was taken so that finer part of the sediments should be preserved. pH of the water samples were measured by pH paper on the spot.

Also, samples were taken from inside the phosphorite mines located in Durmala and Maldeota and from the sludge at different locations till it joins the main Bandal River running along the mining complex. During sampling care was taken so that it should represent total input of phosphate to the nearby stream and the environmental impact can be known.

Few samples of underground water were taken to know the input of phosphate content in the underground water and hence to know the total environmental impact of phosphrite mines. Sample location for Maldeota-Durmala has been given in Fig. 2.1 to 2.3.

Water Analysis

The pH, conductivity and alkalinity of the water samples were measured immediately after the samples were brought to the laboratory. Water was filtered to analyse the various constituents i.e. silicate, sulphate, phosphate, chloride etc. and various elements.

The methods adopted to analyse different constituents of water are as follows -

pH

Elico pH meter model LI-10T; was set for standard pH-7 buffer at temperature 23°C then the pH of each water sample was measured. Cross checking was done for verification.

Conductivity:

Specific conductivity was measured in mMH0/cm using systronic direct reading conductivity meter-303. The instrument was calibrated and set for 0.1 KCl. standard. The measurement was made at 23°C.

Alkalinity:

The alkalinity was measured in the laboratory just after the samples were brought there. It (alkalinity) was measured in terms of bicarbonate.

The bicarbonate was determined in the laboratory by potentiometric titration method. Here no indicator was used. On the otherhand the pH of samples as well as that of standard solutions were maintained at 4.5 to signify the end point, by adding HCl (0.1 N). Standard solution between 5 to 250 ppm was used. The standard graph was plotted and the alkalinity content was measured.

Chloride:

Chloride was estimated by titrating standard chloride solution of various concentrations (6.25 to 250 ppm) against silver nitrate (AgNO_3) solution (0.01 N). The samples were titrated with the same concentration of AgNO_3 . Potassium chromate (K_2CrO_4) was used to indicate the end point. Standard graph was plotted against the concentration of AgNO_3 . From the graph concentration of chloride in the samples were determined.

Fluoride:

For the estimation of fluoride, corning pH/I-on meter-135 was used. The instrument was calibrated for

the standard fluoride. 5 c.c. Sample was taken and 45 c.c. TISAB (Sodium chloride-1M, Acetic acid - 0.25 M, Sodium acetate-0.75 M, sodium citrate - 0.001 M) was added to dilute the samples 10 times and mixed thoroughly to suppress the interference of the other ions. Direct reading was taken to know the fluoride content in ppm.

Silica:

The silica content was determined by the Molybdo-silicate Method.

Standard solutions were prepared by dissolving Na_2SiF_6 by diluting the samples in various proportion. 25 c.c. of standard solution and same amount of water samples were taken out. In each sample 10 c.c. ammonium molybdate solution (the solution was prepared by dissolving 2 gm. of ammonium molybdate in 10 c.c. of DDW and adding 6 c.c. of conc. HCl and the total volume was made 100 c.c. by further diluting it with DDW) and 15 c.c. of reducing reagent (prepared by mixing 100 c.c. of metal sulphite solution, 60 c.c. of 10% oxalic acid and 120 c.c. of 25% H_2SO_4 and making the total volume 300 c.c. by adding distilled water) was added. Metal sulphite solution was prepared by dissolving 5 gms. of metal in 210 c.c. of DDW. Again 3 gms. of sodium sulphite was added and dissolved and DDW was added to make the volume 250 c.c.

The samples were stirred properly and kept for 3 hours to let the reaction complete. The optical density was measured for standard and water samples at 812 nm using Beckman model 34 spectrophotometer. A standard graph was plotted for standard silica concentrations versus optical density (absorption). The silica in the water samples were estimated by comparing their optical density values with the standard graph.

Sulphate:

Sulphate was determined by direct titration with barium perchlorate in 80% ethenol with thorin as the indicator. The samples were prepared by passing through an Dowex cation exchange resin to remove interfering cations.

Reagents:

- Anala R absolute ethenol.
- Thorin solution, 0.2% w/v.
0.2 gm. of thorin (disodium salt) was dissolved in deionised water and the volume was made 100 c.c.
- Hydrochloric acid, 10% v/v.
- Sulphuric acid, 0.005 M.
- Perchloric acid - Anala R perchloric acid (HC10_4 , S.G. 1.66).
- Cation exchange resin.
- Dowex 50 w - x 820 - 50 mesh resin.

Standardisation of barium perchlorate
in 80% ethenol 0.005 M.

2.0 gm. of barium perchlorate $Ba(ClO_4)_2 \cdot 3H_2O$ was dissolved in 200 c.c. of deionised water in a litre volumetric flask and 800 c.c. of ethenol was added. The pH was adjusted to 3.5 by adding perchloric acid dropwise. 10 c.c. of 0.005 M H_2SO_4 was taken in a conical flask and 40 c.c. of ethenol and 4 drops of thurin solution were added. In a burette 25 c.c. of barium perchlorate solution was taken. The initial burette reading was noted down and barium perchlorate with constant swirling was added till the solution just turned from yellow to pink. The final reading was recorded. This step was repeated 3-5 times. Then by the following formula the molarity of barium perchlorate was calculated.

$$\text{Molarity of } Ba(ClO_4)_2 = \frac{10 \times \text{molarity of } H_2SO_4}{\text{Volume of } Ba(ClO_4)_2}$$

Sulphate standard solution

1.4787 gm. of sodium sulphate was dissolved in deionised water and was diluted to 1 litre. From this, by proper dilution, standard solutions of various concentrations (6.25 to 1000 ppm) were made.

Method

An air-free ion-exchange column was prepared. In order to activate the resin, 30 c.c. of 10% HCl was passed through the column. After that, it was rinsed with 100 c.c. DDW. Approximately 70 c.c. of unacidified standard and sample was passed through the column. The first 40 c.c. of sample and standard was discarded and then rest were collected for the analysis. 10 c.c. of treated samples were taken into a conical flask and 40 c.c. of ethenol and 4 drops of therin were added. In the burette 0.005 M barium perchlorate solution was taken. The initial burette reading was noted and then barium perchlorate was added to the sample with constant swirling of the flask until the solutions changed colour from yellow to pink. The burette reading was recorded when the first permanent colour change occurred.

The column was regenerated after every three or four samples by passing 10% HCl and rinsed thoroughly. A graph for standard sulphate solution was prepared, and from that the sulphate concentration of samples were inferred.

Phosphate:

The phosphate was determined by the Ascorbic acid method. Phosphate standard solution of different concentration ranging from 0.0625 ppm to 6.2 ppm were prepared

from potassium dihydrogen phosphate (KH_2PO_4). 40 c.c. of samples and standard solution were pipetted out into a 100 c.c. volumetric flask and 5 c.c. of Molybdate solution, 2 c.c. of ascorbic acid solution, 3 c.c. of DDW was added and mixed well. After adding reagents samples were kept for 3 hours and extinction was measured at 882 nm by Beckman model 34 spectrophotometer.

Molybdate solution was prepared by dissolving 4.8 gms. of ammonium molybdate ($(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) and 0.1 gm. of sodium anti-monytartarate ($\text{NaSbOCuH}_4\text{O}_6$) in 400 c.c. of $4\text{NH}_2\text{SO}_4$ and making the total volume upto 500 c.c. with the same H_2SO_4 . Ascorbic acid (about 0.1 M) was prepared by dissolving 2 gms. of ascorbic acid in 100 c.c. DDW. This solution could be used only for one week when it was kept in the refrigerator.

Major elements (Na, K, Ca, Mg)

Major elements sodium, potassium were analysed in emission mode and calcium, magnesium were analysed in absorption mode by Carl Zeiss AAs-I spectrophotometer. The values of the samples were compared with standard graph to get the concentration of these elements. Standard solutions between 5 to 100 ppm for Ca, Mg & Na and 0.5 to 5 ppm for K were used.

Bed Sediments Analysis

Mineralogy:

The X-ray slides were prepared from the bed sediments by "drop on slide" technique (Gibbs, 1967) after removing the organic contents. The X-ray diffractographs were taken by Phillips X-ray diffractometer using $\text{CuK}\alpha$ radiation and Ni filter. The chart drive was 1 cm./min. and intensity $R = 4 \times 10^2$ TC = 2. The minerals identification and their abundances were done by following the methods of Biscaye (1965) and Carrol (1970).

Major and trace elements:

Trace elements Cu, Cr, Ni and Ag. were partially analysed in absorption mode by Perkin Elmer double beam AAS in Delhi University. The values of the samples were compared with standard graph to get the concentration of trace elements.

For the trace elements analysis sediment samples were treated with H_2O_2 to remove the organic content. Again the organic content removed sediment were digested by bombs. For the bomb digestion 1 gm. fine grained sample was taken in the bomb. 2.5 c.c. of perchloric acid and 7.5 c.c. of HNO_3 were added and kept it in the oven at

100°C for one hour. The bombs were kept out and were cooled down at room temperature. Now half of the crucible was filled up with DDW and bombs were kept in the oven for another half an hour. Bombs were cooled down and diluted the sample to 100 c.c. by adding DDW. Bomb digested samples were filtered with the help of filtered paper and the filtered samples were kept for AAS. Total analysis by XRF for major & trace elements were done for three samples in Belgium by Dr. V. Subramanian.

Fluoride and Phosphate
in the Sediments:

One gram of fine grained, organic matter removed sample, was taken in a teflon crucible and 2.5 c.c. of perchloric acid and 7.5 c.c. of HNO_3 was added and kept the bomb in the oven for one hour at 100°C. DDW was added to the crucible after the bomb gets cooled and was kept again in the oven for one hour and then cooled and diluted to 100 c.c.

To measure the fluoride content in the sediments bomb digested samples were taken and corning pH/Ion Meter-135 was used. The instrument was calibrated for the standard fluoride. 5 c.c. Sample was taken and 45 c.c. TISAB (Sodium Chloride-IM, Acetic acid - 0.25 M, Sodium Acetate - 0.75 M, Sodium citrate - 0.001 M) was added to dilute the samples 10 times and mixed thoroughly to suppress the

interference of the other ions. Direct reading was taken to know the fluoride content.

The phosphate content of the bomb digested samples were done by the ascorbic acid method. The bomb digested samples were diluted with DDW to 100 to 1000 times because the colour developed was so strong that it was out of range for spectrophotometer 40 c.c. of diluted samples and standard solutions (0.125 to 10 ppm) were pipetted out into a 100 c.c. volumetric flask and 50 c.c. of DDW was added and mixed well. After adding reagents, samples were kept for 3 hours and extinction was measured at 882 nm by Beckman model 34 spectrophotometer. The details about the preparation of molybdate solution and ascorbic acid have already been discussed in detail in the methodology section for the analysis of dissolved phosphates.

RESULT AND DISCUSSION

WATER CHEMISTRY

WATER CHEMISTRY

The chemical environment in fresh water is being controlled by the major dissolved ions of Ca^{+2} , Mg^{+2} , Na^+ , K^+ , HCO_3^- , SO_4^{-2} and Cl^- with the pH but other elements may further define the environment. The chemical composition of Bandal river (Table- 4.1) is described below:-

pH

pH generally varies from 8 to 8.3. This shows that water is slightly alkaline, which is the characteristic features of most of the Indian rivers. Fig. 4.2(a) shows the variation of pH with dissolved phosphate. Handa (1972), Subramanian and Dalavi (1978) have reported alkaline water for the Ganges and the Ganges and Yamuna respectively. In Maldeota-Durmala region all the samples show slightly alkaline nature except one; Bandal river is having pH-7. This lower pH may be because phosphoric acid coming out from the phosphorite mine may decrease the pH of river water. One more reason may be association of pyrite with phosphate minerals. Pyrite easily changes by oxidation to an iron sulphate or to the hydrated oxide, limonite, with sulphuric acid set free. The release of sulphuric acid may decrease the pH of water.

Table 4.1 Chemical composition of water concentration in (ppm)

Sample locations arranged in the order of down stream flow of the river	pH	Conductivity $\mu\text{MHO/cm}$	Cl^-	F^-	HCO_3^-	SO_4^{--}	PO_4^{---}	SiO_2	Ca^{++}	Mg^{++}	Na^+	K^+	TDS
Adt-1 (Durmala) (200 m)	8.1	0.75	4	1.3	173	265	0.48	2.0	21.5	29.0	22.0	4.9	523
Adt-2 (Durmala) (500 m)	8.0	1.50	6	1.0	145	795	0.06	1.5	127.0	78.0	51.0	5.2	1210
Junction mine water (Durmala) (1600 m)	8.1	1.30	5	2.1	145	1020	0.07	1.0	150.0	68.0	45.5	4.8	1441
100 meter below junction mine water (Durmala) (1700 m)	8.1	1.10	4	1.1	173	754	0.06	1.4	28.5	45.5	29.5	2.9	1040
200 meter below junction mine water (Durmala) (1800 m)	8.1	1.10	4	1.3	145	577	0.36	1.7	150.0	62.0	34.0	4.0	979

Contd...

Sample locations arranged in the order of down stream flow of the river	pH	Conduct- ivity mMHO/cm	Cl ⁻	F ⁻	HCO ₃ ⁻	SO ₄ ⁻	PO ₄ ⁻	SiO ₂	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	TDS
Junction Bandal River+Mine water (Durmala)(2000m)	8.2	0.4	4	1.3	155	73	0.24	1.5	56.0	18.0	15.0	3.4	353
100 meter below Bandal River (Durmala)(2100m)	8.2	0.4	4	1.0	219	40	0.06	1.5	10.5	19.0	17.0	1.6	314
Bandal River (Maldeota) (15000 m)	7.0	0.5	6	1.4	191	40	0.15	1.7	7.0	17.0	9.0	2.4	276
Adt-2 inside mine (Maldeota) (15000 m)	8.2	0.4	4	1.3	164	48	0.3	1.3	7.0	19.0	7.0	2.0	254
Outside Adt-2 (Maldeota) (15000 m)	8.1	0.7	5	1.3	109	125	0.06	1.4	18.0	31.0	16.0	3.5	310
Junction Adt-2 +Bandal River (Maldeota) (15200 m)	8.2	0.4	5	1.6	155	40	0.06	1.7	10.5	13.0	14.0	2.7	244

Contd...

Sample locations arranged in the order of down stream flow of the river	pH	Conduct- ivity mMHO/cm	Cl ⁻	F ⁻	HCO ₃ ⁻	SO ₄ ⁻	PO ₄ ⁻	SiO ₂	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	TDS
Adt-1 inside mine (Maldeota) (15800 m)	8.0	0.8	5	1.4	145	354	0.18	2.0	21.5	50.0	15.0	4.0	598
Outside Adt-1 (Maldeota) (15800 m)	8.0	1.0	4	1.4	155	118	0.12	2.0	127.0	58.0	39.0	4.0	509
Tube-well water (Maldeota) (15800 m)	8.3	0.4	4	1.3	109	65	0.06	1.7	23.5	15.0	14.0	3.0	237
Quarry (Maldeota) (15900 m)	8.0	1.2	5	1.6	155	804	1.32	1.4	118.0	78.0	66.0	8.8	1239
Junction Bandal River+Adt-1+ Adt-2+Quarry (Maldeota) (16000 m)	8.2	0.4	4	1.3	159	40	0.06	1.8	18.5	19.0	18.0	3.0	265

Contd...

Sample locations arranged in the order of down stream flow of the river	pH	Conduct- ivity mMHO/cm	Cl ⁻	F ⁻	HCO ₃ ⁻	SO ₄ ⁻	PO ₄ ⁻	SiO ₂	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	TDS
Junction Bandal River + Mashan Nala (Maldeota) (16800 m)	8.2	0.4	4	1.3	155	48	0.42	1.0	14.5	14.0	15.0	2.5	256
Junction Bandal River+Jagdish Mool (Maldeota) (17000 m)	8.2	0.4	4	1.4	164	57	0.12	1.6	13.5	15.0	23.5	3.5	284
Bandal River 100 m. below Jagdish Mool (Maldeota) (17100 m)	8.2	0.5	5	1.3	173	116	0.06	1.6	8.0	14.0	18.0	2.7	340
Bandal Canal (Maldeota) (19000 m)	8.1	0.4	5	1.4	145	34	0.06	1.5	15.0	19.0	6.0	2.8	230

Contd...

Sample locations
arranged in the
order of down
stream flow of
the river

	pH	Conduct- ivity mMHO/cm	Cl ⁻	F ⁻	HCO ₃ ⁻	SO ₄ ⁻⁻	PO ₄ ⁻⁻⁻	SiO ₂	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	TDS
Song Canal (Maldeota) (19000 m)	8.0	1.0	4	1.4	119	438	0.06	2.1	110.0	30.0	56.0	4.0	765
Junction Bandal Canal + Song Canal(Maldeota) (19100 m)	8.0	1.0	4	1.3	122	335	0.06	2.0	31.0	31.0	43.0	2.5	572
Tap water (Dehradun) (35000 m)	8.0	0.6	5	1.3	155	125	0.06	1.4	28.5	15.0	14.0	3.0	348

Table 4.2 Comparison of chemical composition of Maldeota-Durmala water with the World average (all values in ppm)

Chemical composition	Maldeota Durmala	World Average
Cl ⁻	4.5	7.8
F ⁻	1.4	-
HCO ₃ ⁻	153.0	58.4
SO ₄ ⁻⁻	274.0	11.2
PO ₄ ⁻⁻⁻	0.2	π
SiO ₂	2.0	13.1
Ca ⁺⁺	48.0	15.0
Mg ⁺⁺	33.0	4.1
Na ⁺	25.0	0.3
K ⁺	3.5	2.3
TDS	547.0	120.0

Source: Livingstone, 1963) (adapted from Krauskopf, 1967).

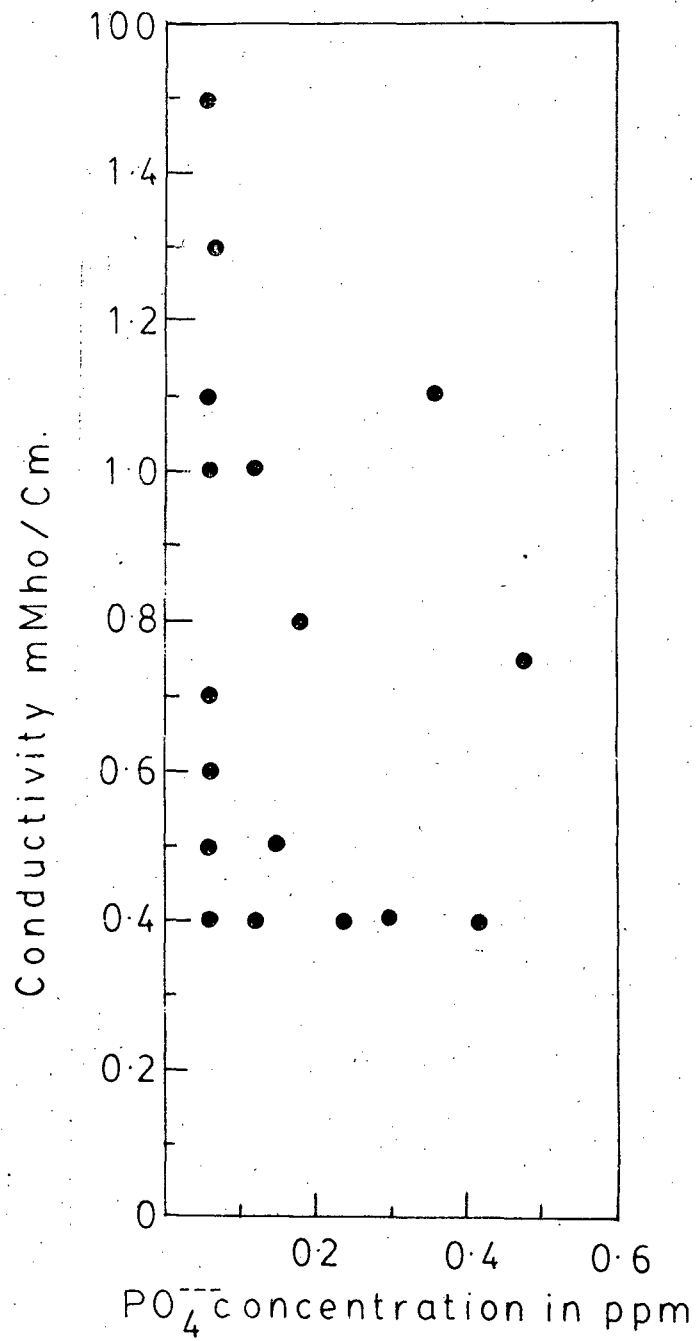


Fig.4.1 Graph showing the variation of conductivity with phosphate.

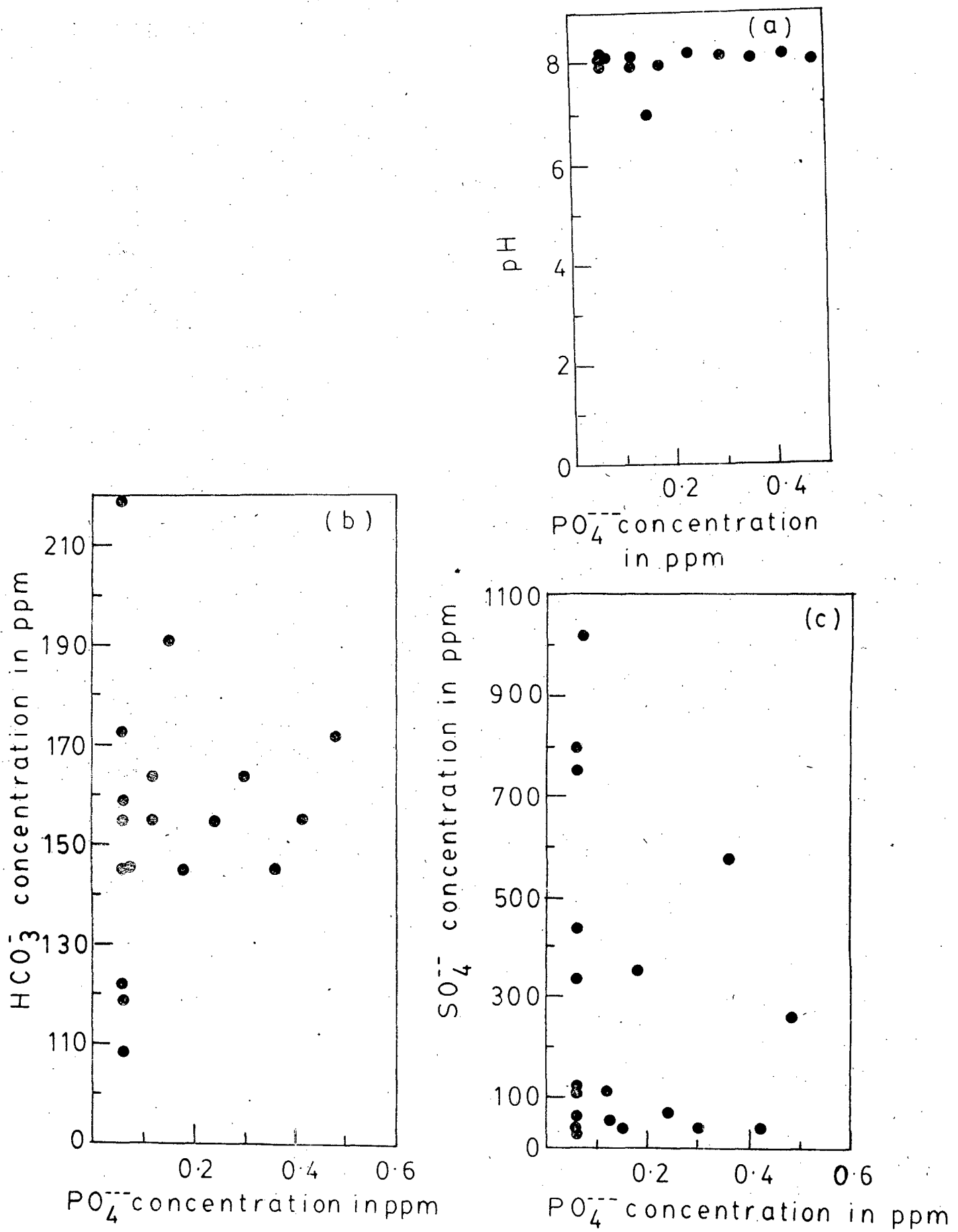


Fig:4:2.Graph showing the variation of HCO_3^- , pH and SO_4^{2-} with phosphate.

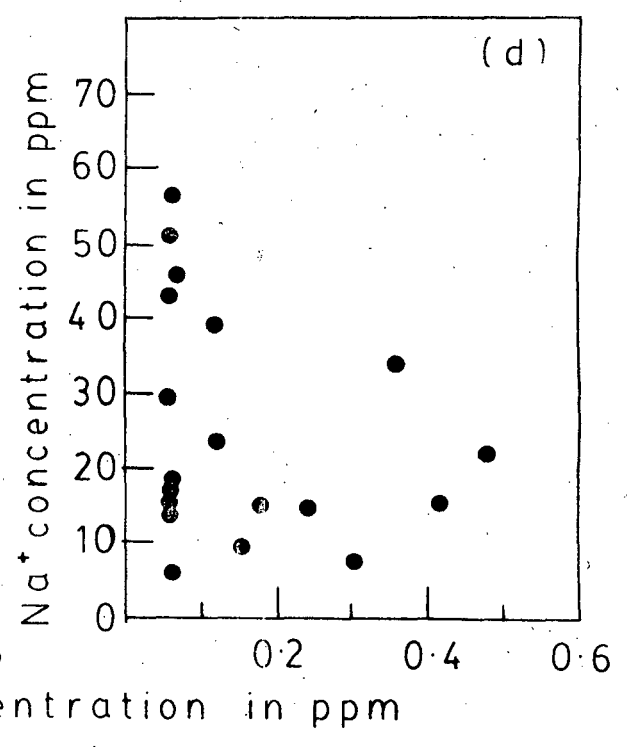
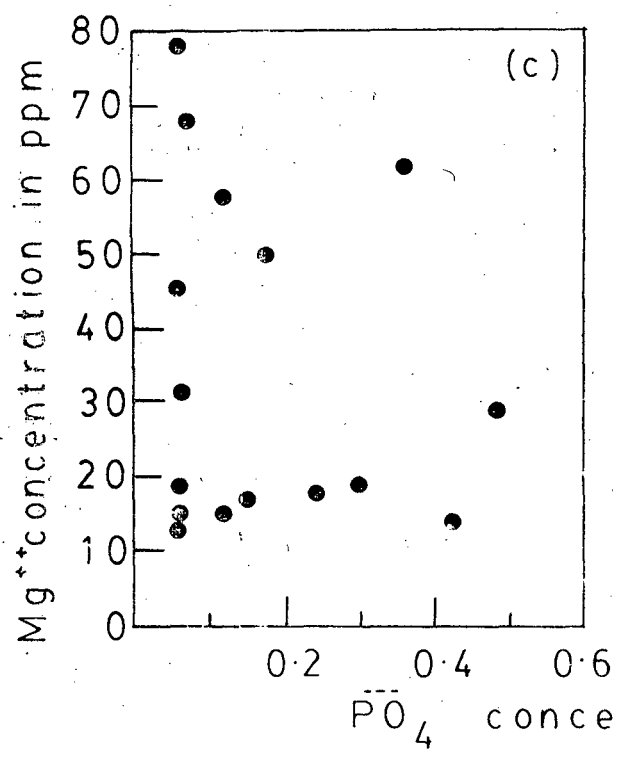
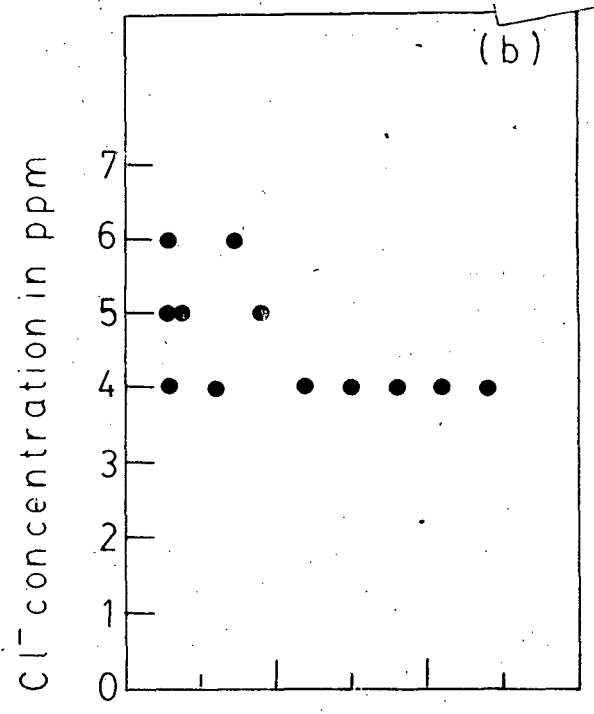
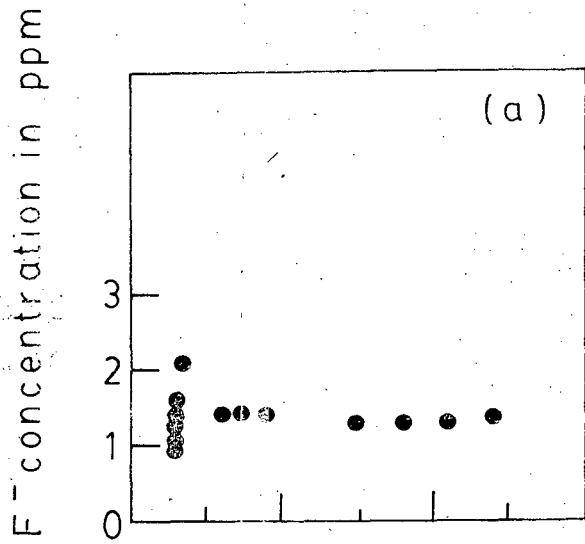


Fig.4-3. Graph showing the variation of Mg^{++} , F^- , Na^+ and Cl^- concentration with phosphate.

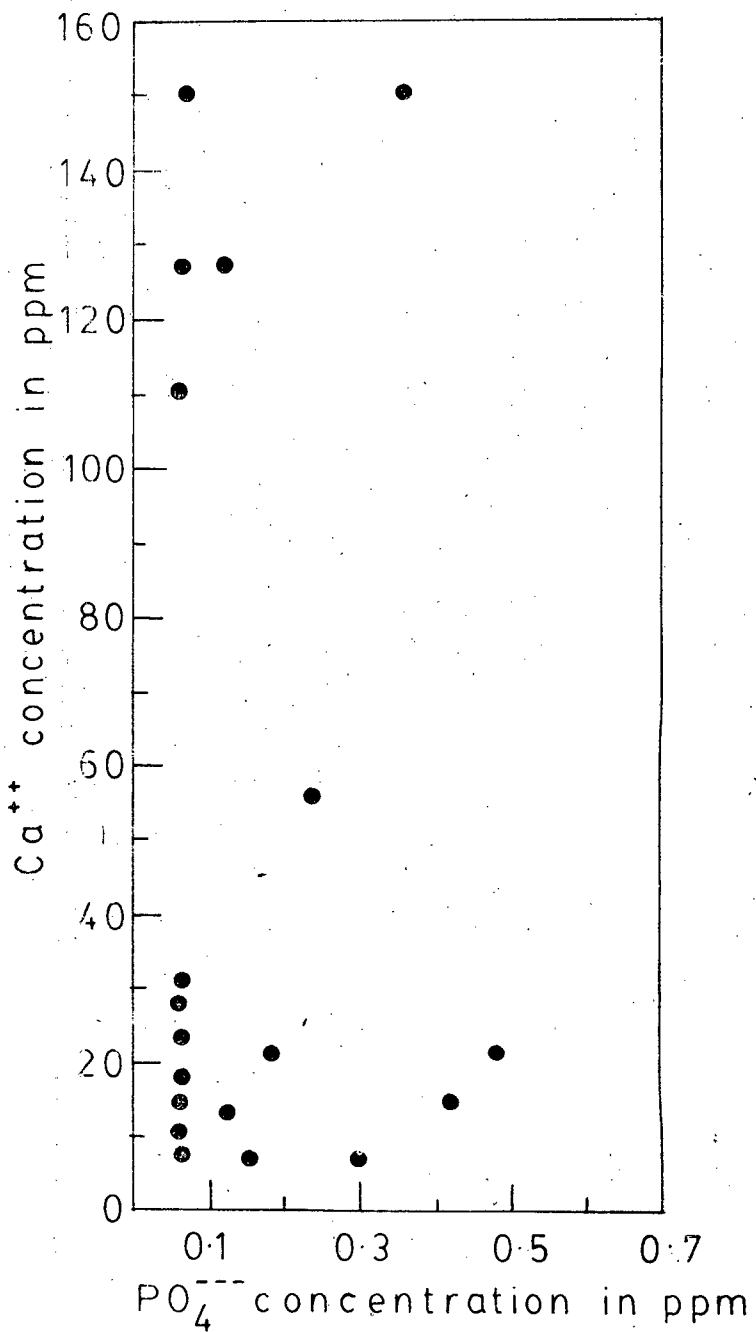
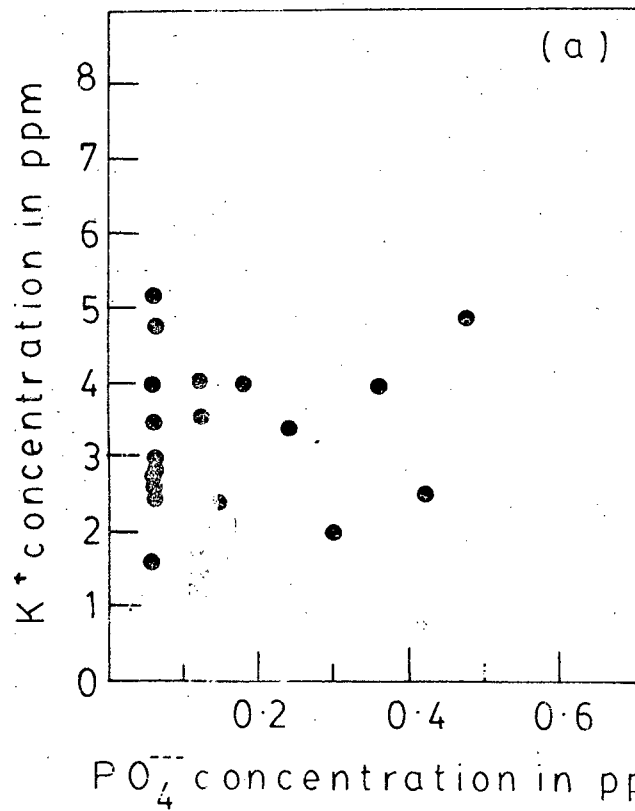
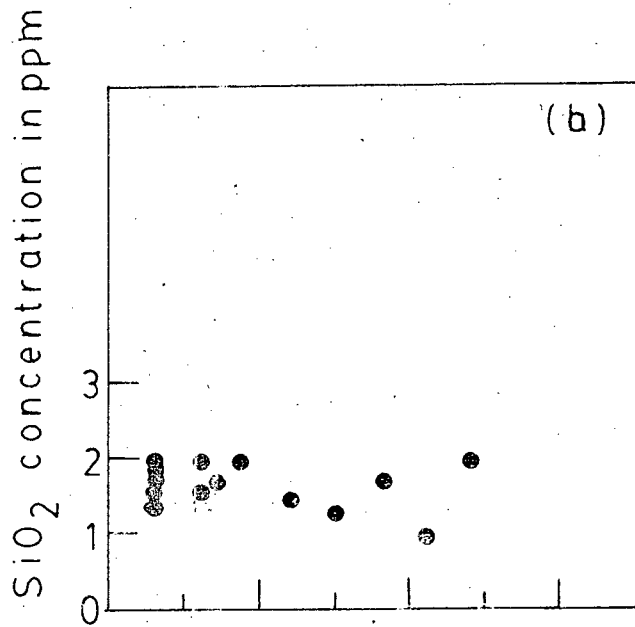


Fig.4:4. Graph showing the variation of Ca⁺⁺ concentration with phosphate.



Graph showing the variation of K⁺ and SiO₂ concentration with phosphate. (Fig. 4-5)

Subramanian (1979) has observed in the Indian rivers that pH buffering mechanism of carbonate equilibria controls the pH. In the Bandal river also the pH buffering mechanism of carbonate equilibrium is the controlling factor of pH in the aqueous system, due to the narrow range of pH.

Conductivity:

The specific conductivity varies from 0.4 to 1.5 mMH0/cm. It shows increase of conductivity with the increase of TDS. Abbas (1982) and Jha (1983) have reported down stream increase of conductivity in Ganga river water and Hooghly estuary respectively. In the Bandal river down stream increase of conductivity has not been observed. The irratic behaviour of conductivity may be due to irratic behaviour of dissolved major elements, because, the conductivity of any water depends upon dissolved major elements. Golterman and Kouwe (1980) have also reported that the conductivity of any water is roughly proportional to the concentration of its dissolved major elements. Fig. 4.1 shows the variation of conductivity with phosphate.

Alkalinity:

The alkalinity was measured as bicarbonate. The average bicarbonate concentration in the Bandal river is 153 ppm, which is higher in comparison to the world average (58.4 ppm) HCO_3^- concentration in the river water. The higher concentration is because the river flows through the terrain rich in limestone. The weathering of these carbonates releases HCO_3^- in water. Garrels and Mackenzie (1971) have reported alkaline water for chemically active rivers. Subramanian (1979) has also reported the same for Indian rivers. He has reported average of 90.77 ppm HCO_3^- in the Indian rivers. Subramanian (1979) after the observations of the composition of world average river water given by Livingstone (1963) and average composition of Indian rivers reports that HCO_3^- and Ca^{+2} contents differ significantly for the two average waters, suggesting that chemical weathering is intense in the Indian subcontinent.

Abbas (1982) and Jha (1983) have reported increase of HCO_3^- with the down stream for the Ganges river and Hooghly estuary respectively. In the Bandal river HCO_3^- does not show streamline variation. Variation of HCO_3^- with phosphate has been given in Fig. 4.2(b).

Talling & Talling (1965) have observed that with the increase of conductivity HCO_3^- increases. In Bandal river conductivity and bicarbonate show irratic change. The irratic changes may be due to unequal variations of different ions in the aguous system.

Chloride:

The Cl^- concentration does not show much variation. The average Cl^- concentration is 4.5 ppm. The Cl^- concentration of average river water is 7.8 ppm. The low concentration in the fresh water is because the Cl^- in rivers are derived from the sea spray and recycled through the atmosphere. Hence river water near to the sea will be having higher concentration of Cl^- . A graph (Fig. 4.3,b) was plotted to see the relationship between Cl^- & PO_4^{3-} .

✓ Golterman and Kouwe (1980) have observed that Cl^- increases with increasing conductivity. In Bandal river this relationship was not found. The Cl^- concentration is almost constant. Golterman and Kouwe (1980) have derived relationship between different cations and anions in the fresh water. They observed that Cl^- exceeds the other anions in a way parallel to that in which Na^+

dominates the cations. In Bandal river this relationship was not found. It may be due to unsystematic distribution pattern of different ions in the Bandal river.

Sulphate:

The concentration of SO_4^{-2} varies from 34 ppm in Bandal Canal (Maldeota) to 1020 ppm. in the Junction of mine water Durmala. The average concentration in the Bandal river is 274 ppm. Generally, it has been noticed that the SO_4^{-2} content in the water coming out from the mine is very high (118 to 1020 ppm) On the other hand as soon as the mine water joins Bandal river, the SO_4^{-2} concentration decreases drastically. It clearly shows that higher concentration of SO_4^{-2} in the Bandal river is due to high SO_4^{-2} concentration of water coming out from the phosphorite mines. In the mineralogical composition pyrite has been found associated with phosphorite. Pyrite readily changes by oxidation to an iron sulphate or to the hydrated oxide, limonite, with sulphuric acid set free, thus SO_4^{-2} in the water increases.

Dissolved silica:

Most of the dissolved silica is derived by weathering. Dissolved silica in the Bandal river is very low. The average SiO_2 concentration is 2 ppm, which is much lower

in comparison to the average SiO_2 concentration in the world river water (13.1 ppm). Table- 4.2 gives the average composition of world rivers.

Siever (1971) has reported for the water having $\text{pH} < 9$ that the dissolved silica is present as silicic acid (H_4SiO_4). Bandal river is having pH between 8.0 to 8.3, which indicates that in Bandal river water also dissolved silica is present as silicic acid. Maeda (1952), Makimoto et al (1955) have found linear relationship between dissolved silica and chlorinity. It is not observed in Bandal river. The linear relationship between silica and chlorite is the characteristic feature of marine & estuarine environment. Bandal river represents fresh water environment.

Dissolved phosphate (measured as orthophosphate)

The phosphate concentration in the most part of Bandal river is constant. It gives the phosphate concentration of 0.06 ppm. The variation of PO_4^{-3} between 0.06 to 0.48 ppm is because dissolved PO_4^{-3} from the mine is coming to the river. Basically PO_4^{-3} is not highly soluble in water. That is the reason for very less concentration of PO_4^{-3} in the outcoming mine water. Inside

the river where the phosphate concentration is of the order of 0.12 to 0.48 ppm. water outside the mine contains 0.06 - 0.07 ppm of phosphate. This concentration of PO_4^{-3} is being maintained in the entire course of river.

The analysis of canal water also shows 0.06 ppm concentration of PO_4^{-3} . Sampling for underground water was done. It also shows the same concentration of PO_4^{-3} . The water from canal goes to Dehradun where it is being used for drinking purposes. Analysis of Dehradun tap water shows some concentration of PO_4^{-3} . Sometimes slightly higher concentration of PO_4^{-3} upto 0.38 ppm has been observed in the Bandal river. It may be due to addition of PO_4^{-3} from the nearby field. The phosphorite fertilizer is being used in the field, when the rain falls the dissolved PO_4^{-3} goes to the river with the rain water.

On the other hand quarry shows very high concentration of PO_4^{-3} , the phosphate concentration is 1.32 ppm. The reason may be that the rock types in the quarry are not homogeneous on the other hand water is moving. Water passing through phosphorite weathers phosphate and PO_4^{-3} concentration increases.

Calcium has a great influence on the phosphate concentration, especially at high pH values and suggests that hydroxylapatite co-precipitation is involved (Viner, 1975). If calcium carbonate is precipitating, phosphate may be absorbed as well, causing thus a further reduction of the phosphate concentration (Golterman, 1973).

Effect of pH on phosphorus removal was studied by Narkis & Meiri (1981) and it was found that acidic alumina showed a better removal capacity than the basic alumina. At pH 9 Ca^{++} and Mg^{++} ions present in effluents are responsible for the precipitation of calcium hydroxylapatite and formation of phosphate salts and complexes of Ca^{++} and Mg^{++} overcoming the differences among the various types of alumina.

Subramanian (1976) reported that in the hydrosphere the fresh water contains only 0.02 ppm P and the sea water 0.062 ppm P, the weathering of primary phosphatic minerals, the transport of phosphorus in the aquatic environment and the precipitation and removal of P from the water are important rather than the dissolved ionic form of P. He further states that increase of pH causes precipitation of both calcite and apatite, when both are coprecipitated, the calcite/apatite ratio will be higher, since Ca^{++} , PO_4^{---}

and CO_3^{--} all have single valance states, changes in Eh cannot produce separation into carbonate rich and phosphate rich layer; hence the individual environment will have to take place within a narrow pH range. The solubility product of apatite is 1.3×10^{-30} . Hence in the pH range 7-7.6, apatite precipitates.

Fluoride:

In Bandal river F^- content varies from 1.0 to 2.1 ppm. surface water usually contain 0.1 ppm or less of naturally occuring fluoride, and occurs from 0.7 to 1.4 ppm. The variation of F^- with PO_4^{--3} has been plotted in Fig. - 4.3(a). Jha and Jha (1982) have reported that in India higher values, upto 12 ppm have been observed in surface water and 20 ppm in well water, this is equal to the concentrations in the US rivers and extuaries near individual pollution source.

The natural fluoride content of water in different areas varies according to the source of water, geology, the amount of rainfall and the quality of water lost by evaporation. The higher concentration of fluoride content may be due to phosphorite mine. Fluoride is the common constituents of fluorapatite. Fluorapatite is widely distributed in Maldeota-Durmala region. It will give fluoride ion after dissolution.

For drinking water fluoride content is safe maximum upto 0.5 ppm (WHO). In Maldeota in the tube well water it has been found 1.3 ppm. In Dehradun tap water also fluoride concentration has been found 1.3 ppm. Near the junction mine water Durmala, concentration of F^- is 2.1 ppm. This higher concentration may be because some of the audit in Durmala, which is not functional, shows higher concentration of fluoride in the sediments. Water coming from those mines will bring higher concentration of fluoride. This higher concentration of F^- may increase the concentration of fluoride at the junction where different mine water come together.

Major elements (Na^+ , K^+ , Ca^{+2} , Mg^{+2})

The variation of concentration of different major elements is interesting. In both Durmala mines and the junction of mine water, all the four major elements shows comparatively higher concentration. 100 meter below the junction of mine water the concentration decreases but all of a sudden at 200 meter below the junction mine water the concentration increase. The reason may be that some other water sources coming out from different mines with higher concentration of these ions join this mine water.

As soon as the Bandal river joins the mine water the concentration decreases. In the Bandal river this low concentration is being maintained throughout.

In the quarry again comparatively higher concentration of all the four major elements is being found. One interesting thing is noticed in Maldeota mines that in comparison to water inside the mine is having less concentration of all the four major elements than water outside the mine. The reason may be that the rock types are not homogeneous. On the other hand water is moving. The concentration of different ions depend on rock types through which the water passes. Fig.- 4.3(c), (d); Fig. - 4.4 & 4.5(a) show the variation of Mg^{++} , Na^{+} , Ca^{++} & K^{+} respectively with PO_4^{-3} .

Na^{+} , K^{+} :

Bandal river water shows higher Na^{+} concentration to K^{+} . It is common for all the water systems. The reason given by Millot (1970) for the water systems is that Na^{+} ion is more mobile when the weathering phenomena takes place; due to which higher amount of Na^{+} is being incorporated in the water, whereas, the K^{+} ion is being adsorbed by the sediments. Millot (1970) has also reported that less amount of K^{+} is being incorporated in the water and its volume is three times smaller than that of Na^{+} .

The relationship between conductivity and Na^+ has been established. In Bandal river generally increase of sodium with increasing conductivity is apparent. Talling and Talling (1965) have also observed a pronounced continuous increase of sodium with increasing conductivity in many African waters.

Ca^{+2} , Mg^{+2}

Ca^{+2} and Mg^{+2} throughout the Bandal river course shows higher concentration of Mg^{+2} to Ca^{+2} . The lithology of the area shows wide distribution of phosphorite and limestone. Weathering of these rocks releases Ca^{+2} ion. High amount of Ca^{+2} is being discharged into the water. But the result shows higher concentration of Mg^{+2} to Ca^{+2} . The reason may be that Ca^{+2} is being precipitated as CaCO_3 and thus Ca^{+2} ion is removed.

The $\text{Ca}^{+2}/\text{Mg}^{+2}$ ratio in audit-2, Durmala and junction mine water, Durmala is quite different. The Ca^{+2} ratio is very high in comparison to Mg^{+2} ratio. In Song Canal, under-ground water Maldeota and tap water Dehradun also the Ca^{+2} concentration is higher in comparison to Mg^{+2} concentration. Generally, the higher concentration of Ca^{+2} in the water may be due to weathering of apatite and calcite minerals.

Inside the mine, Maldeota it shows lower concentration of Ca^{+2} and Mg^{+2} in comparison to outside the mine. In the quarry concentration of both Ca^{+2} and Mg^{+2} is again high. The higher concentration of Ca^{+2} and Mg^{+2} outside the mine may be because the sample was collected, where the phosphate is being dumped.

Talling and Talling (1965) have observed in the African waters that Ca^{++} and HCO_3^- concentrations are around 0.2 m mol l^{-1} at the lower conductivity values and increase upto conductivity values between $100-500 \mu\text{scm}^{-1}$, above which generally Ca^{++} decreases and bicarbonate and carbonate still increase. In the Bandal river generally increase of Ca^{++} with increasing conductivity have been observed Mg^{+2} also increases with increasing conductivity. The reason is that conductivity of water is roughly proportioned to the dissolved major elements.

TDS

The average TDS concentration in the Bandal river is 547 ppm, which is higher than the world average (120 ppm). Generally water coming out from the mine is having higher TDS than the TDS concentration in the Bandal river. The higher value of TDS is due to higher concentration of SO_4^{-2} , Ca^{+2} , and Mg^{+2} . These three ions are having great

variations in different regions. As soon as the mine water joins Bandal river the concentration of these ions decrease due to dilution of water. Other ions like Na^+ , K^+ , PO_4^{3-} also get diluted but Ca^{+2} and Mg^{+2} and SO_4^{-2} make a drastic change.

Gibbs (1967), Carbonnel & Meyback (1975), Bikshamaiah and Subremanian (1980), Abbas (1982), have reported higher TDS down streams. This relationship is not being found in Bandal river. It may be due to the mining which abruptly changes the chemical composition of river water. Different audits situated at different altitude is discharging different amount of cations and anions, higher concentration of SO_4^{--} , PO_4^{---} , and Ca^{++} is due to the mine. It is also discharging sulphuric and phosphoric acid. Due to the precipitation and dissolution of different compounds the water chemistry of river may varies.

Apart from it the reason for irratic nature of the composition of water may be because water is a moving body; on the other hand lithology of the area is not homogeneous. Chemical composition of water depends on rock types through which the river passes. Carbonnel and Meybeck (1975) and Bikshamaiah (1979) have also reported for Mekong and

Godavari river respectively that rock types control the TDS. Subramanian and Dalavi (1978) have also observed for Ganges and the Yamuna rivers that TDS depends on the extent of chemical weathering and the rock types.

Gibbs (1967) has reported for Amazon river that its TDS is being controlled by elevation. But it is not common for all rivers. In the Indian context it has been observed in Yamuna river by Subramanian and Dalavi (1978). The water chemistry of Bandal river is not being governed by the relief, human activities predominates. Exploitation of phosphate, limestone and its transportation control the water chemistry of Bandal river.

RELATIONSHIP BETWEEN IAP & K FOR DIFFERENT PHOSPHATE MINERALS

The ion activity product of a given solution is denoted by IAP & the state of saturation of a solution with respect to a solid is defined as:

$IAP > K =$ Supersaturated

$IAP = K =$ Saturated

$IAP < K =$ Undersaturated

In the present study, ion activity product (IAP) and equilibrium constant (K) has been calculated assuming

Table - 4.3 Table showing IAP & IAP/K ratio for Apatite

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K, where K for apatite= 10^{-30}
Adt-1 (Durmala) (200 m)	4.300×10^{-8}	4.300×10^{22}
Adt-2 (Durmala) (500 m)	1.629×10^{-8}	1.629×10^{22}
Junction mine water (Durmala) (1600 m)	1.220×10^{-8}	1.220×10^{22}
100 meter below junction mine water (Durmala) (1700 m)	3.655×10^{-8}	3.655×10^{22}
200 meter below junction mine water (Durmala) (1800 m)	1.190×10^{-7}	1.190×10^{23}
Junction Bandal River+Mine water (Durmala) (2000 m)	5.380×10^{-8}	5.380×10^{22}
100 meter below Bandal River (Durmala) (2100 m)	3.570×10^{-8}	3.570×10^{22}

Contd...

Sample locations arranged in
the order of down stream
flow of the river

IAP

IAP/K

Bandal River (Maldeota) (15000 m)	5.950×10^{-9}	5.950×10^{21}
Adt-2 inside mine (Maldeota) (15000 m)	1.190×10^{-8}	1.190×10^{22}
Outside Adt-2 (Maldeota) (15000 m)	6.130×10^{-9}	6.130×10^{21}
Junction Adt-2 + Bandal River (Maldeota) (15200 m)	3.570×10^{-9}	3.570×10^{21}
Adt-1 inside mine (Maldeota) (15800 m)	1.550×10^{-8}	1.550×10^{22}
Outside Adt-1 (Maldeota) (15800 m)	6.095×10^{-8}	6.095×10^{22}
Tube well water (Maldeota) (15800 m)	8.000×10^{-9}	8.000×10^{21}
Quarry (Maldeota) (15900 m)	6.510×10^{-7}	6.510×10^{23}

Contd....

Sample locations arranged in
the order of down stream
flow of the river

IAP

IAP/K

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K
Junction Bandal River + Adt-1 + Adt-2 + Quarry (Maldeota) (16000 m)	6.300×10^{-9}	6.300×10^{21}
Junction Bandal River + Mashan Nala (Maldeota)(16800 m)	3.620×10^{-8}	3.620×10^{22}
Junction Bandal River + Jagdish Mool (Maldeota) (17000 m)	9.190×10^{-9}	9.190×10^{21}
Bandal River 100 m below Jagdish Mool (Maldeota) (17100 m)	2.723×10^{-8}	2.723×10^{22}
Bandal Canal (Maldeota) (19000 m)	5.110×10^{-9}	5.110×10^{21}
Song Canal (Maldeota)(19000 m)	2.640×10^{-8}	2.640×10^{22}
Junction Bandal Canal + Song Canal (Maldeota) (19100 m)	7.420×10^{-9}	7.420×10^{21}
Tap water (Dehradun) (35000 m)	9.700×10^{-8}	9.700×10^{22}

Table - 4.4 Table showing IAP & IAP/K ratio for Carbonate apatite

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K, where K for Carbonate apatite = $10^{-118.3}$
Adt-1 (Durmala) (200 m)	1.30×10^{-19}	$1.30 \times 10^{99.3}$
Adt-2 (Durmala) (500 m)	1.85×10^{-19}	$1.85 \times 10^{99.3}$
Junction mine water (Durmala) (1600 m)	4.50×10^{-20}	$4.50 \times 10^{98.3}$
100 meter below junction mine water (Durmala) (1700 m)	8.65×10^{-21}	$8.65 \times 10^{97.3}$
200 meter below junction mine water (Durmala) (1800 m)	3.42×10^{-20}	$3.42 \times 10^{98.3}$
Junction Bandal River+Mine water (Durmala) (2000 m)	1.37×10^{-20}	$1.37 \times 10^{98.3}$
100 meter below Bandal River (Durmala) (2100 m)	1.70×10^{-20}	$1.70 \times 10^{98.3}$
Bandal River (Maldeota) (15000 m)	1.39×10^{-22}	$1.39 \times 10^{96.3}$

Contd....

Sample locations arranged in
the order of down stream
flow of the river.

	IAP	IAP/K
Adt-2 inside mine (Maldeota) (15000 m)	3.51×10^{-20}	$3.51 \times 10^{98.3}$
Outside Adt-2 (Maldeota) (15000 m)	2.10×10^{-20}	$2.10 \times 10^{98.3}$
Junction Adt-2 + Bandal River (Maldeota) (15200 m)	1.93×10^{-20}	$1.93 \times 10^{98.3}$
Adt-1 inside mine (Maldeota) (15000 m)	4.19×10^{-20}	$4.19 \times 10^{98.3}$
Outside Adt-1(Maldeota) (15800 m)	1.12×10^{-19}	$1.12 \times 10^{99.3}$
Tube well water (Maldeota) (15800 m)	3.98×10^{-20}	$3.98 \times 10^{98.3}$
Quarry (Maldeota) (15900 m)	1.37×10^{-18}	$1.37 \times 10^{100.3}$
Junction Bandal River + Adt-1 + Adt-2 + Quarry (Maldeota) (16000 m)	2.80×10^{-20}	$2.80 \times 10^{98.3}$

Contd...

Sample locations arranged in
the order of down stream
flow of the river

IAP

IAP/K

Junction Bandal River +
Mashan Nala (Maldeota) (16800 m)

1.53 x 10⁻¹⁹

1.53 x 10^{99.3}

Junction Bandal River + Jagdish
Nool (Maldeota) 17000 m)

4.61 x 10⁻²⁰

4.61 x 10^{98.3}

Bandal River 100 m below Jagdish
Nool (Maldeota)(17100 m)

1.34 x 10⁻²⁰

1.34 x 10^{98.3}

Bandal Canal (Maldeota)
(19000 m)

1.43 x 10⁻²⁰

1.43 x 10^{98.3}

Song Canal (Maldeota) (19000 m)

3.72 x 10⁻¹⁹

3.72 x 10^{99.3}

Junction Bandal Canal + Song Canal
(Maldeota) (19100 m)

10⁻²⁰

10^{98.3}

Tap water (Dehradun) (35000 m)

1.70 x 10⁻²⁰

1.70 x 10^{98.3}

Table - 4.5 Table showing IAP & IAP/K ratio for Fluorapatite

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K, where K for Fluorapatite = 10^{-120}
Adt-1 (Durmala) (200 m)	6.62×10^{-11}	6.62×10^{109}
Adt-2 (Durmala) (500 m)	1.83×10^{-11}	1.83×10^{109}
Junction mine water (Durmala) (1600 m)	2.74×10^{-10}	2.74×10^{110}
100 meter below junction mine water (Durmala) (1700 m)	4.41×10^{-12}	4.41×10^{108}
200 meter below junction mine water (Durmala) (1800 m)	1.70×10^{-10}	1.70×10^{110}
Junction Bandal River + Mine Water (Durmala) (2000 m)	1.73×10^{-9}	1.73×10^{111}
100 meter below Bandal River (Durmala) (2100 m)	1.45×10^{-12}	1.45×10^{108}
Bandal River (Maldeota) (15000 m)	1.01×10^{-11}	1.01×10^{109}

Contd....

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K
Adt-2 inside mine (Maldeota) (15000 m)	1.89×10^{-11}	1.89×10^{109}
Outside Adt-2 (Maldeota) (15000 m)	9.70×10^{-12}	9.70×10^{108}
Junction Adt-2 + Bandal River (Maldeota) (15200 m)	6.97×10^{-12}	6.97×10^{108}
Adt-1 inside mine (Maldeota) (15000 m)	2.56×10^{-11}	2.56×10^{109}
Outside Adt-1 (Maldeota) (15800 m)	10^{-10}	10^{110}
Tube well water (Maldeota) (15800 m)	1.27×10^{-11}	1.27×10^{109}
Quarry (Maldeota) (15900 m)	1.23×10^{-9}	1.23×10^{111}
Junction Bandal River + Adt-1 + Adt-2 + Quarry (Maldeota) (16000 m)	10^{-11}	10^{109}

Contd....

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K
Junction Bandal River + Mashan Nala (Maldeota) (16800 m)	5.73×10^{-11}	5.73×10^{109}
Junction Bandal River + Jagdish Mool (Maldeota)(17000 m)	1.57×10^{-11}	1.57×10^{109}
Bandal River 100 m below Jagdish Mool (Maldeota) (17100 m)	1.44×10^{-12}	1.44×10^{108}
Bandal Canal (Maldeota) (19000 m)	8.70×10^{-12}	8.70×10^{108}
Song Canal (Maldeota) (19000 m)	4.37×10^{-11}	4.37×10^{109}
Junction Bandal Canal + Song Canal (Maldeota) (19100 m)	1.14×10^{-11}	1.14×10^{109}
Tap water (Dehradun) (35000 m)	5.22×10^{-12}	5.22×10^{108}

Table - 4.6 Table showing IAP & IAP/K ratio for Hydroxylapatite

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K, where K for Hydroxylapatite = 10^{-115}
Adt-1 (Durmala) (200 m)	1.35×10^{-11}	1.35×10^{104}
Adt-2 (Durmala) (500 m)	4.07×10^{-13}	4.07×10^{102}
Junction mine water (Durmala) (1600 m)	3.85×10^{-12}	3.85×10^{103}
100 meter below junction mine water (Durmala) (1700 m)	1.15×10^{-10}	1.15×10^{105}
200 meter below junction mine water (Durmala) (1800 m)	3.74×10^{-12}	3.74×10^{103}
Junction Bandal River+Mine water (Durmala)(2000 m)	2.12×10^{-12}	2.12×10^{103}
100 meter below Bandal River (Durmala) (2100 m)	1.41×10^{-11}	1.41×10^{104}
Bandal River (Maldeota) (15000 m)	1.01×10^{-11}	1.01×10^{104}

Contd....

Sample locations arranged in
the order of down stream
flow of the river

IAP

IAP/K

Sample locations arranged in the order of down stream flow of the river	IAP	IAP/K
Adt-2 inside mine (Maldeota) (15000 m)	4.71×10^{-13}	4.71×10^{102}
Outside Adt-2 (Maldeota) (15000 m)	1.93×10^{-13}	1.93×10^{102}
Junction Adt-2 + Bandal River (Maldeota) (15200 m)	1.41×10^{-13}	1.41×10^{102}
Adt-1 inside mine (Maldeota) (15000 m)	6.11×10^{-13}	6.11×10^{102}
Outside Adt-1 (Maldeota) (15800 m)	1.52×10^{-12}	1.52×10^{103}
Tube well water (Maldeota) (15800 m)	3.63×10^{-13}	3.63×10^{102}
Quarry (Maldeota) (15900 m)	1.63×10^{-11}	1.63×10^{104}
Junction Bandal River + Adt-1 + Adt-2 + Quarry (Maldeota) (16000 m)	2.50×10^{-12}	2.50×10^{103}

Contd....

Sample locations arranged in
the order of down stream
flow of the river

IAP

IAP/K

Junction Bandal River +
Mashan Nala (Maldeota) (16800 m)

1.43×10^{-12}

1.43×10^{103}

Junction Bandal River +
Jagdish Mool (Maldeota)
(17000 m)

3.63×10^{-12}

3.63×10^{103}

Bandal River 100 m below
Jagdish Mool (Maldeota)
(17100 m)

1.08×10^{-11}

1.08×10^{104}

Bandal Canal (Maldeota)
(19000 m)

1.61×10^{-13}

1.61×10^{102}

Song Canal (Maldeota) (19000 m)

6.60×10^{-11}

6.60×10^{104}

Junction Bandal Canal +
Song Canal (Maldeota) (19100 m)

1.86×10^{-11}

1.86×10^{104}

Tap water (Dehradun) (35000 m)

2.43×10^{-11}

2.43×10^{104}

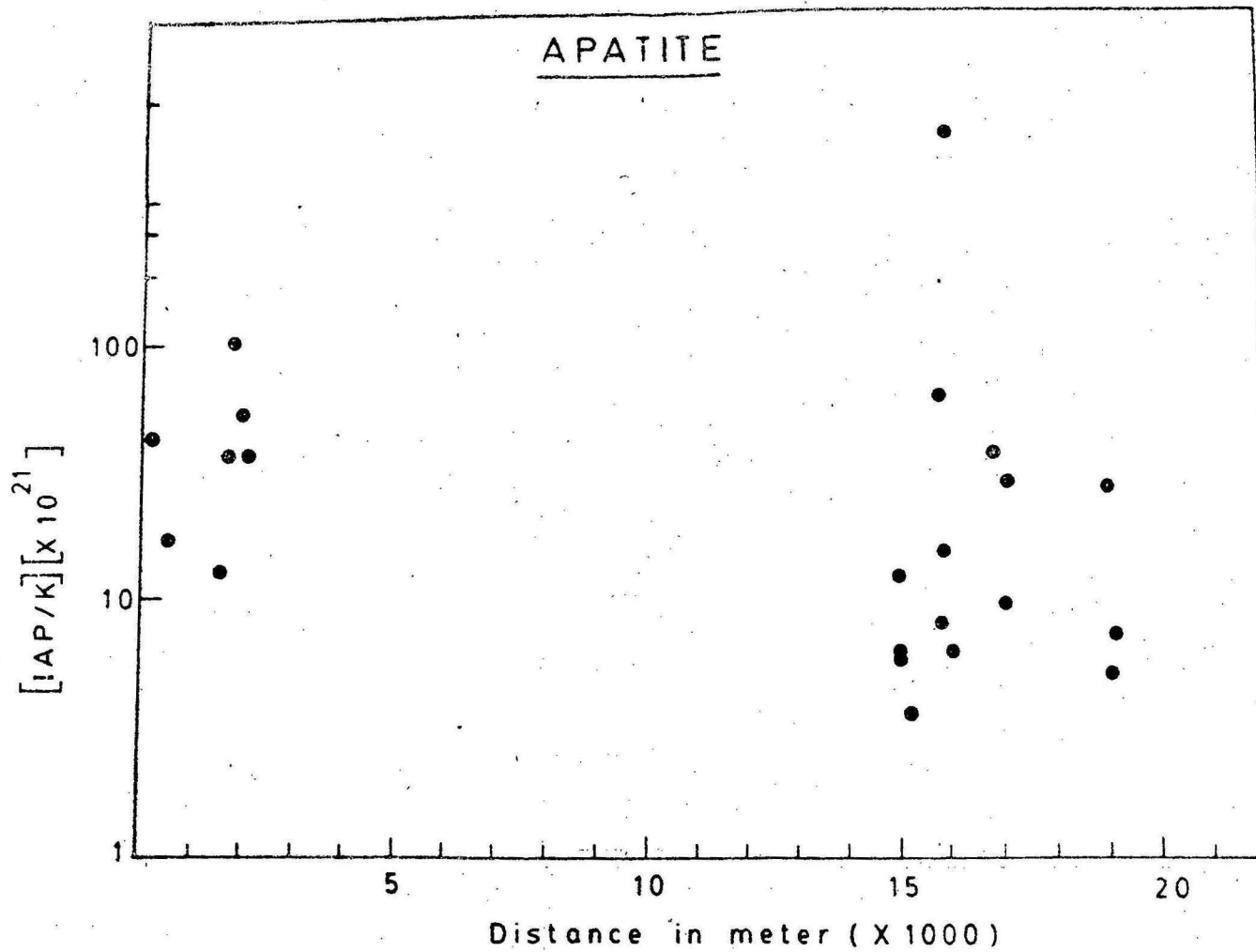


Fig. 4.6. Graph showing the variation IAP/K of apatite with distance

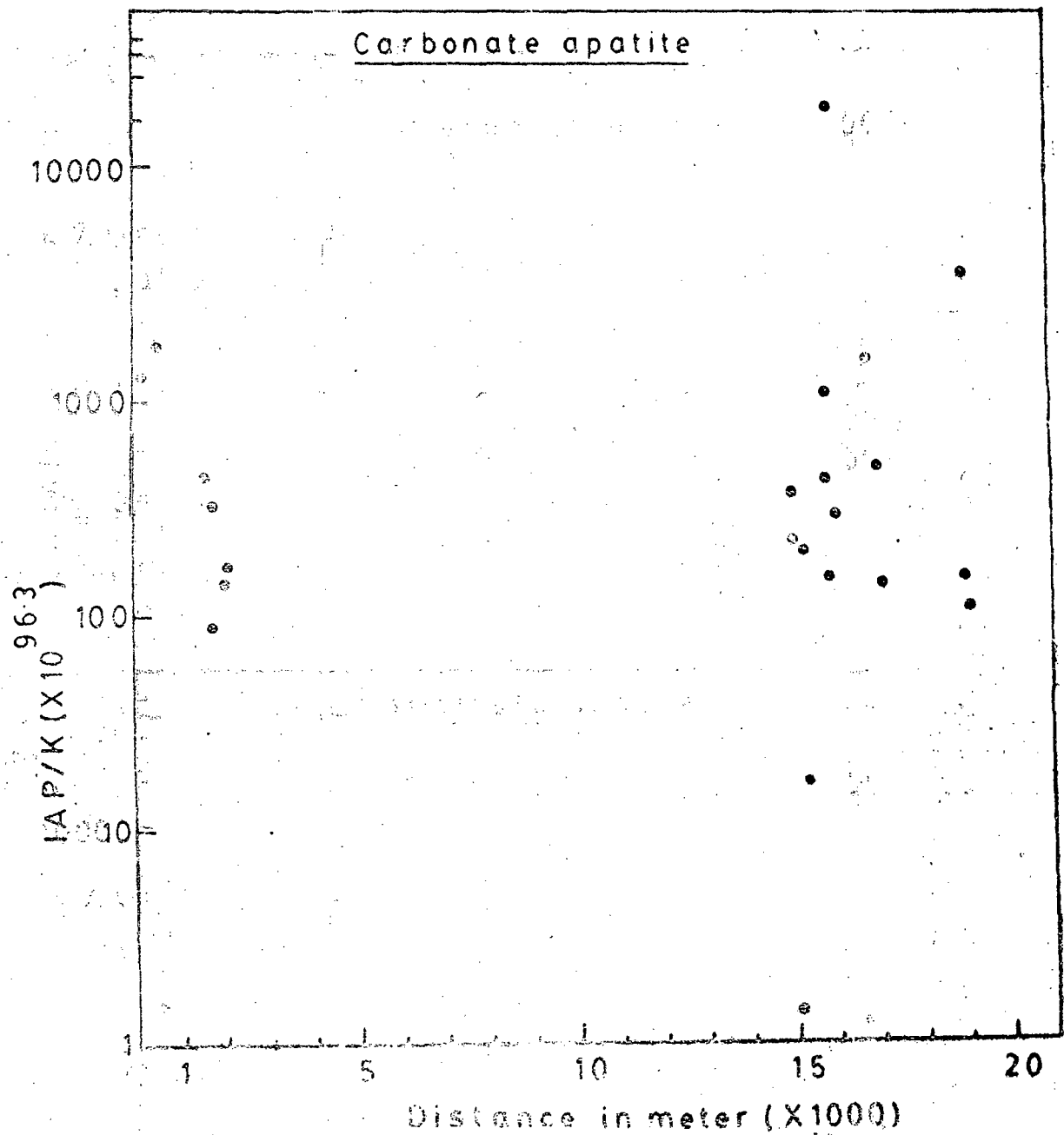


Fig. 47. Graph showing the variation of IAP₆/K of carbonate apatite with distance.

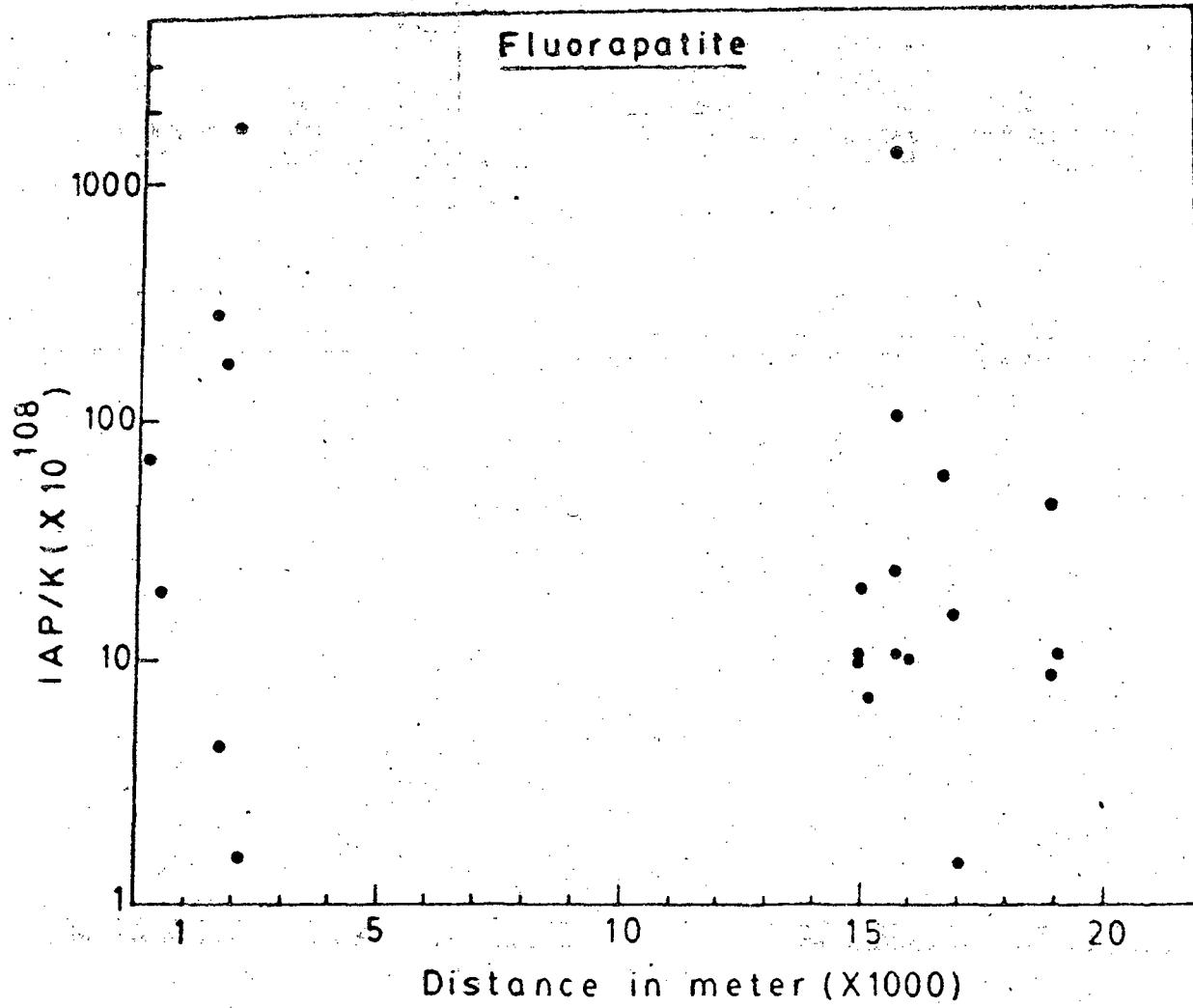


Fig. 4.8. Graph showing the variation of IAP /K of Fluorapatite with distance.

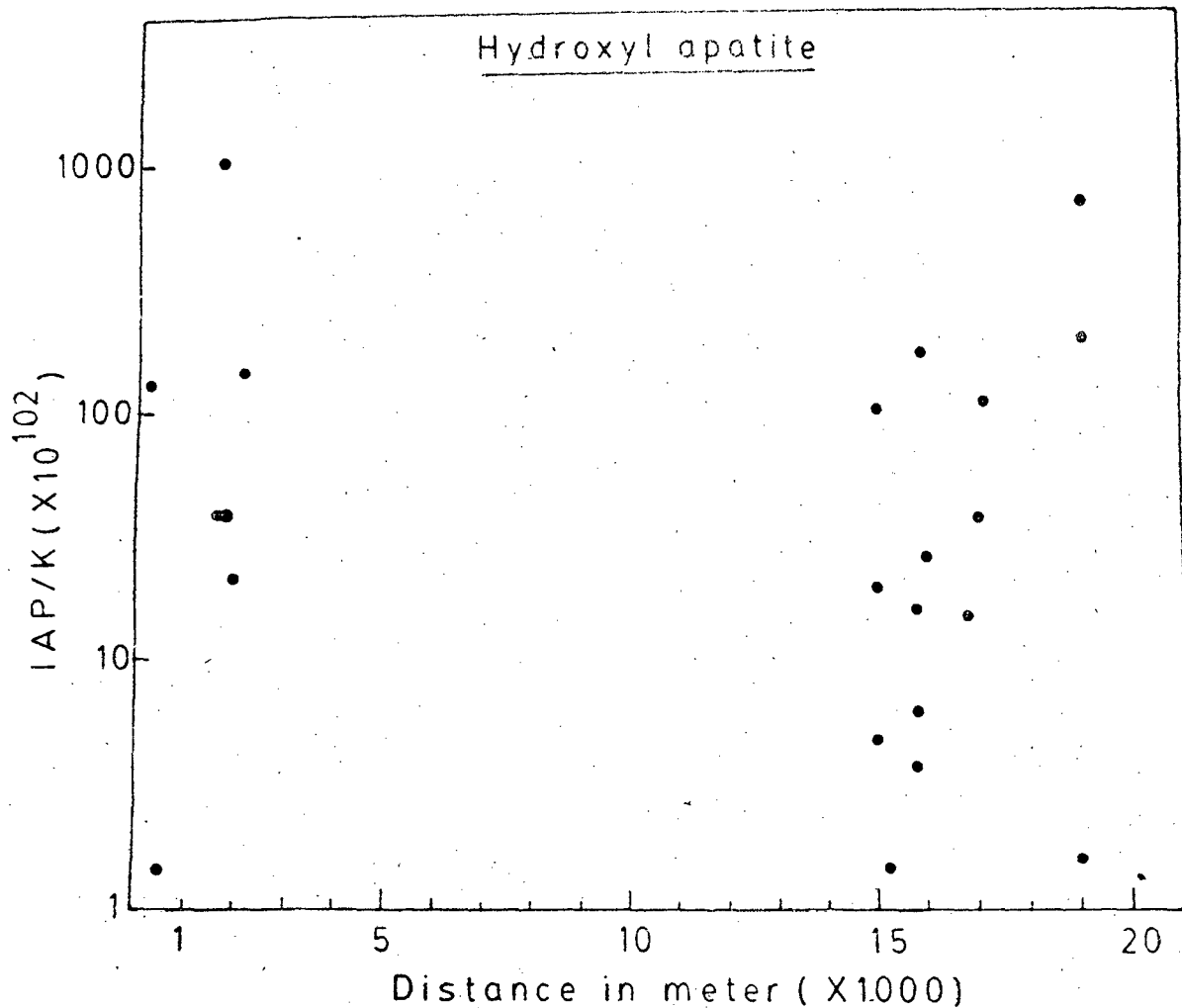


Fig. 4.9. Graph showing the variation of IAP/K of hydroxy apatite with distance.

constant temperature (T 25°C) and pressure (1 atm.) (Table - 4.3 to 4.6). The activity and the equilibrium constant are the functions of temperature pressure and chemical composition. These factors govern the solubility, precipitation and stability of various minerals in the aqueous environment.

Kinetic conditions also govern the aquatic system. Garrels and Mackenzie (1967) shows that natural waters are supersaturated with respect to quartz but due to kinetic effects, the actual crystallization of quartz from the water is not observed. Thus, for understanding the actual chemical reaction, the Kinetic approach is essential along with the thermodynamic approach. However, the discussion and application of Kinetics is beyond the scope of the present work.

There are four types of phosphate minerals common in the fresh water system apatite, fluorapatite, hydroxyapatite and carbonate apatite. Valyasko et al (1968) has reported that all these four phosphate minerals are supersaturated in the fresh water. In Bandal river also phosphate minerals are found supersaturated. It is evident by its IAP/K ratio which is > 1 . Fig.-4.6 to 4.9 shows the variation of IAP/K ratio of different phosphates with distance.

The solubility of different phosphate minerals varies in fresh water. The least soluble of apatite is fluorapatite. The solubility of phosphate rock, in terms of kinetic and equilibrium dissolution, depends on the carbonate substitution in apatite structure as reported by Chien and Black (1975, 1976). The solubility of hydroxyl fluorapatite increases from fluorapatite to hydroxylapatite as reported by Mc Cann (1968) and Wier et al (1972).

Hydroxyl-fluorapatite is generally considered to be solid solution of hydroxylapatite and fluorapatite. Wier et al (1972) showed that hydroxylapatite was transformed to less soluble fluorapatite after the former apatite had been equilibrated with solid fluoride. On the other hand, Mc Cann (1968) reported that for pure fluorapatite equilibrated with aqueous solutions at pH 6.4 and above, the ion activity product $(Ca^{++}) (PO_4^{---}) (F^-)$, exceeded the solubility product constant determined for fluorapatite and the value increased as the pH increased. Mc Cann's findings indicate that hydroxyl ions may partially substitute for fluoride in fluorapatite to form a solid solution of hydroxyl-fluorapatite if the solution is relatively alkaline.

It seems likely, therefore that hydroxyl substitution is also an important factor to be considered in order to understand the solubility behaviour of apatite mineral in certain phosphate rocks.

Hydroxyl-fluorapatite, being a compound of constant composition dissolves congruently in water. The activity products of apatites decrease with increasing temperature, i.e., apatite becomes more stable as temperature rises. Therefore, the capacity of the hydrothermal solutions to extract apatite from the rocks and transport its component increases with decreasing temperature. The transport of calcium and phosphorus in equivalent amount by aqueous solutions becomes more difficult at higher temperatures, and hydrothermal apatite is more likely to form at elevated temperatures by interaction between phosphorus bearing solutions and calcium bearing rocks.

BED SEDIMENT ANALYSIS

MINERALOGY

The X-ray analysis of Maldeota-Durmala samples reveals the presence of different phosphate minerals, carbonate minerals, clay minerals, quartz, felspar & pyrite. Table - 4.10 shows the mineralogical composition of Maldeota-Durmala. Table - 4.11 shows the percentage of different minerals. The detail study of mineralogy has been described below:

Quartz and Felspar:

Quartz is present in all the samples. The percentage of quartz varies from about 3% to 56%. The variation of quartz with phosphate minerals has been shown in Fig - 4.18(a). Gibbs (1967) reported that quartz is less abundant in mountainous environment. In case of samples from Mussoorie, the quartz percentage is very high (31%). The high percentage of quartz in this region may be due to breaking down of quartz by some physical processes. The less abundance of quartz observed by Gibbs may be because the mountainous region in the Andes may not be having abundance of quartz minerals in the host rocks. The percentage of felspar is very small. It varies from 1.1 to 6.3%. The

Table 4.10 Mineralogy of the bed sediments
(in percentage)

Sample locations arranged in the order of down stream flow of the river	Dolomite	Calcite	Felspar	Qtz.	Montmori- llonite	Chlorite	Kaolinite	Illite	Pyrite	Carbonate apatite	Flour.+Hydroxyl +Chlor- apatite	Francolite
Adt-1A (Durmala) (100 m)	x	4.3	6.3	2.7	x	x	x	x	4.9	x	24.3	57.6
Adt-1 (Durmala) (200 m)	x	x	x	23.5	x	x	x	x	14.8	x	28.4	33.3
Adt-2B (Durmala) (300 m)	x	x	2.2	5.4	x	x	x	5.1	x	10.1	47.4	29.8
Adt-2A (Durmala) (400 m)	x	x	x	9.5	x	x	x	x	x	40.7	22.4	27.4
Adt-2 (Durmala) (500 m)	x	x	4.9	21.2	x	x	x	x	x	9.7	23.4	40.9

Contd...

Sample locations
arranged in the
order of down
stream flow of
the river

	Dolomite	Calcite	Felspar	Gtz.	Montmori- llonite	Chlorite	Kaolinite	Illite	Pyrite	Carbonate apatite	Flour. + Hydroxyl. + Chlor-apatite	Francolite
Adt-3 (Durmala) (600 m)	x	17.3	x	50.4	x	x	x	x	32.4	x	x	x
200 meter below junction mine water (Durmala) (1800 m)	x	17.6	5.3	36.5	x	x	x	4.4	3.5	27.5	3.5	x
Adt-2 (Maldeota) (15000 m)	x	2.6	x	42.5	x	x	x	x	x	32.0	2.8	20.0
Adt-1 (Maldeota) (15800 m)	x	11.6	x	38.9	x	x	x	x	1.0	36.4	8.4	3.7
Quarry (Maldeota) (15900 m)	x	x	x	56.3	6.3	20.3	x	6.3	3.6	x	x	7.2

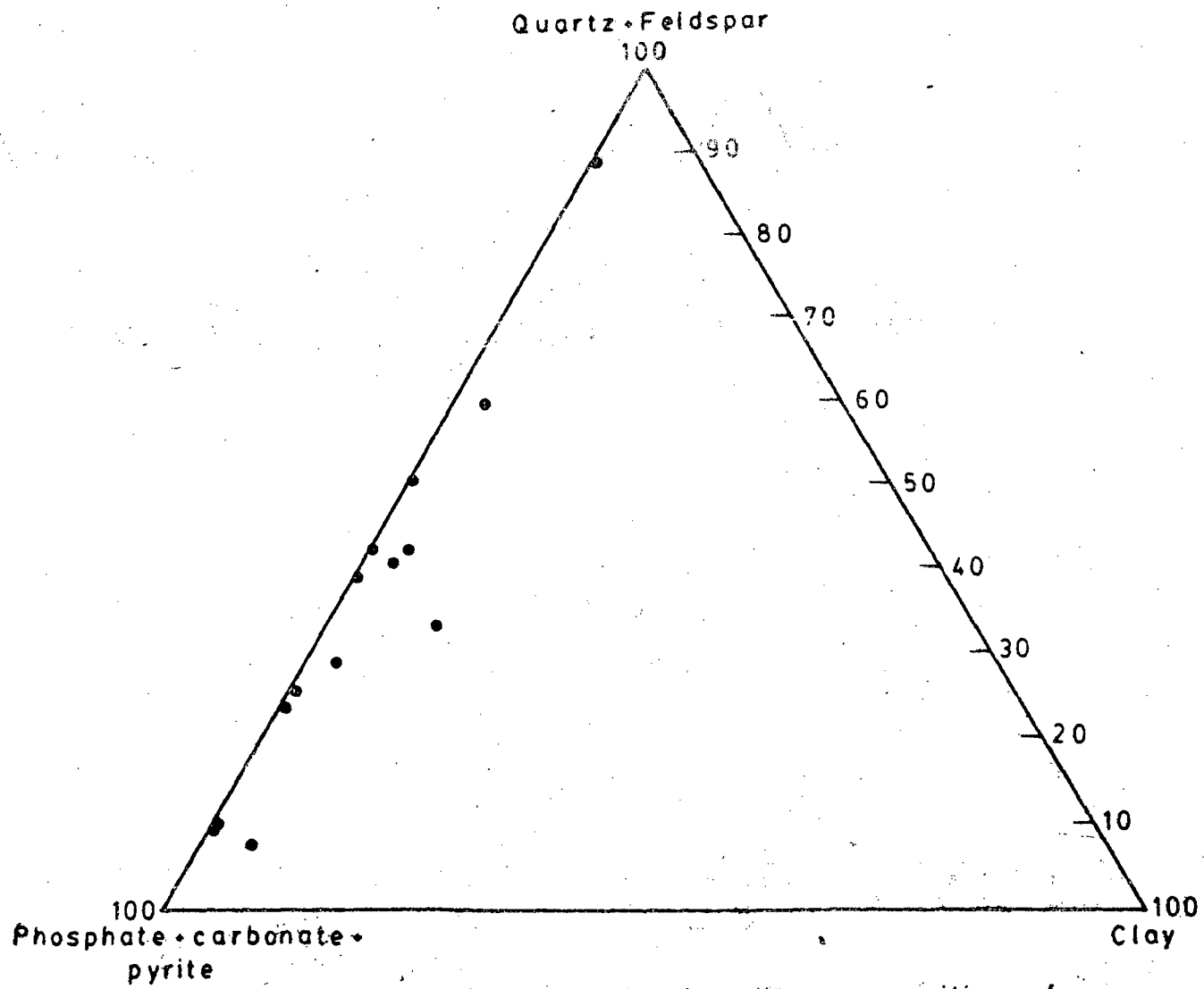
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Sample locations
arranged in the
order of down
stream flow of
the river

	Dolomite	Calcite	Felspar	Qtz.	Montmori- llonite	Chlorite	Kaolinite	Illite	Pyrite	Carbonate apatite	Flour. +Hydro- xyl.+Chlor- apatite	Francolite
Junction Bandal River + Mashan Nala (Maldeota) (16800 m)	1.7	13.9	x	23.4	x	x	x	x	14.9	x	29.8	16.2
Dry Bandal River (Maldeota) (19000 m)	x	40.3	x	27.9	x	x	x	2.8	5.0	x	7.0	17.0
Soil nearby field of Song Canals (Maldeota)(19000 m)	x	x	3.3	55.8	x	1.9	0.7	0.7	1.1	x	16.9	19.7
Song River Doiwala (35000 m)	x	10.7	1.1	39.3	x	x	x	2.9	17.0	x	29.0	x

Table 4.11 Table showing Average (%) of different minerals in Maldeota-Durmala region

Phosphate minerals	51
Quartz	31
Carbonate minerals	15
Pyrite	9
Clay minerals	8
Felspar	4



Triangular diagram showing the composition of the bed sediments.

Fig.4.15.

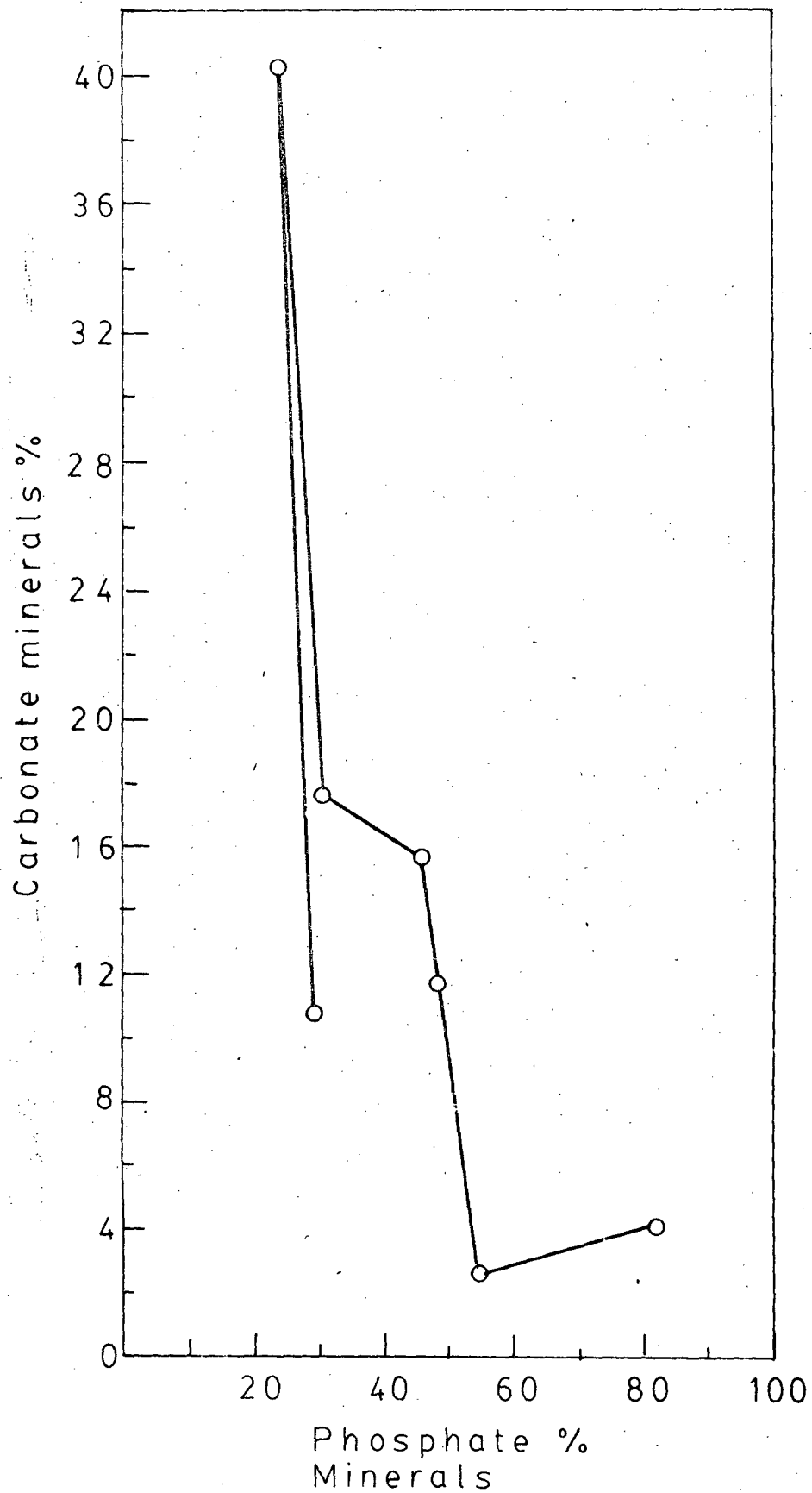


Fig.4-16. The graph showing the relationship between phosphate and carbonate minerals

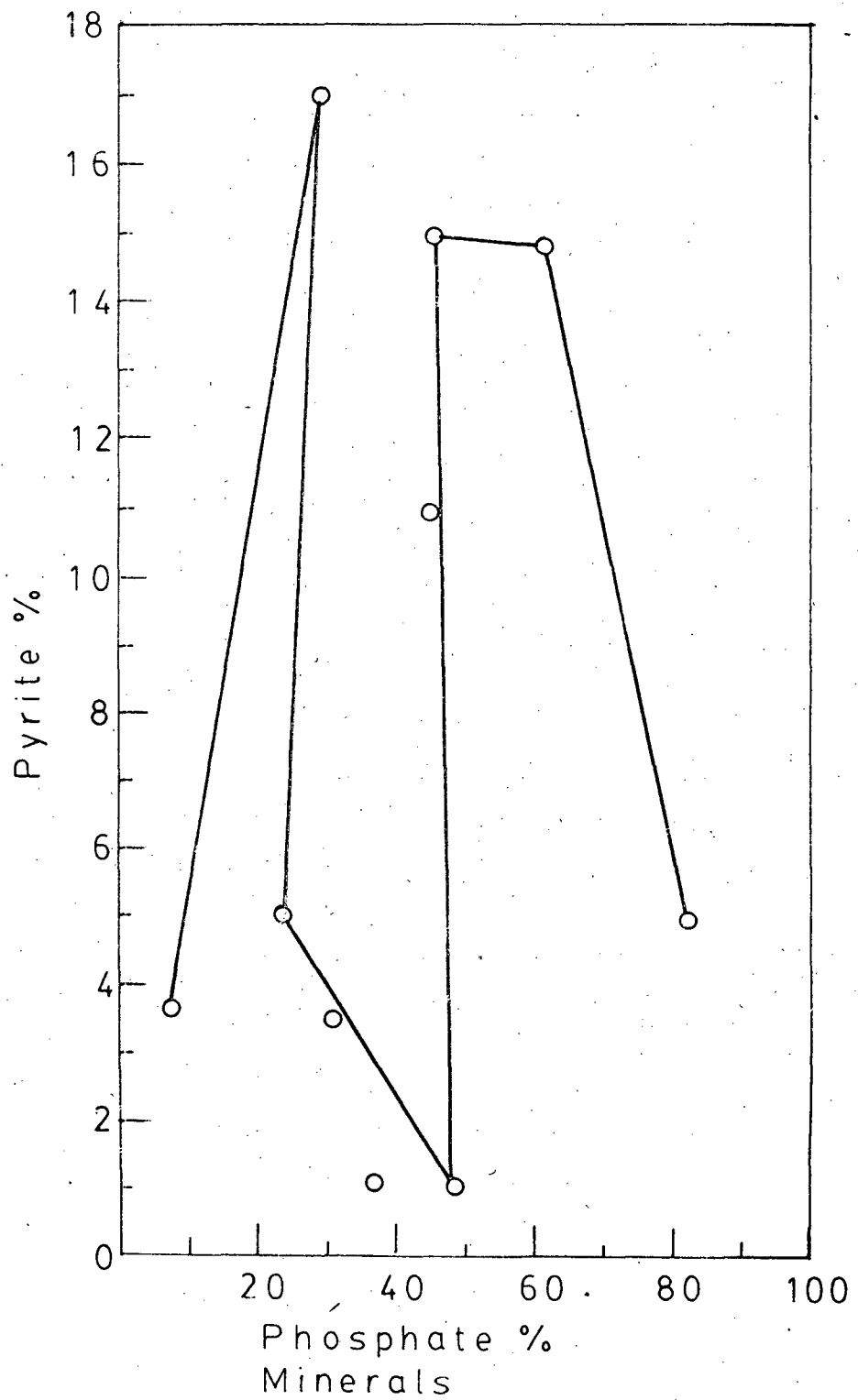


Fig. 4-17. The graph showing the relationship between phosphate and pyrite minerals

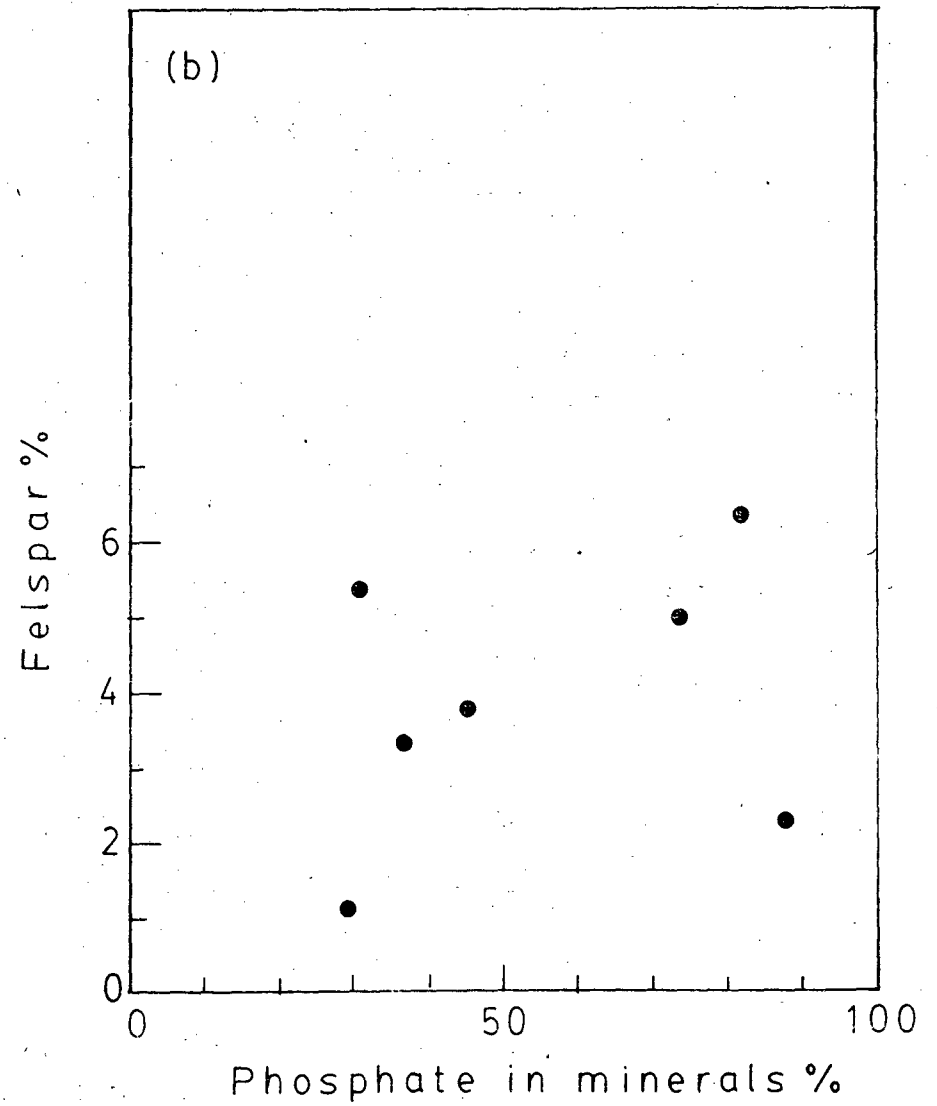
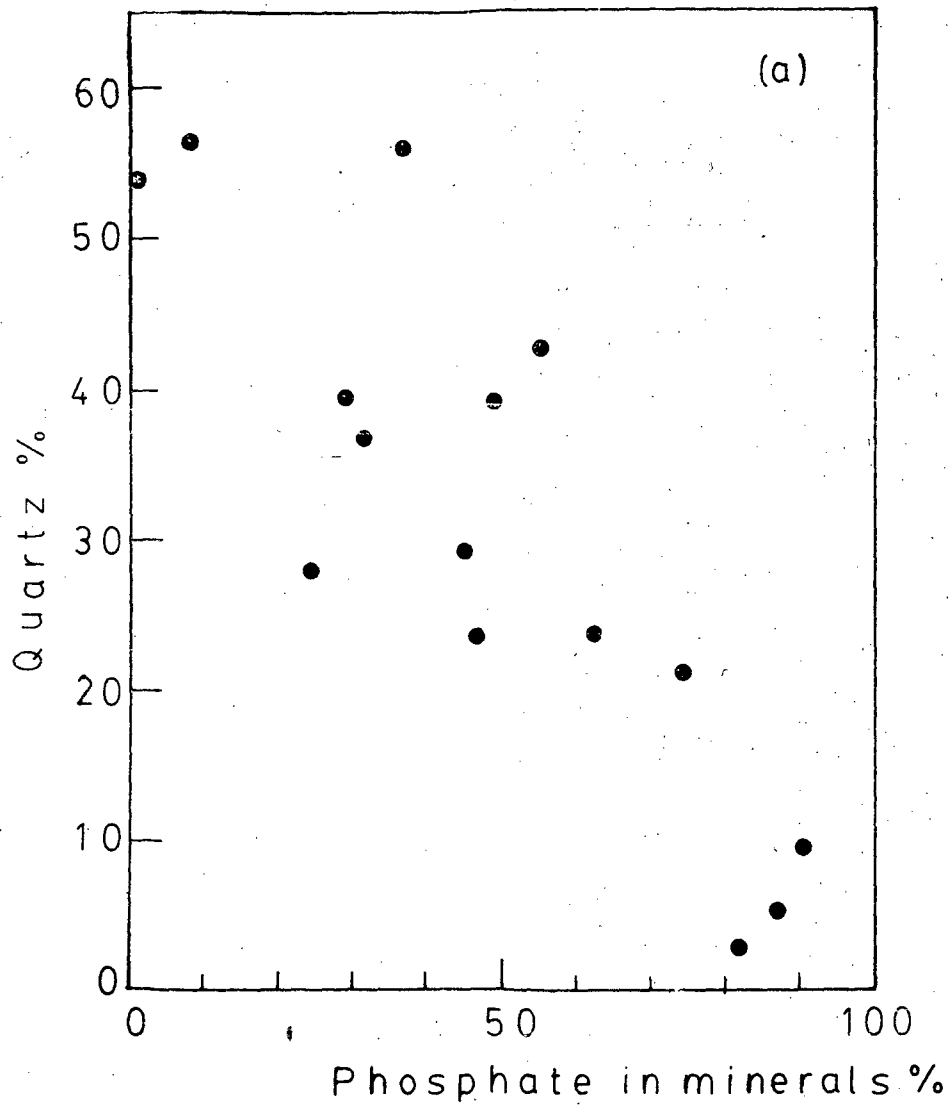


Fig. 4.18 showing the variation of Quartz & Feldspar with phosphate minerals.

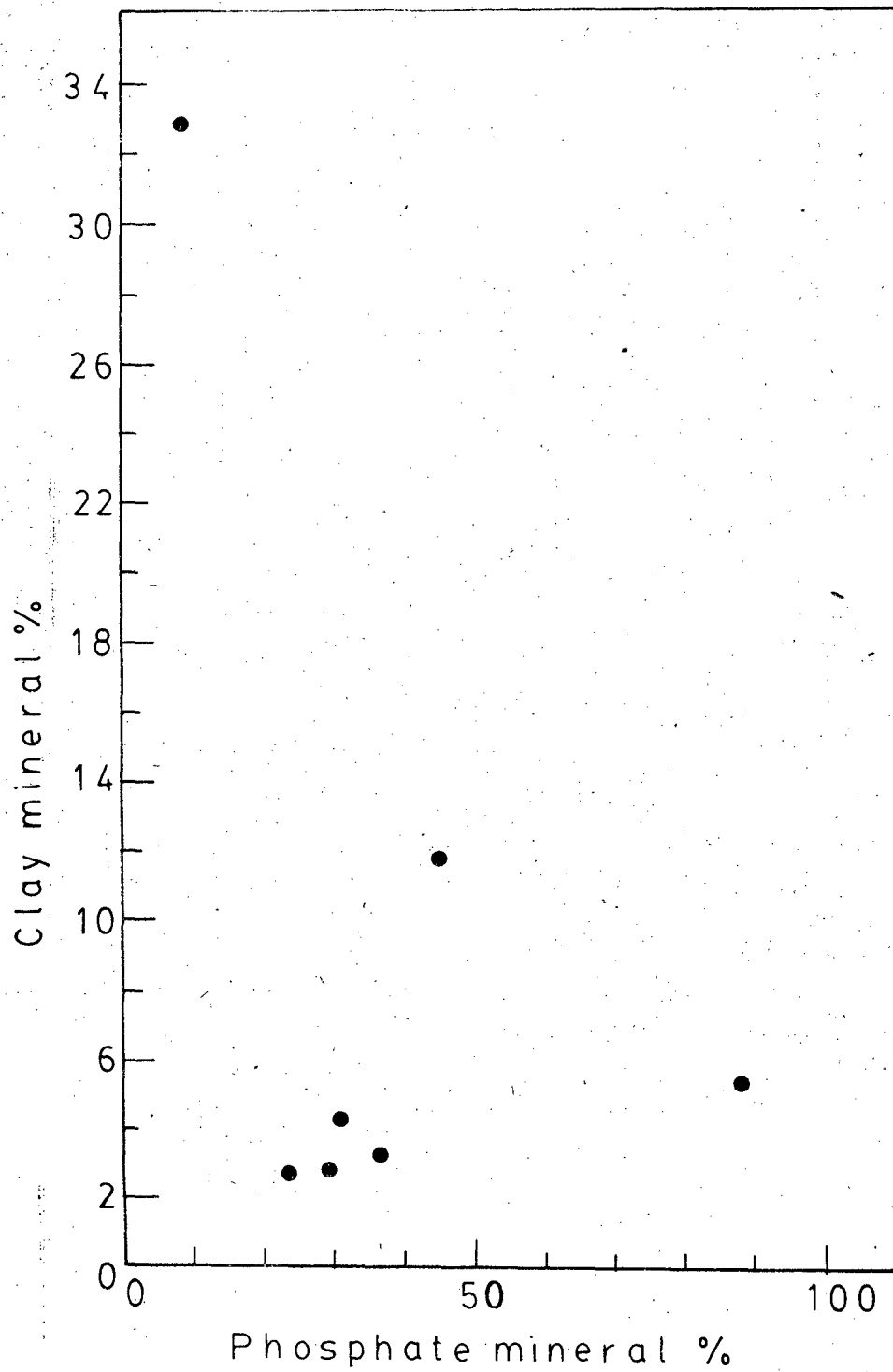


Fig. 4-19. Graph showing the variation of clay minerals with phosphate minerals.

variation of felspar with phosphate minerals has been shown in Fig - 4.18(b), Generally felspar is absent.

Jha (1983) has observed for Hooghly estuary that quartz decreases down stream, whereas felspar shows an increase. This relationship was not found. It may be because the relief is high. Quartz and Felspar are the product of mechanical breakdown of igneous, metamorphic and sedimentary rocks. Due to high velocity of river water all these minerals may be carried away and deposited where water body is quiet.

Carbonates:

Calcite is the chief carbonate minerals in both the Durmala and Maldeota blocks. It varies from 3% to 40%. Dolomite is very rare. According to Mehrotra et al (1981) dolomite predominates in Durmala and calcite predominates in Maldeota block. But the bed sediments along with Bandal river rarely contains dolomite. Both in Durmala block as well as Maldeota block calcite predominates. Calcite varies from 3% to 40%. Fig - 4.16 shows the variation of carbonate minerals with the phosphate minerals.

Jha (1983) reports that both the calcite and dolomite show the down stream decrease in their abundance. In Bandal river also it shows the same trend. The abnormal increase of calcite in the lower region of dry Bandal river (where calcite percentage is 40%) may be because the course of river is almost flat and the sediments are being deposited. Again the downward decrease of calcite is being maintained because the calcite content in the Song River near Doiwala (which is about 20 kms. from Maldeota) shows decrease in calcite percentage.

Clay Minerals:

Clay minerals varies from 3% to 4% throughout the course of river. The region for low concentration of clay minerals is that the relief is very high and therefore most of the finer part of the sediments is being carried away. Clay minerals are more abundant in low relief environment than the high relief environment. Clay minerals are the product of low relief chemical weathering.

The sediments from different audits generally show absence of clay minerals. It is because inside the mine or near the mine loose phosphorite materials dominate. The high percentage of clay minerals and low percentage of

phosphate minerals in the quarry (Maldeota) may be due to sampling error. Fig - 4.19 shows the variation of clay minerals with the phosphate minerals.

Among the clay minerals illite is most common. Montmorillonite, chlorite and Kaolinite are very rare. The freshwater sediments generally contains 17% to 20% illite, 4% to 64% Kaolinite, 1% to 3% chlorite. High percentage of illite has been reported in the Ganges river by (Subramanian, 1980; Abbas, 1982).

Pyrite:

Pyrite is very widespread in its occurrence being the common sulphide. It occurs in rocks of all ages and types, being most common in the metamorphic and sedimentary rocks. It is generally associated with phosphate minerals. In Maldeota-Durmala region, it varies from 1% to 32%. The variation of pyrite with phosphate has been shown in Fig - 4.17. Dubey and Parthasarathy (1975) after mineralogical study of phosphorite in Durmala have reported pyrite intimately associated with collophane forming irregular alternate bands in some of the thin sections.

These sulphides can be formed through the action of hydrogen sulphide, although the reducing action of

carbonaceous materials may also at times be of importance. The association of pyrite with phosphorite in Maldeota-Durmala region is important in the sense, it may be one of the region for higher concentration of sulphate in the mines & Bandal river water. It easily oxidises to an iron sulphate or to hydrated oxide, limonite, with sulphuric acid set free.

Phosphate Minerals:

Among the phosphate minerals francolite, carbonate apatite, fluor and hydroxyl-apatite dominate. Dubey and Parthasarathy (1975), have also observed carbonate-apatite and carbonate substituted variety of apatite-francolite in Durmala region. Mehrotra et al. (1981) have reported hydroxyl fluor-apatite i.e. francolite as the main phosphate mineral with minor amount of dahllite, brushite and uraninite in Mussoorie region.

The overall phosphate content vary from 7% to 91% whereas francolite varies from 4% to 58%, fluor and hydroxyl apatite varies from 3% to 47% and carbonate apatite varies from 10% to 36%.

Subramanian (1980) has observed that apatite precipitates in the pH range of 7 to 7.6. He further states

that increase of pH causes precipitation of both calcite and apatite, when both are co-precipitated the calcite/apatite ratio will be higher.

Various authors have studied the solubility behaviour of apatite mineral in certain phosphate rocks. Mc Cann (1968) (adapted from Chien, 1977), observed that hydroxyl ions may partially substitute for fluoride in fluor-apatite to form a solid solution of hydroxyl-fluor-apatite in the alkaline solution. Wier et al. (1972) (adapted from Chien, 1977) have observed that by addition of fluoride to hydroxyl-apatite it changes to fluor-apatite.

A triangular diagram was plotted to show the overall mineralogical composition of Maldeota-Durmala sediments. Fig - 4.15 shows the mineralogical composition of the area. The figure indicates that except for some samples dominated by quartz, rest of the samples are dominated by phosphate minerals. Clay minerals are not very significant in this region.

Chemical Composition of the Bed Sediments

To study the chemistry of the sediments two methods were adopted (details are given in the methodology section)-

Table 4.7 Chemical composition of bed sediments
concentration in (ppm)

Sample locations arranged in the order of down stream flow of the river	P ₂ O ₅	F	Cu	Ni	Cr	Ag
Adt-1A (Durmalā) (00 m)	4300.	1100.	6.1	16.8	37.7	1.1
Nala under Adt-1A (Durmalā) (100 m)	2300	217	4.8	12.2	40.0	1.2
Adt-1 (Durmalā) (200 m)	2375.	154	9.9	27.2	62.6	1.5
Adt-2B (Durmalā) (300 m)	3725	453	7.6	12.7	42.6	1.2
Adt-2A (Durmalā) (400 m)	3400	684	3.6	8.7	28.8	0.9
Adt-2 (Durmalā) (500 m)	1375	100	7.7	12.7	x	x
Adt-3 (Durmalā) (600 m)	2425	265	5.2	23.0	40.1	0.9
Junction mine water (Durmalā) (1600 m)	1325	132	7.3	16.6	14.8	1.9

Contd....

Sample locations arranged in
the order of down stream
flow of the river

P₂O₅

F

Cu

Ni

Cr

Ag

100 meter below junction
mine water (Durmala)
(1700 m)

295

46

6.5

24.2

9.6

0.8

200 meter below junction
mine water (Durmala)
(1800 m)

452

45

5.9

20.5

12.1

0.7

Bandal River (Durmala)
(2000 m)

75

47

1.8

2.1

9.8

0.8

Soil Silla Village
(Durmala) (2000 m)

150

10

2.9

5.4

9.4

1.0

100 meter below junction
Bandal River + Mine water
(Durmala) (2100 m)

7500

101

2.4

5.8

8.4

0.6

Soil 100 meter below Silla
Village (Durmala) (2100 m)

132

50

3.1

5.2

15.5

0.4

Contd...

Sample locations arranged in
the order of down stream
flow of the river

	P ₂ O ₅	F	Cu	Ni	Cr	Ag
Bandal River (Maldeota) (15000 m)	62	10	1.0	x	4.2	0.2
Adt-2 inside mine (Maldeota)	1200	156	20.4	16.1	22.99	2.1
Outside Adt-2 (Maldeota) (15000 m)	1475	121	19.0	x	52.0	0.5
Adt-1 inside mine (Maldeota) (15800 m)	2500	190	7.5	12.1	70.1	1.0
Outside Adt-1 (Maldeota) (15800 m)	3350	296	7.0	8.5	86.5	1.0
Quarry (Maldeota) (15900 m)	675	55	3.8	28.2	40.0	3.0
Junction Bandal River + Adt-1 + Adt-2 + Quarry (Maldeota) (16000 m)	467	100	5.2	11.7	14.6	0.7

Contd...

Sample locations arranged in
the order of down stream
flow of the river

	P ₂ O ₅	F	Cu	Ni	Cr	Ag
Junction Bandal River + Mashan Nala (Maldeota) (16800 m)	340	60	4.1	5.9	16.3	0.6
Junction Bandal River + Jagdish Mool (Maldeota) (17000 m)	170	75	1.8	2.5	8.8	1.1
100 meter below junction Bandal River + Jagdish Mool (Maldeota) (17000 m)	150	58	14.0	12.0	8.5	0.3
Dry Bandal River (Maldeota) (19000 m)	195	50	x	x	x	x
Soil nearby field Song Canal (Maldeota) (19000 m)	35	19	2.3	1.2	6.0	0.3
Song River Doiwala (35000 m)	37	54	3.0	4.0	8.3	0.3

Table 4.8 XRF data for major and trace elements
Ca through Ti in (%); rest in (ppm)

Sample locations arranged in the order of down stream flow of the river	Ca	K	Fe	Mn	Ti	V	Cr	Co	Ni	Cu	Zn	Pb	Sr	Ba
100 meter below junction Bandal River + Mine water(Durmala) (2100 m)	1.6	0.1	0.4	0.01	0.01	30.0	9.0	<2.0	15.0	6.0	19.0	5.0	14.0	69.0
Outside Audit-2 (Maldeota) (15000 m)	20.7	0.1	2.2	0.03	0.06	65.9	40.3	1.2	9.0	18.6	15.0	2.8	30.7	327.5
100 meter below junction Bandal River + Jagdish Mool (Maldeota) (17100 m)	33.8	1.4	2.6	0.04	0.11	21.1	6.6	1.5	6.9	7.8	14.9	3.3	31.2	116.7

Table - 4.9 Comparison of average concentration of elements in the Maldeota-Durmala sediments obtained by XRF with the world average concentration in phosphorite and average concentration in Mussoorie phosphorites (value in ppm)

Element	XRF value Maldeota- Durmala	World ¹ average sediments	World ² average phosphorite	Mussoorie ³ Phosphorite	Mussoorie ⁴ Phosphorite
P	344	1150	x	x	x
F	170	x	x	x	x
Ca	190000	21500	x	x	<10
K	5000	20000	x	x	x
Fe	20000	48000	x	x	x
Mn	300	1050	30	1354	x
Ti	600	5600	00.04	1015	x
Cu	11	100	100	313	74

Contd....

Element	XRF value Maldeota- Durmala	World ¹ average sediments	World ² average phosphorite	Mussoorie ³ Phosphorite	Mussoorie ⁴ Phosphorite
Ni	11	90	100	1906	79
Cr	19	100	1000	662	91
Ag	x	x	x	x	x
V	39	170	300	1090	306
Co	1.5	200	2	89	<8
Zn	16	350	300	743	100
Pb	4	150	20	658	37
Sr	25	150	1000	1136	700
Ba	171	600	100	2868	725

- 1 Adapted from Martin & Meybeck (1978).
2 & 3 Adapted from Saraswat et al. (1970).
4 Adapted from PPCL (1981).

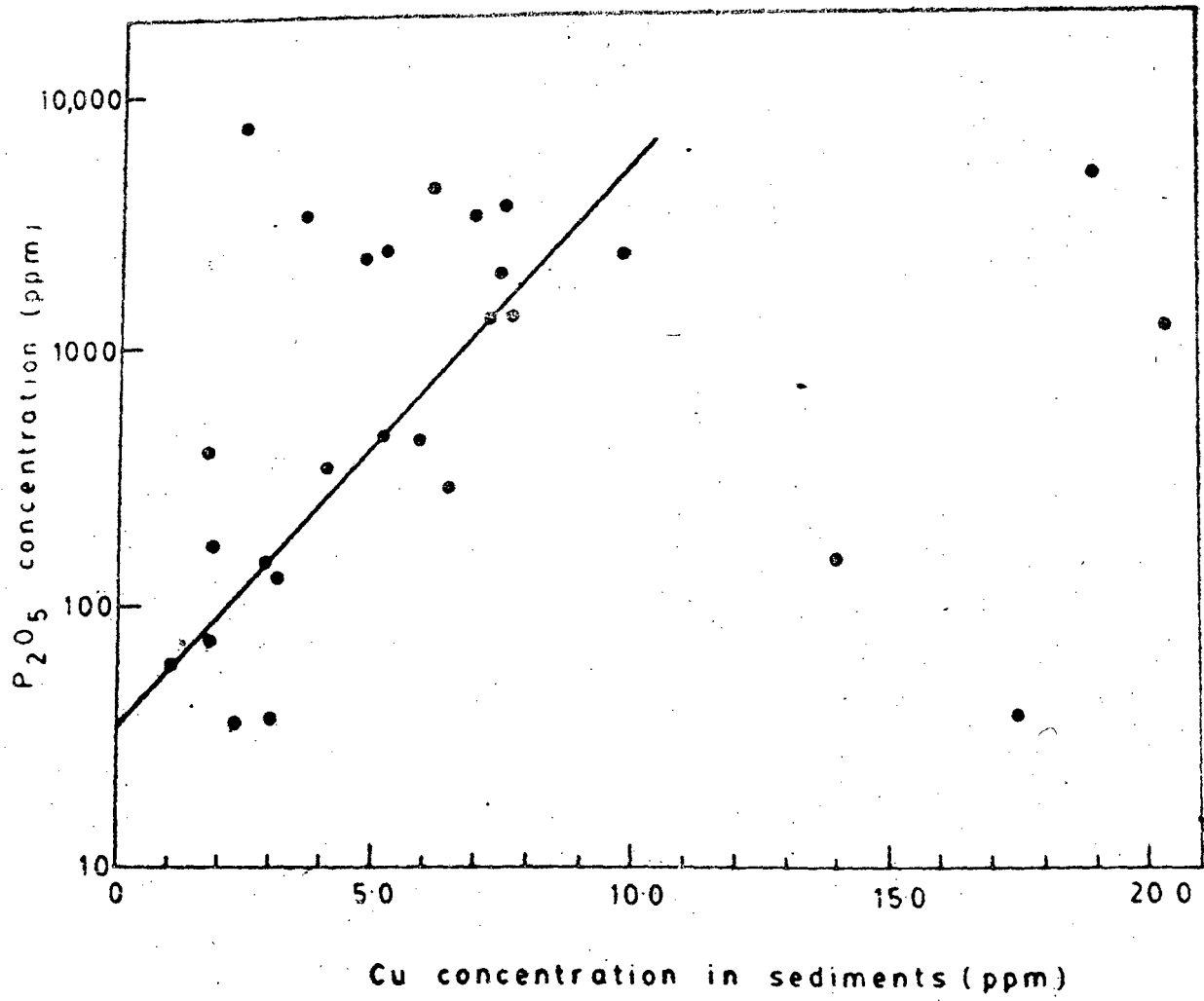


Fig. 4.10. Graph showing the variation of Cu with P₂O₅

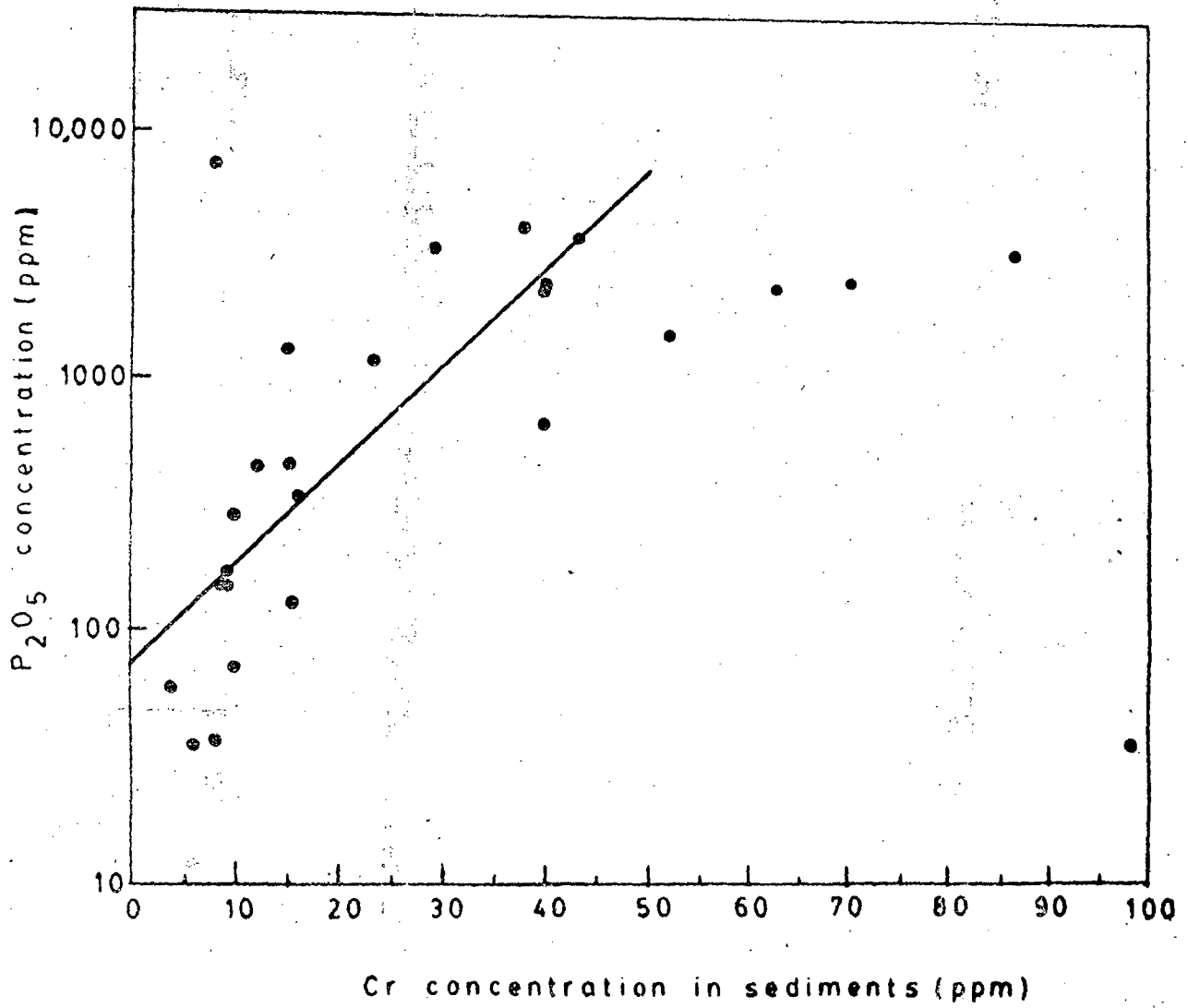


Fig4.11. Graph showing the variation of Cr with P₂O₅

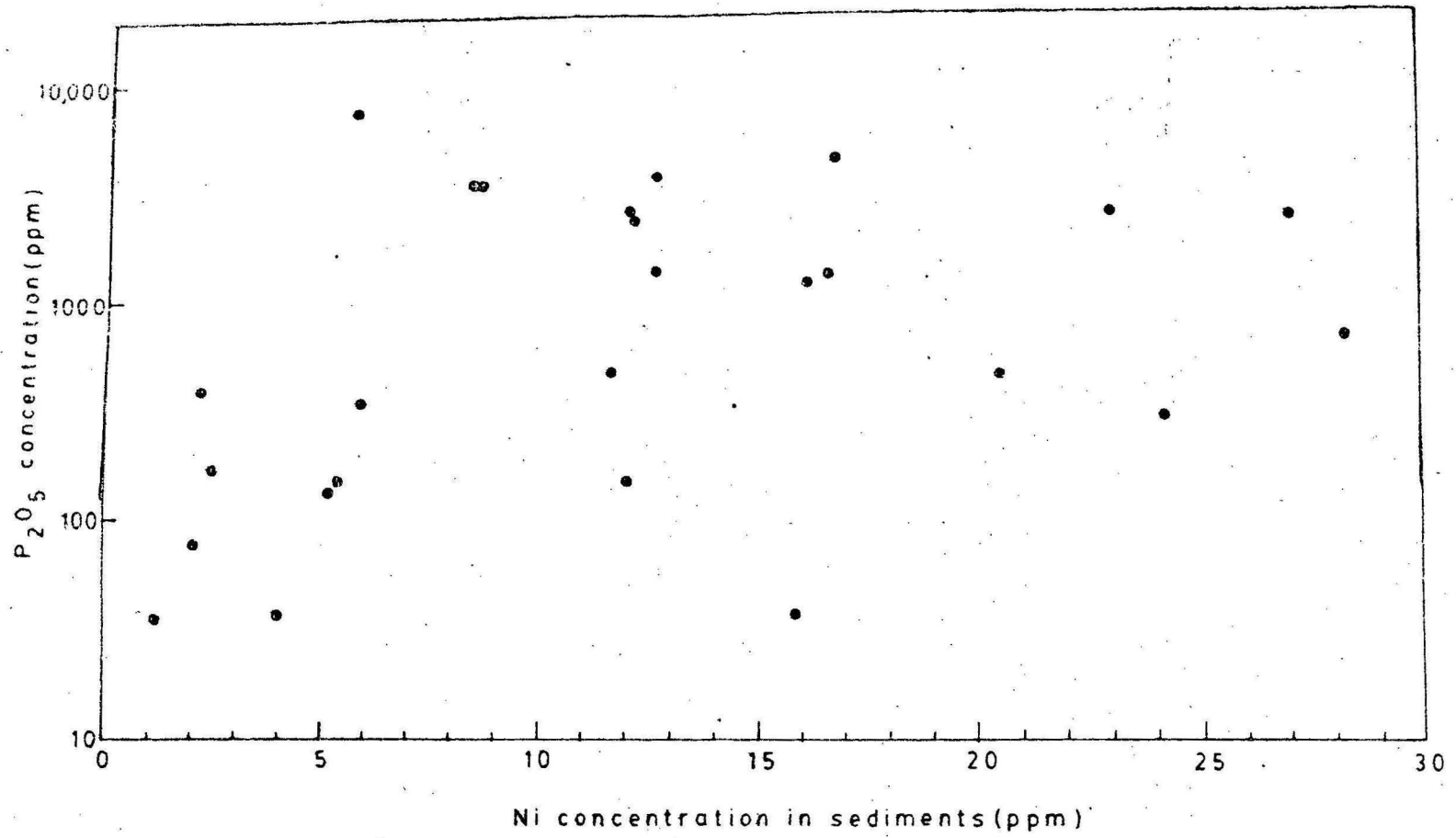


Fig. 4.12. Graph showing the variation of Ni with P₂O₅.

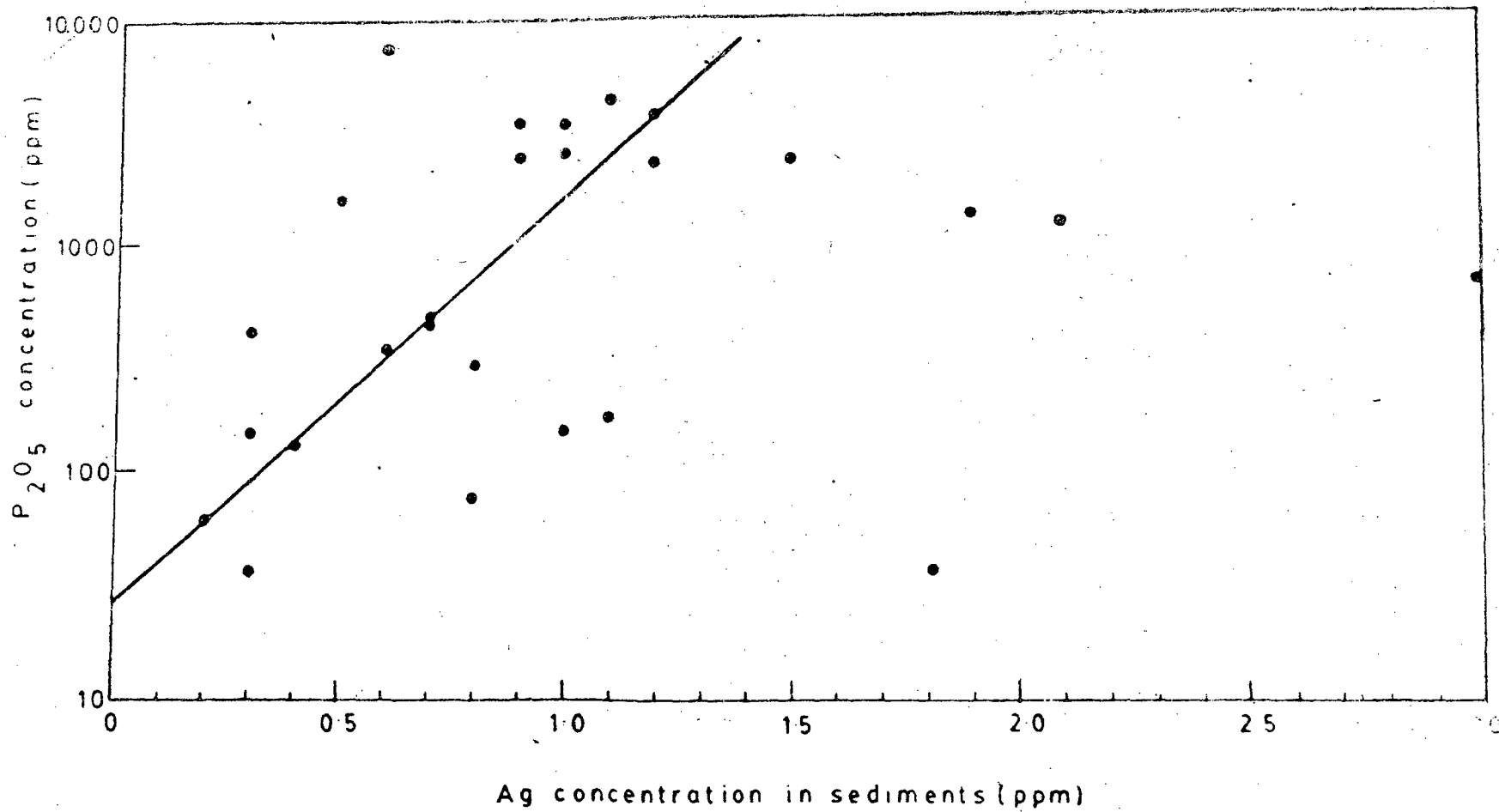


Fig. 4.13. Graph showing the variation of Ag with P₂O₅

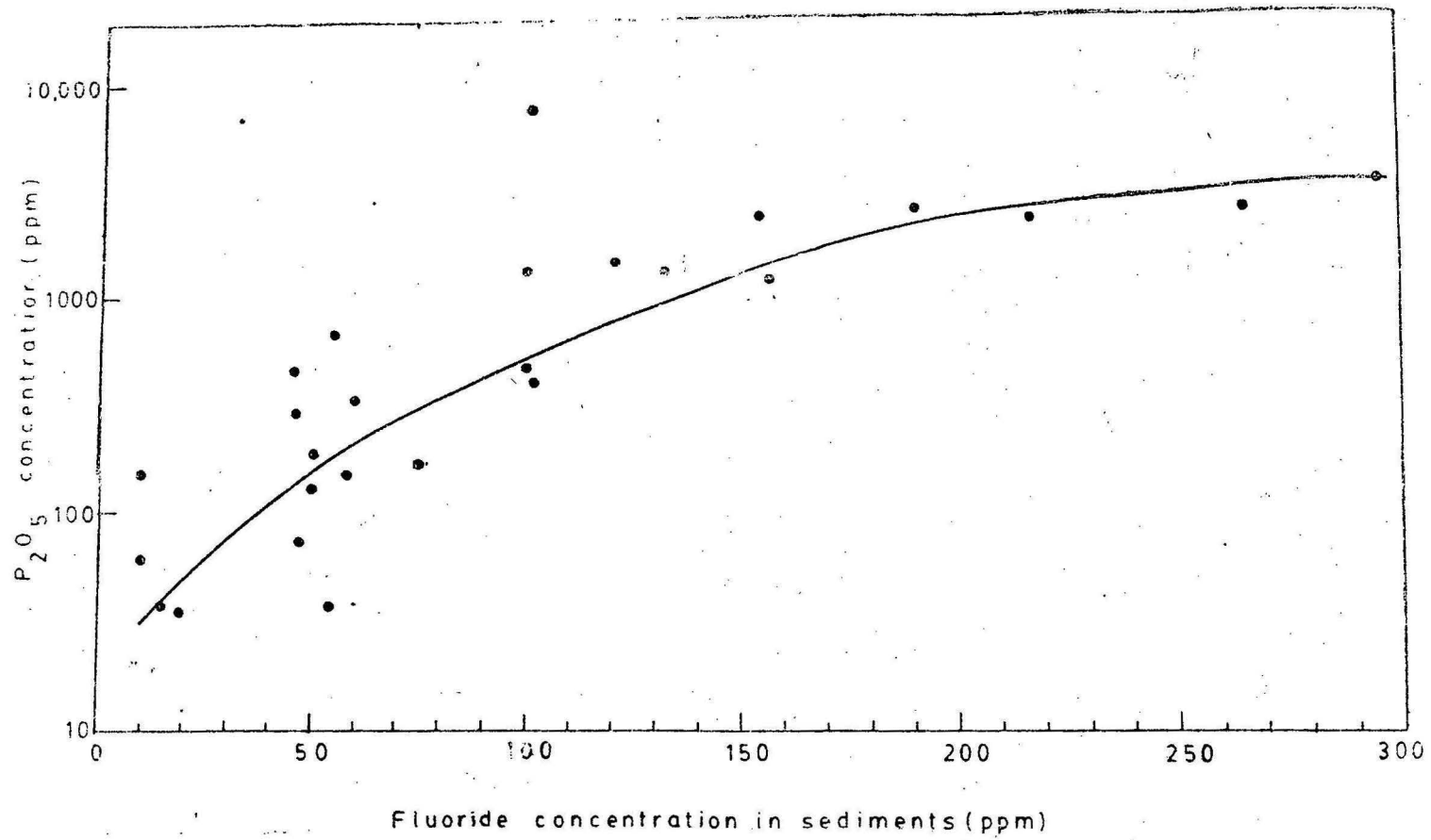


Fig. 4.14. Graph showing the variation of Fl with P₂O₅

(1) For the analysis of P, F, Cu, Cr, Ni and Ag perchloric acid was used for partial digestion of samples, which gives much lower value (Table - 4.7) Compared to the total elemental levels given by different authors (Table - 4.9). The reason is that my analysis does not reflect the complete chemistry of the sediments. The chemistry of an extract will depend on the nature of extractant used.

(2) However for comparison purposes three samples were analysed to know the total concentration of Ca, K, Fe, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Sr and Ba using XRF (bulk analysis) techniques (by my supervisor in Belgium) (Table - 4.8).

Major Elements

Phosphorus:

The phosphorous was analysed in the laboratory as orthophosphate and the value was converted into P_2O_5 . The economic importance of phosphorite deposit is based on the total P_2O_5 content. On the basis of percentage of P_2O_5 in the whole rock Basu (1976) has classified the phosphorite deposits as follows:-

> - 35% P ₂ O ₅	-	Very rich phosphate
28 - 35% P ₂ O ₅	-	Rich phosphate
18 - 28% P ₂ O ₅	-	Medium phosphate
10 - 18% P ₂ O ₅	-	Poor phosphate
5 - 10% P ₂ O ₅	-	Very poor phosphate
< - 5% P ₂ O ₅	-	Phosphate bearing rocks

The P₂O₅ concentration in Maldeota-Durmala regions shows very low concentration in comparison to the host rocks. There are no agreement among the different authors on the P₂O₅ content in Maldeota-Durmala region due to the following reasons:-

- (1) Different authors have analysed only a limited number of samples from different regions. The concentration of P₂O₅ is not homogeneous throughout. It varies from region to region. Thus the values given by them do not reflect the average P₂O₅ concentration in the phosphorite rocks.
- (2) The differences may also be due to different analytical techniques used by different authors. The overall P₂O₅ percentage in Maldeota-Durmala region given by PPCL is 19-20%. This is much higher in comparison to

the average percentage of P_2O_5 in the sediments analysed by me (0.15%). On the other hand much higher value is expected in the Maldeota-Durmala sediments also. However, this aspect could not be confirmed since I was able to do only partial analysis of the sediments and also P could not be done by XRF for the whole sediments due to technical reasons.

The average P_2O_5 concentration in the Maldeota-Durmala sediments is 1460 ppm. The concentration of P_2O_5 in the audit sediments is higher in comparison to the river bed sediments. The reason is that in the audits phosphorite is being explored. The sediment collected from the audits generally represents the phosphate minerals.

Ravi Shanker (1976) has analysed the Maldeota phosphorite rocks. He has found average P_2O_5 concentration 19.2%. The corresponding grade in the surface d , being ricker due to leaching out of carbonate, varies between 20 to 30% P_2O_5 . My analysis of the sediments shows average 0.15% P_2O_5 . It shows that very little amount of phosphate is coming to the river bed sediments. The sample from Bandal river (Maldeota), which is about 15000 m. away from Durmala mine, shows only 0.006% P_2O_5 .

The sediment sample from junction of Bandal river and Jagdish Mool, which is about 2000 m. from Maldeota phosphorite mine, shows only 0.02% of P_2O_5 ; which is much lower in comparison to the P_2O_5 content in the Maldeota rivers 0.15 to 0.34%.

Rao and Rao (1971) and Mehrotra et al (1981) have analysed the Mussoorie phosphorite. Both have reported higher P_2O_5 content in Mussoorie phosphorite (38-39% and 21-31% respectively) in comparison to Maldeota phosphorite (19.2%). Mehrotra et al have found highest value of P_2O_5 in stromatolitic phosphorites, whereas the lowest value is observed in fragmental variety. But the information collected from PFCL (1983) does not show much variation of P_2O_5 between Maldeota and Durmala region. In Maldeota underground mine the P_2O_5 content is 17 to 18%, whereas the underground mine (Durmala) shows 19-20% P_2O_5 . The higher concentration reported by them may be because they have analysed only few core samples. Again, PFCL report shows higher concentration of P_2O_5 (20% and 25-30% respectively) in Maldeota-Durmala open cast mine in comparison to the underground mines. My analysis of Maldeota quarry sediments shows lesser amount of P_2O_5 (0.07%) in comparison to the mine samples (0.1 to 0.3%).

The reason may be that this sample does not represent phosphorite rock samples. The sample was taken from nearby the quarry. This discrepancy prevails when we compare P_2O_5 content of inside the mine Maldeota and outside the mine Maldeota. The data given in the table clearly shows that the samples outside the river are having higher P_2O_5 concentration. This is expected because this sample was collected, where the phosphorite are being dumped. The inside sample shows lower concentration which may be because the sample represents the associate rocks not the phosphorite rocks.

Ravi Shanker (1976) has established reciprocal relationship between acid insolubles and P_2O_5 . The value for acid insolubles generally vary from 2% to 10% and rarely upto 13% in the phosphate zone, whereas the samples, from overlying and underlying zones, give values ranging between 30% to 75%.

Fluoride:

Super phosphate production is one of the major source of fluoride. From Maldeota-Durmala region an average of 170 ppm of fluoride has been analyzed. Generally the fluoride concentration is higher in the mine sediments

(Table 4.7), in the river bed sediments it is quite low. The reason is that fluoride is the essential constituent of fluor-apatite, which is dominating in the mine. The concentration of phosphate minerals will decrease gradually away from the mine, thus F concentration will decrease.

Rao and Rao (1971) by the analysis of phosphorite rocks (Mussoorie) have found 4% of fluoride. Ravi Shanker (1976) has found 0.76 to 1.38% of fluoride content in the Maldeota phosphorite rocks. The analysis of sediments show only 0.02% of average fluoride concentration.

A graph (Fig 4.14) was plotted to study the relationship between fluoride and P_2O_5 . It is well known that the F : P_2O_5 ratio is a significant chemical factors because the components are the primary associates of carbonate-fluor-apatite. It was observed that average ratio varies between different areas. It does not show any systematic pattern. The reason for unsystematic pattern may be because my analysis does not reflect the analysis of phosphorite rocks, of which F and P_2O_5 are the associate. On the other hand weathering of rocks other than phosphorite may interfere and change the composition of the sediments.

Calcium:

The XRF data shows average 199000 ppm Ca in the sediment, which is higher to the Ca content of world average (21500 ppm). The higher concentration of Ca content in the sediment of Maldeota-Durmala region may be because it is having different types of apatite and other Ca minerals. Weathering of these minerals release Ca ion, which can be absorbed in the sediments.

Rao and Rao (1971) have analysed few phosphorite rock samples of Mussoorie and have reported 9-10% of calcium. The sediments samples are showing 19% calcium. It clearly indicates that apart from phosphorite rocks, there are some other sources, which enhance the calcium concentration in the sediments. The mineralogy of the sediment indicate abundance of calcite and dolomite apart from phosphorite minerals. Partial dissolution of calcite and dolomite will further add the Ca ion in the sediments. It is interesting to note that ((Table 4.8)) indicates higher value of calcium in the junction Bandu river and Jagdish Mool sample (33.8 ppm) which is far off the mines. in comparison to Audit-2 Maldeota Sample (20.7 ppm). Use of super-phosphate as fertilizer in the nearby field may be one of the reasons for higher calcium concentration.

Potassium:

Potassium concentration is lower to the average composition of potassium in the world average sediments. The world average shows 20000 ppm of potassium whereas in the Maldeota-Durmala region it is 5000 ppm. The lower concentration of potassium in the sediments may be because the lithology of the area is dominated by chert, shale and limestone.

Rao and Rao (1971) have reported 0.03 to 0.07% of potassium in the Mussoorie phosphorite rocks, which is lower in comparison to the potassium content in the sediment samples (average 0.05%). The lower value reported by Rao is because he has analysed the phosphorite rocks, which is carbonate-fluor-apatite. The higher concentration of potassium in the sediments may be due to weathering of potash felspar from shale, in which potassium ions are removed and absorbed in clay minerals.

Iron:

In the Maldeota-Durmala region concentration of iron in the sediment is 20,000 ppm, whereas the world average is higher (48000 ppm) to it. The reason for lower concentration of iron is that the value does not reflect

the average iron content in the sediments. Due to the limited analytical facilities only three samples were analysed. On the other hand higher value is expected because pyrite is associated with phosphorite.

Iron can exist in sediments in clay minerals, in other detrital silicates, in hydrous oxides and in complexes with organic matter, Leland and Shukla (1973) adapted from Singer, 1973) after the mineralogical studies of Lake Superior reported that reduction, upward migration and reprecipitation at the water interface of previously sedimented iron may be important for the concentration of iron. Changes in the clay minerals or in the other detrital silicates do not lead to the higher concentration of iron.

Manganese and Titanium:

The concentration of manganese in the average sediments of the world is higher (1050 ppm) to the concentration of manganese in the sediments of Maldeota-Durmala region (300 ppm). Saraswat et al (1970) have observed higher value (1354 ppm) of Mn in the phosphorite rocks, Mussoorie.

Titanium concentration (600 ppm) shows lower concentration in comparison to the world average (5600 ppm).

Saraswat et al (1970) have noticed 1015 ppm of Ti in the Mussoorie phosphorite rocks.

For Manganese and Titanium higher value is expected. The given value does not reflect the actual average concentration of manganese and titanium.

Trace Elements:

Variations of different elements depend upon the types of weathering and the balance between weathering rate and river transport (Martin and Meybeck, 1978). Heavy metals are generally carried by clay minerals. A generalised sequence of the capacity of solids to sorb heavy metals was found as follows (Guy and Chakrabarti, 1975) -

manganese oxides > humic substances >
 hydrous Fe oxides > clay minerals.

There are different mechanisms of metal accumulation. Gibbs (1973)(adapted from Forstner, 1982) has described five major mechanisms of metal accumulation in the sediments:-

- (1) adsorptive bonding on fine grained substances;
- (2) precipitation of discrete metal compounds;
- (3) Co-precipitation of metals by hydrous Fe and Mn oxides and by carbonates;
- (4) association with organic molecules; and
- (5) incorporation in crystalline minerals.

Saraswat et al (1970) have analysed the trace elements in Mussoorie phosphorite rocks and they have compared it with the world average composition of trace elements in the phosphorite rocks (Table 4.9). They have observed greater amounts of Ba, Co, Cu, Ni and V, lesser amount of Cr and comparable amount of Sr. They have also analysed concentration of trace elements in the shale and limestone and found that V and Ni increase progressively from limestone, through phosphorite to black shale, whereas Cu decreases in the same direction. Sr, Cr, Pb are highest in the phosphorite and are lower in amount in the black shale and limestone.

Ravi Shanker (1976) has also analysed few phosphorite core samples of Maldeota and has reported lower concentration of Ba (> 1000 ppm), Sr. (300-800 ppm), V (100-300 ppm) in comparison to the average concentration reported by Saraswat et al 2868 ppm, 1136 ppm and 1090 ppm respectively. This discrepancy may be because Ravi Shanker has analysed only few samples. The concentration of trace elements may vary from place to place. It may also vary due to different analytical techniques used.

Generally the result obtained by Saraswat shows higher concentration of trace elements in the Mussoorie

phosphorite rocks in comparison to the world average concentration of trace elements in the phosphorite rocks, and the world average concentration in the sediments.

To study the distribution of trace elements in the sediments of Maldeota and Durmala total analysis by XRF and partial analysis of extract was done. In comparison to the Mussoorie phosphorite the concentration of trace elements in the sediments is very low. The XRF data (Table 4.8) and the data obtained from the analysis of extract (table 4.7) are close to each other. The XRF data shows 11 ppm Cu, 11 ppm, Ni and 19 ppm Cr which is very near to the average concentration of trace metals in the extracts 8.3 ppm, 12.4 ppm and 28 ppm respectively, though higher value such as 19 ppm Cu, 40 ppm Cr have been observed in the XRF analysis. XRF is the total analysis of the sediments, whereas, the analysis of extract gives the partial analysis of the sediments; therefore, higher value is expected in the XRF analysis. The lower value may be because the data doesn't reflect the average concentration of trace elements. Due to limited analytical facilities only three samples were analysed. The lower value in the extract is because it is the partial analysis of the sample.

In Table - 4.9 trace elements data obtained by XRF has been compared with world average concentration in the sediments, world average concentration in phosphorite and data given by Saraswat et al (1970) and PPCL (1981). The data indicates that variation of trace elements is very wide. Different graphs to show the variation of different trace elements with P_2O_5 concentration were plotted. The graphs do not show any systematic pattern. Fig. 4.10 to 4.13 show the variation of different elements with P_2O_5 . The wide variation of trace elements in the phosphorite rocks is due to variation of geographical distribution of different elements. The distribution of different elements is not homogeneous. It varies from place to place. The irratic nature of graph is because the fate of heavy metals depend on different factors. In general in the aquatic systems it depends on partitioning between soluble and settleable solid phases and may be influenced by various interaction which include coagulation, adsorption, precipitation, co-precipitation, complexion and biotic uptake (Brussell, 1974) (adapted from Young et al, 1982). These factors are known to be affected by environmental conditions, such as: pH, redox potential, metal concentrations, ionic strength, bioaccumulation and type and concentration of complexing ligands (Heckie and James, 1974) (adapted from Young et al, 1982). According to Young et al (1982) the

aforesaid phenomena is superimposed by kinetic factors which govern reaction rates, particle, sedimentation and hydrodynamics.

CONCLUSION

CONCLUSION

The basic idea of doing this research was to study the environmental impact of mining on water and sediments of Maldeota-Durmala region. Higher quantity of phosphate was expected both in water and the sediments; even though its movement is restricted because of its limited solubility and it is retained by component of Soil and Sediments. The following observations were made:-

- (1) Analysis of water sample shows higher concentration of PO_4^{-3} ; > 0.02 ppm (0.02 ppm phosphorus has been reported by Subramanian, 1980 in the fresh water of the hydrosphere), in the river as well as in the underground water. The PO_4^{-3} concentration in the Bandal river is generally 0.06 ppm. The higher concentration in the sample collected away from the mine may be due to use of fertilizers in the field.

The SO_4^{-2} content of water is very high, comparatively higher concentration of SO_4^{-2} in the mine water than Bandal river water clearly indicates that SO_4^{-2} in the water is being controlled by the mining. On the other hand HCO_3^- is being controlled by the weathering of limestone in the host rocks, because Bandal river water shows higher concentration of HCO_3^- in comparison to the mine water.

Fluoride is the common constituents of fluorapatite. Fluorapatite is widely distributed in Maldeota-Durmala region. The higher concentration of fluoride content in the water may be due to phosphorite mine.

Average Ca^{+2} and Mg^{+2} is higher in the Maldeota-Durmala region. Generally Mg^{+2} is higher than Ca^{+2} though high amount of Ca^{+2} is being released by the weathering of carbonate minerals and phosphate minerals. The reason may be that Ca^{+2} is being precipitated as CaCO_3 and thus Ca^{+2} ion is removed.

- (2) The X-ray analysis of Maldeota-Durmala sediments show phosphate as the dominating minerals, followed by quartz and carbonate minerals. The lesser amount of clay minerals is due to high rate of erosion.
- (3) The P_2O_5 concentration in Maldeota-Durmala regions show very low concentration in the sediments in comparison to the host rocks. More high value is expected. The partial analysis of the extracted sediments gives lower concentration of the major and trace elements. But it does not reflect the actual concentration of different elements in the sediments because it is not the total analysis of the sediments.

The total analysis by XRF shows lower concentration of different elements in the sediments, it is because, it does not represent the average composition of the sediments; and three samples were analysed due to analytical reasons. Higher value is expected both for major and trace elements.

Impact of mining on the water and sediment was expected. Higher amount of phosphate and fluoride in the water and sediments and higher amount of sulphate in the water is due to mining. But the irratic nature of the result does not confirm the impact of mining on the water and sediments. On the other hand impact of transportation of phosphorite rocks. Use of fertilizers in the field, exploitation of limestones in the nearby region, other human activities are the important factors.

The permissible amount of different ions in the drinking water given by PHS (Public Health Service), US (1974) is as follows:-

Cl^-	-	< 250 ppm
F^-	-	1.0 ppm
SO_4^{-2}	-	< 250 ppm
Mg^{+2}	-	125 ppm
$\text{Na}^+ \& \text{K}^+$	-	No standard exist.

In the Bandal river concentration of fluoride and sulphate exceeds the permissible limit (average 1.4 ppm and 274 ppm respectively). The concentration of these ions are more high near the mine. It indicates that river water near the mine is of poor quality. But the concentration of these ions in the underground water and canal water is very close to the value given by PHS. Hence it is safe for domestic purposes. The Indian Standard (IS 3025-1964) for the irrigation water, pH 5.5 to 9; conductivity at 25°C 3000×10^{-6} MHO, TDS (inorganic) 2100 ppm, sulphate 1000 ppm, chloride 600 ppm, is being fulfilled by the Bandal and Song Canal water and are safe for the irrigation purposes.

But the concentration of phosphate in the water is high. The average concentration of phosphate in the Bandal river water (0.2 ppm) is higher in comparison to the value given by Subramanian (1980) for the fresh water (0.02 ppm). However, the data is not sufficient to calculate the input of phosphate in the Bandal river by the mining. More investigations are required to calculate the

- (i) rate of flow of water;
- (ii) the amount of sediments transported;
- (iii) uptake of phosphorus by the plants; and
- (iv) the seasonal variations of phosphate.

Total analysis of the sediments is essential to know the impact of mining on the sediments.

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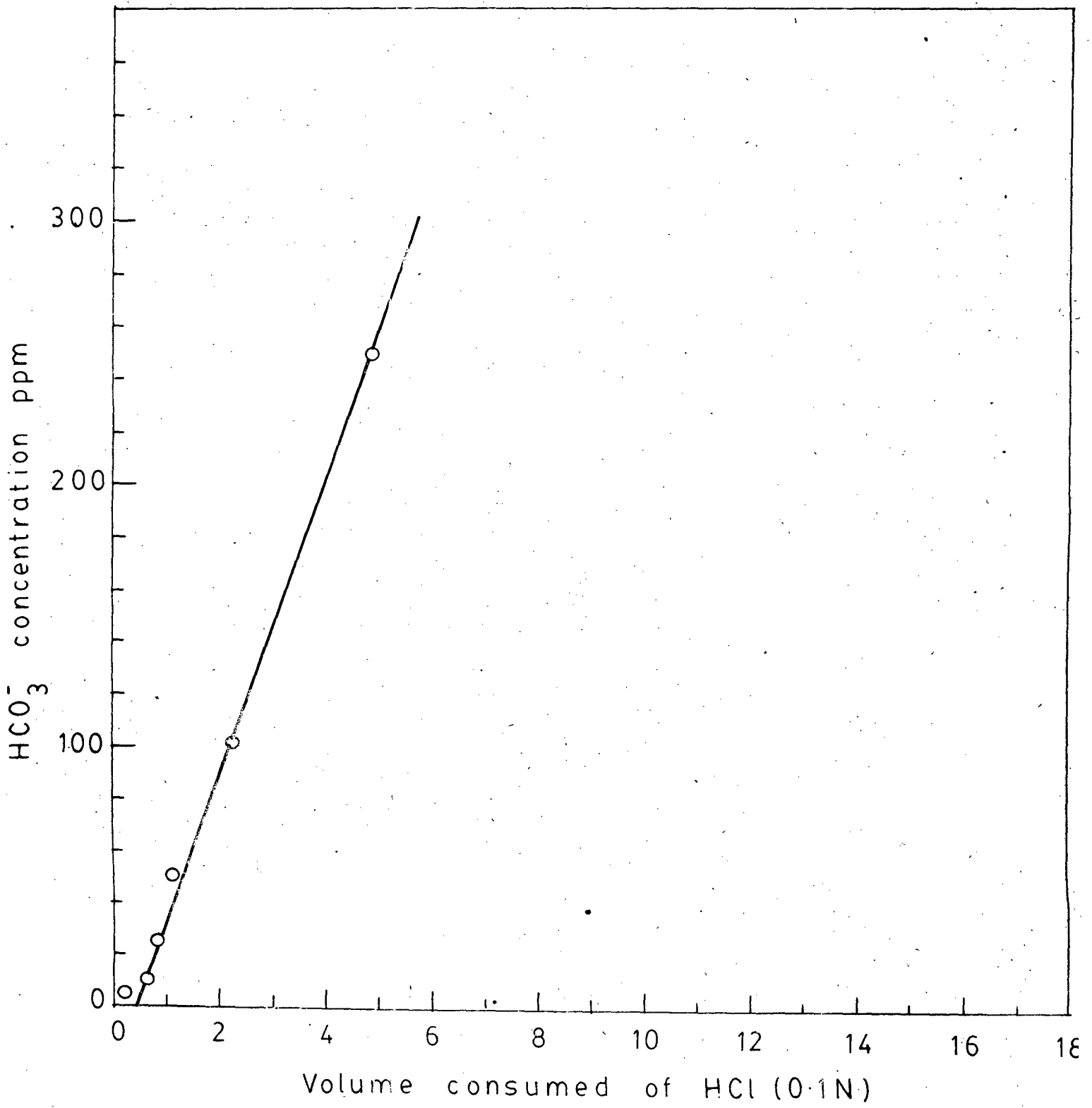
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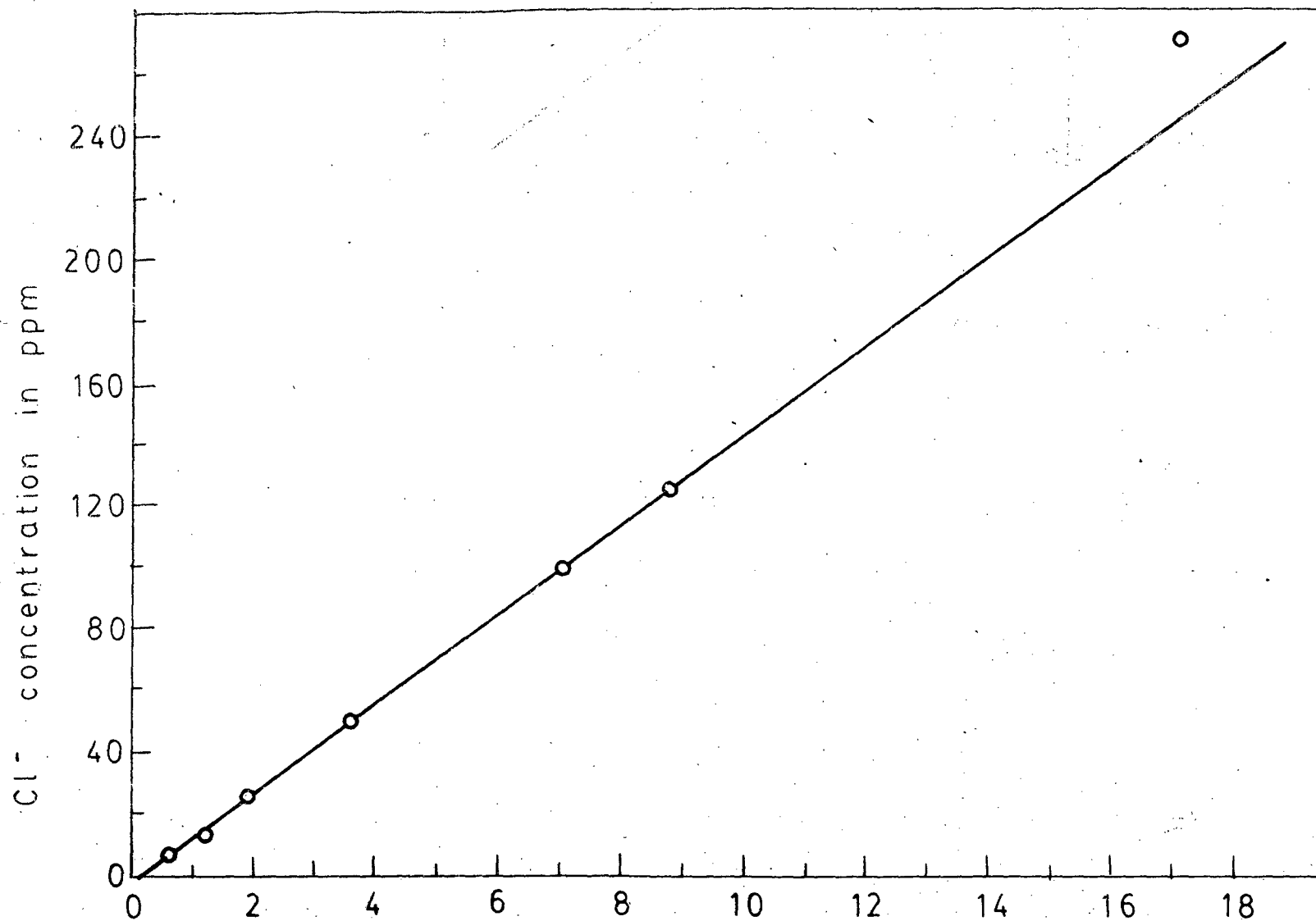
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APPENDICES

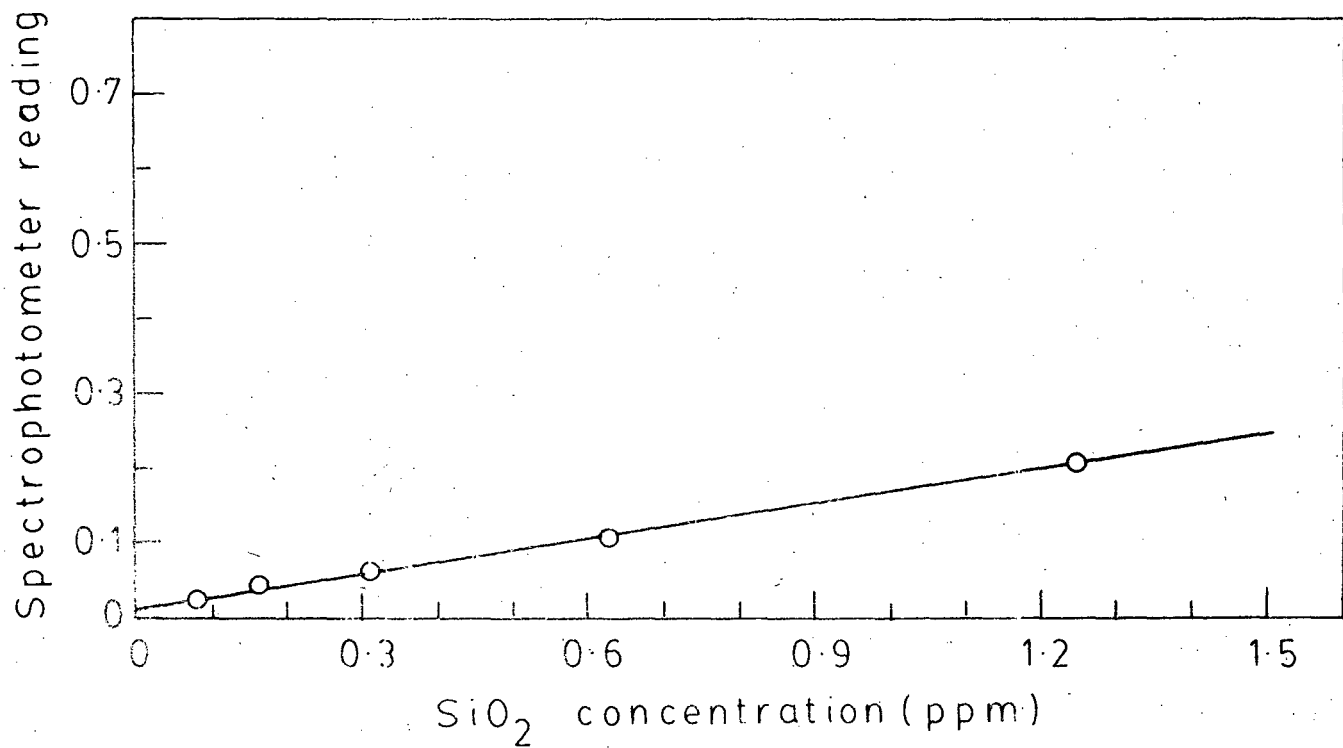


Standard plot of HCO_3^- concentration

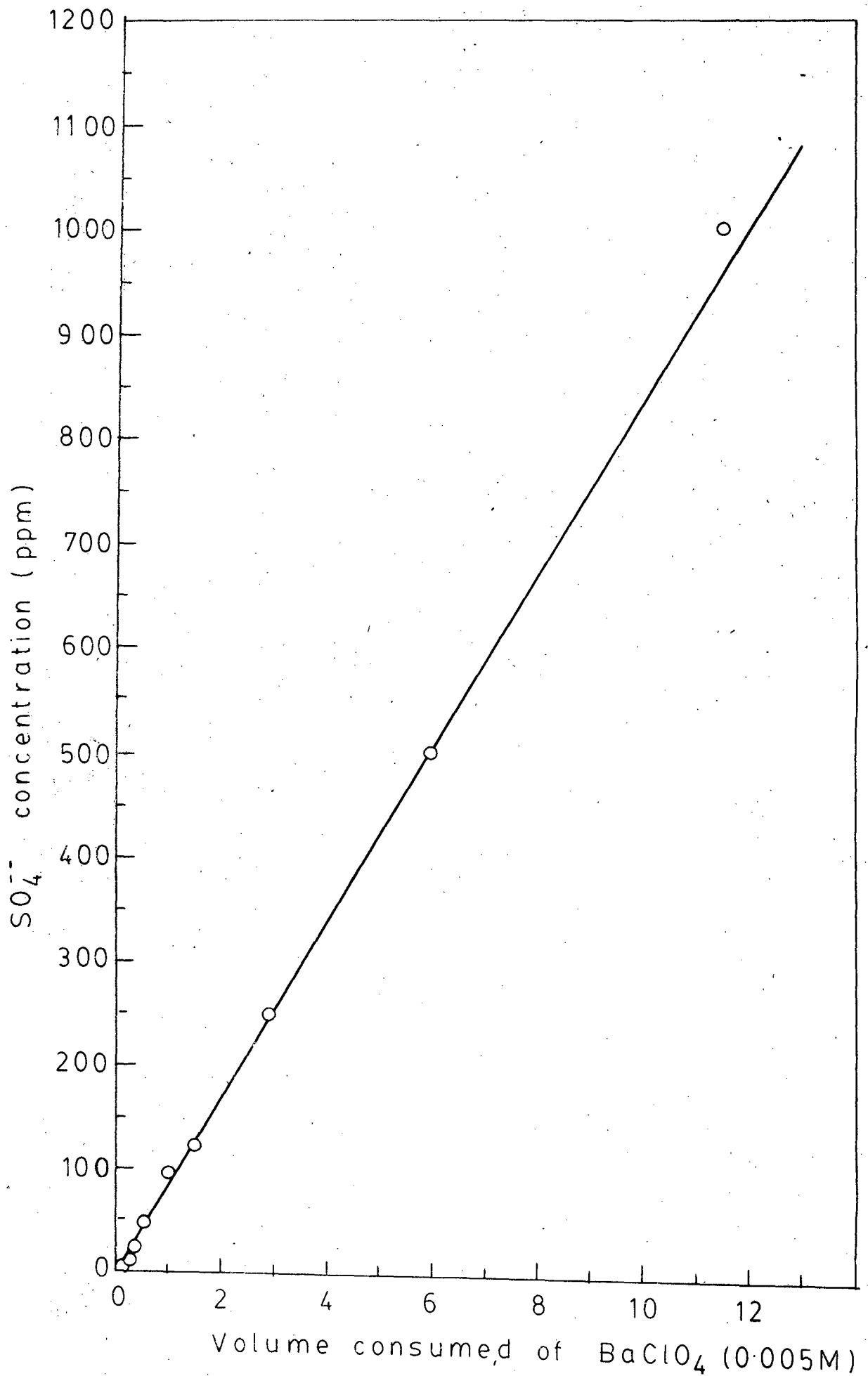


Volume consumed of AgNO₃(0.01 N)

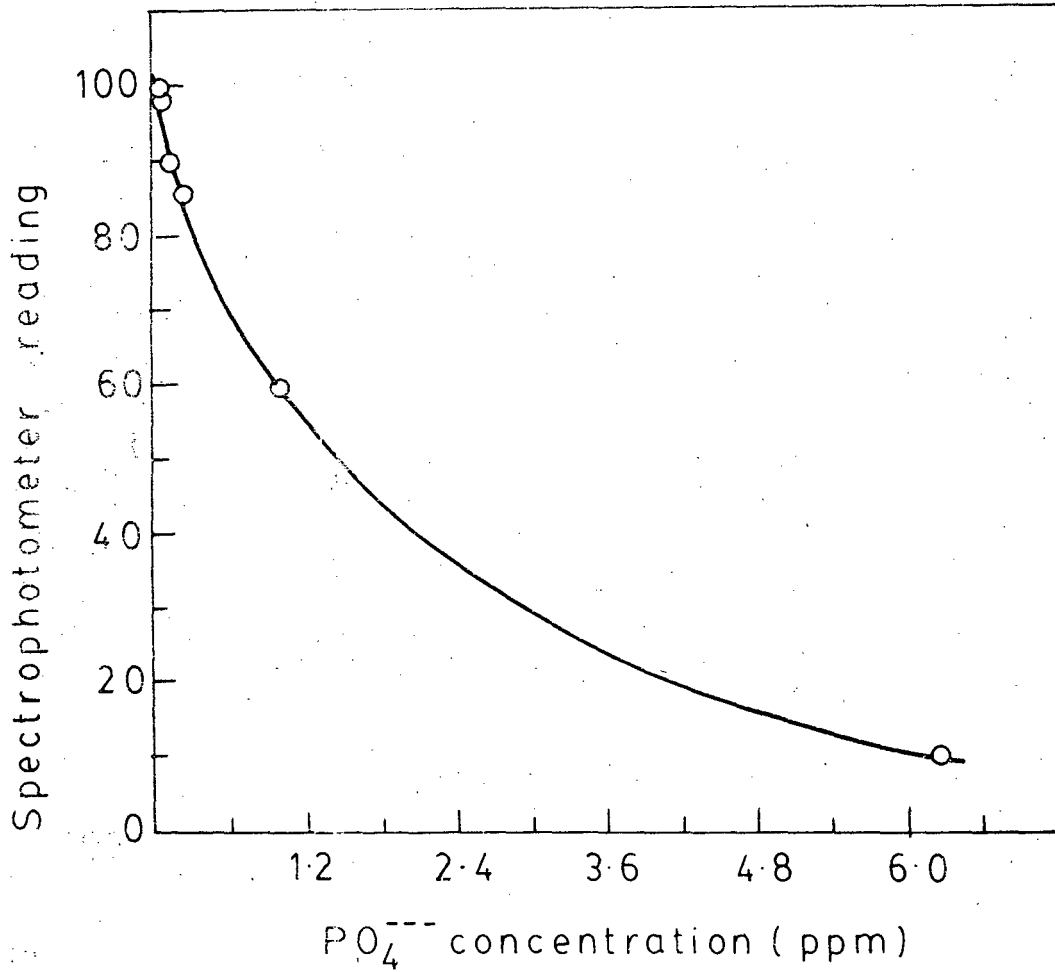
Standard plot of Cl⁻ concentration



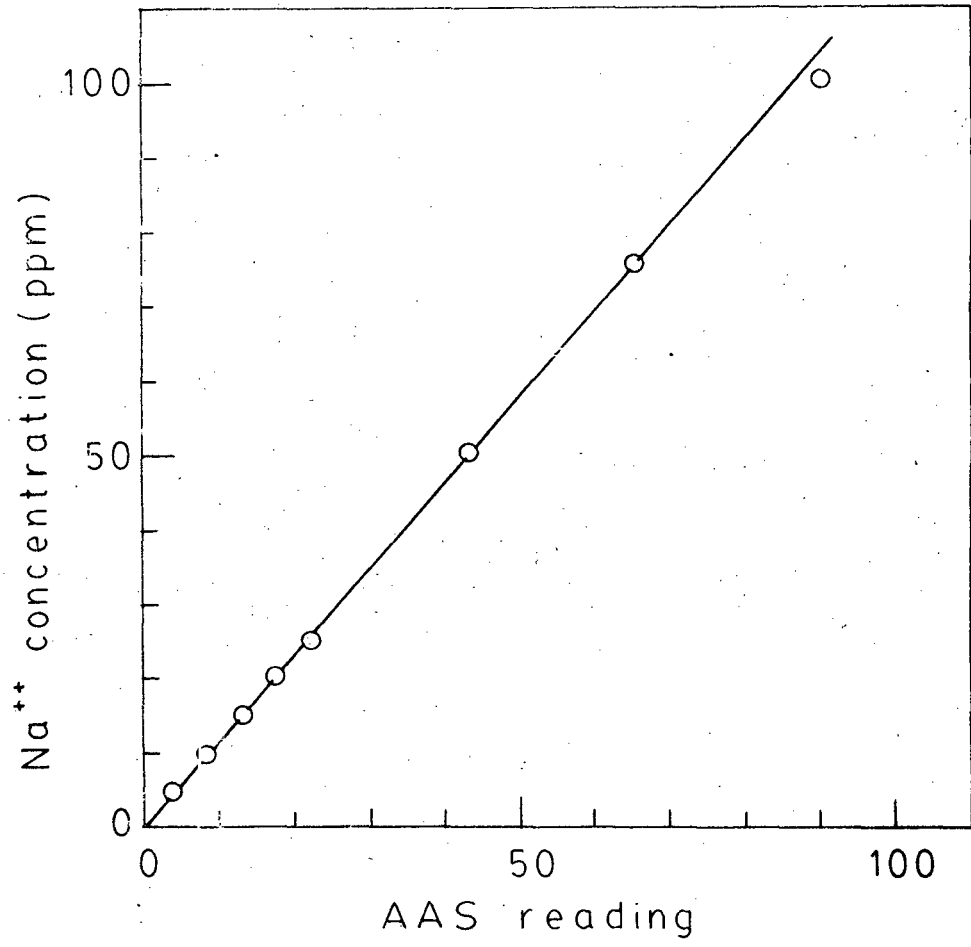
Standard plot of SiO₂ concentration



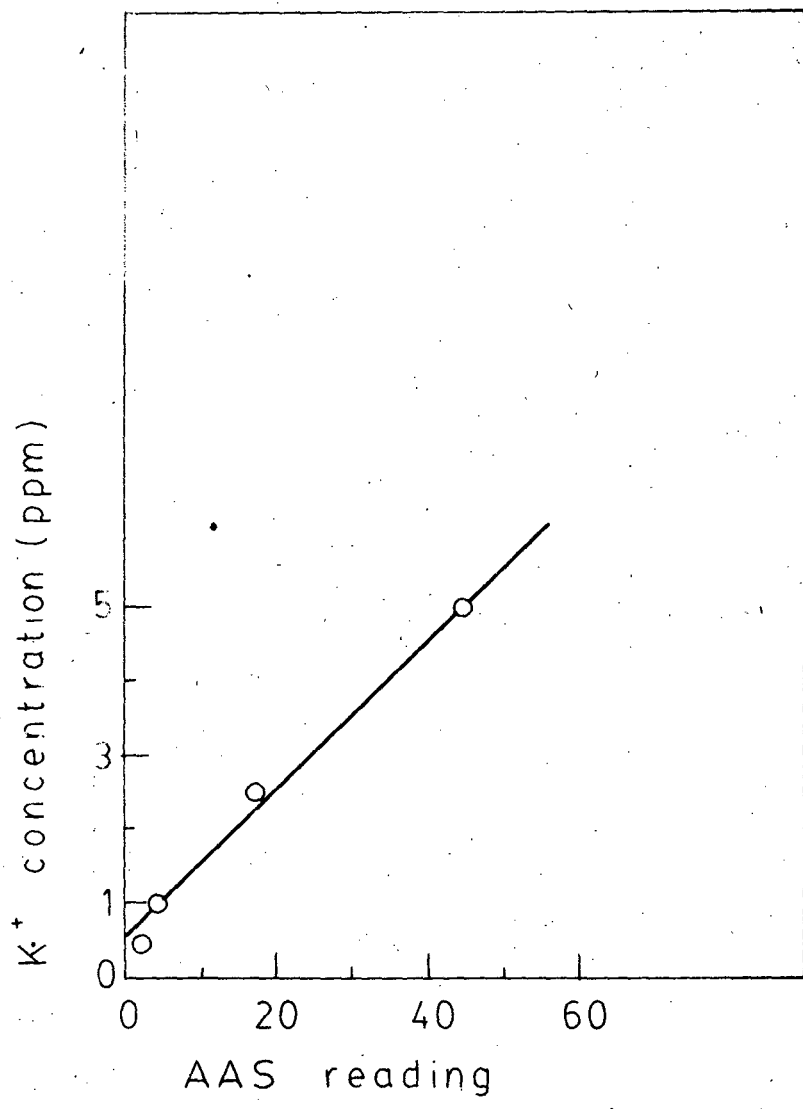
Standard plot of SO_4^{2-} concentration



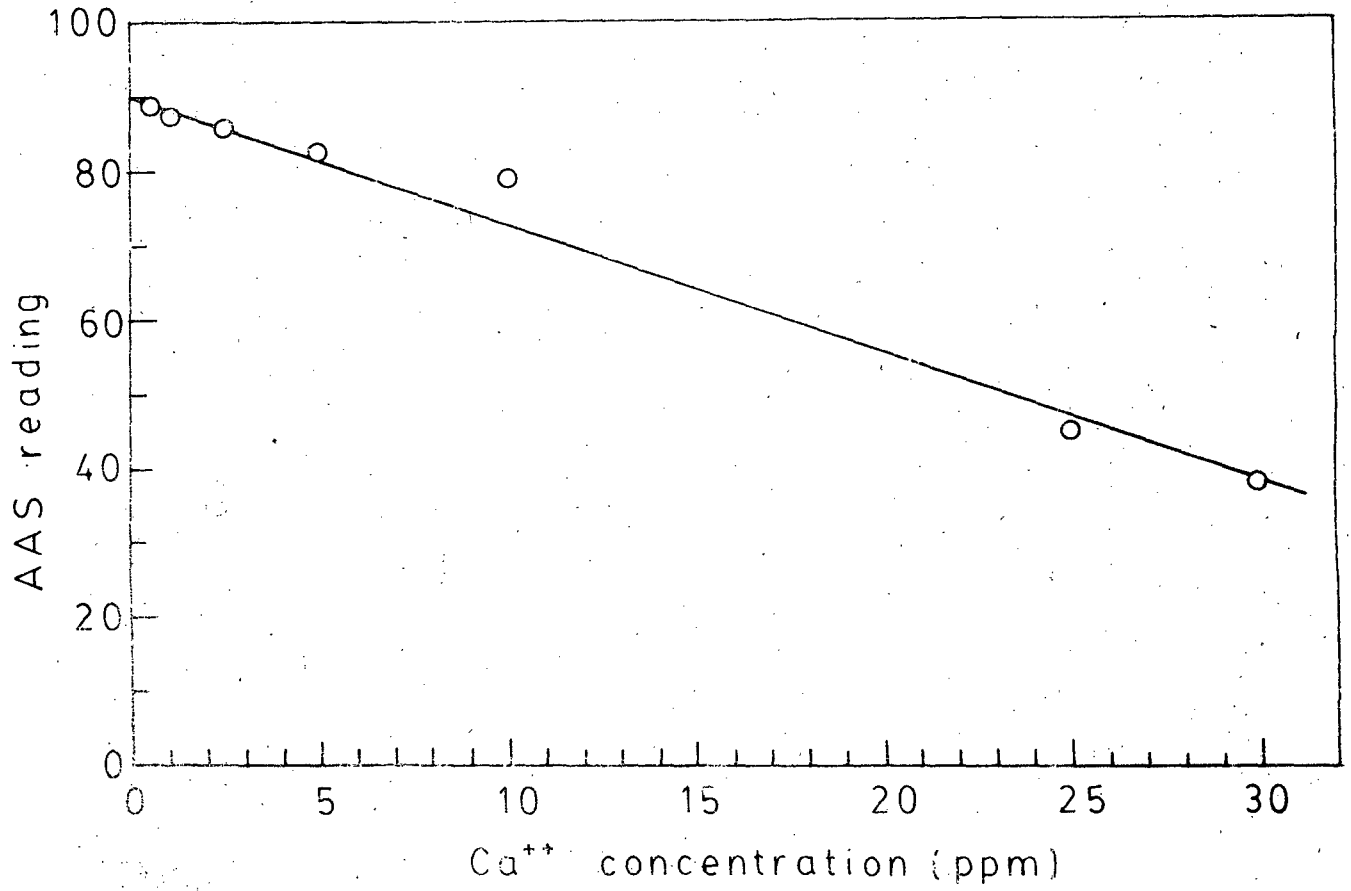
Standard plot of PO_4 concentration (in water)



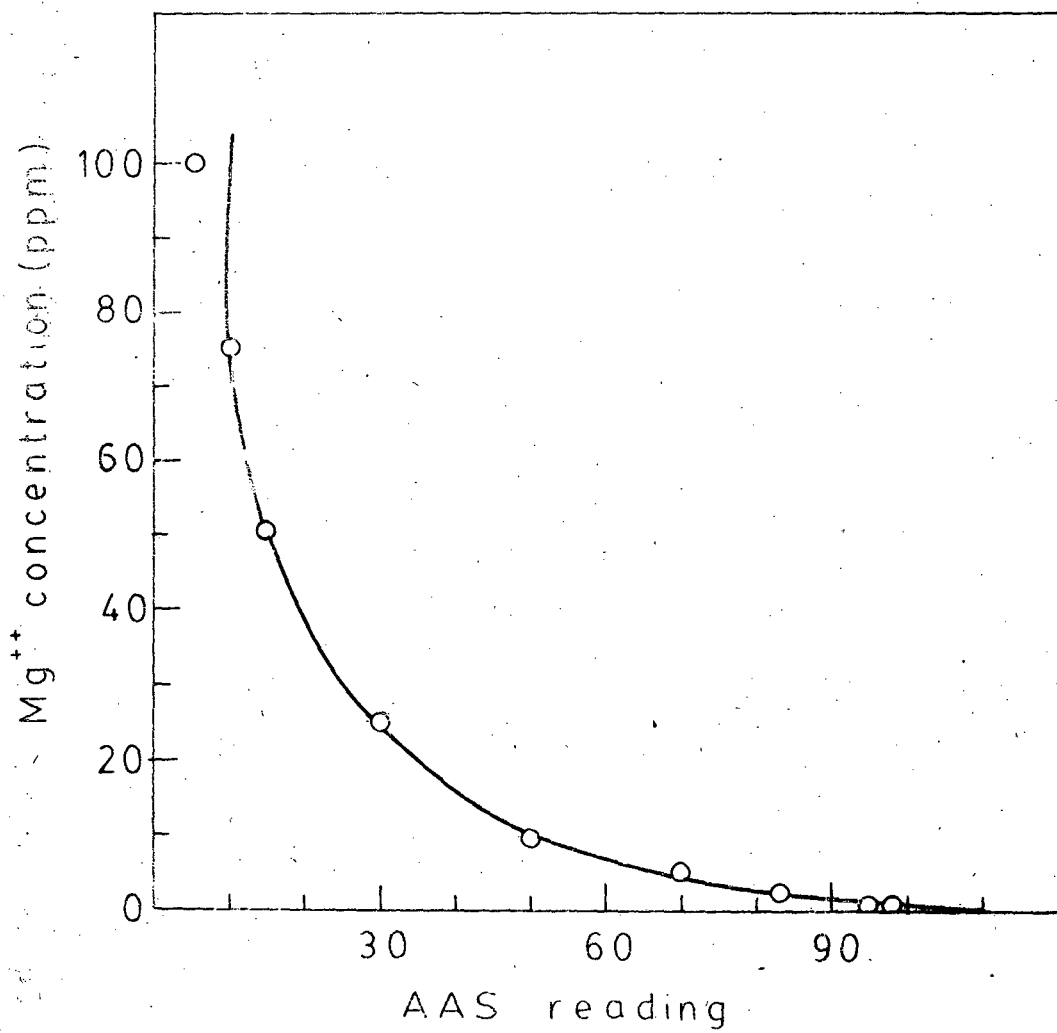
Standard plot of Na⁺ concentration



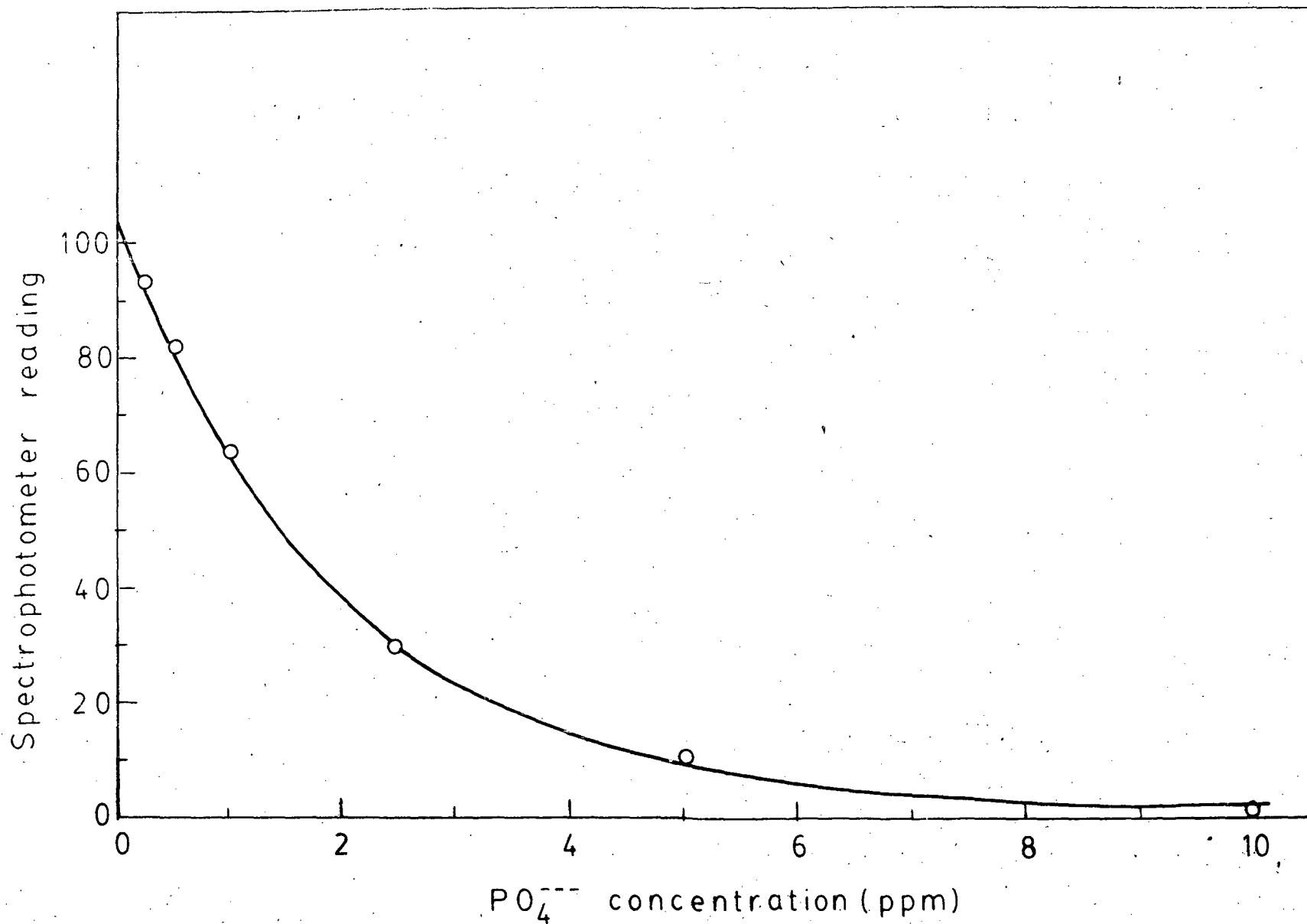
Standard plot of K⁺ concentration



Standard plot of Ca⁺⁺ concentration

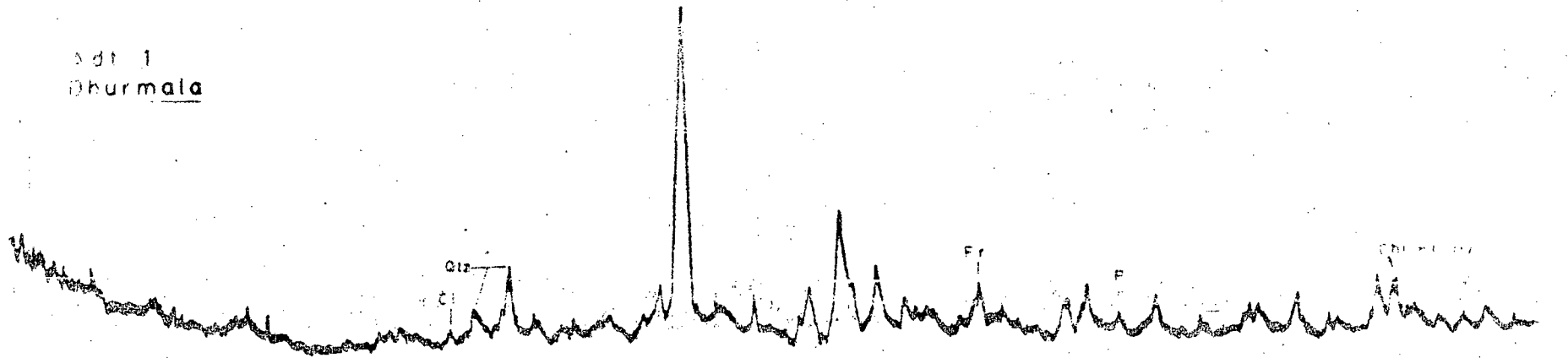


Standard plot of Mg⁺⁺ concentration

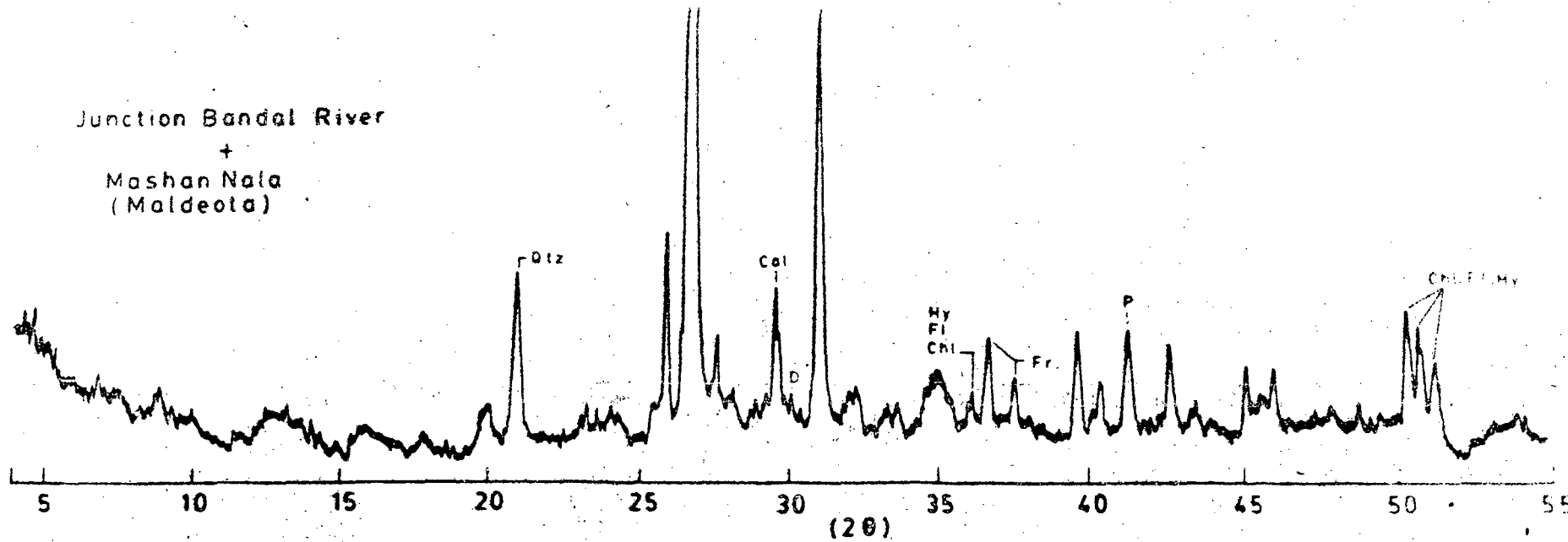


Standard plot of PO_4 (in the sediments)

Sdt 1
Dhurmala



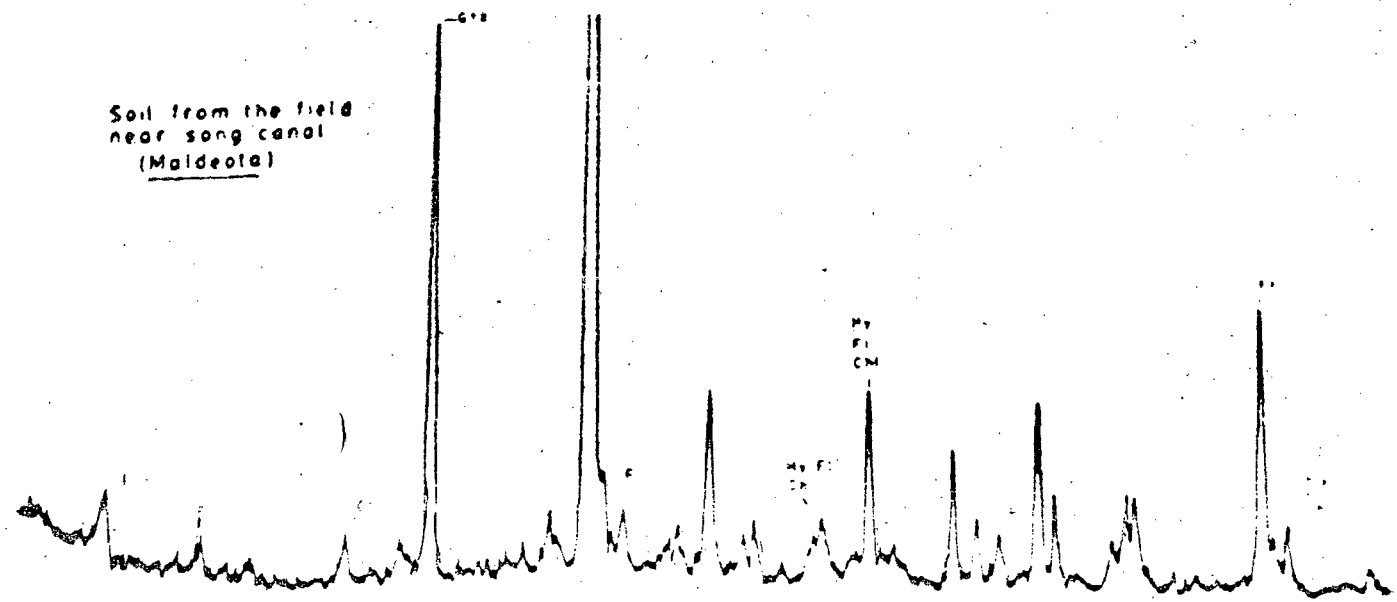
Junction Bandal River
+
Mashan Nala
(Maldeota)



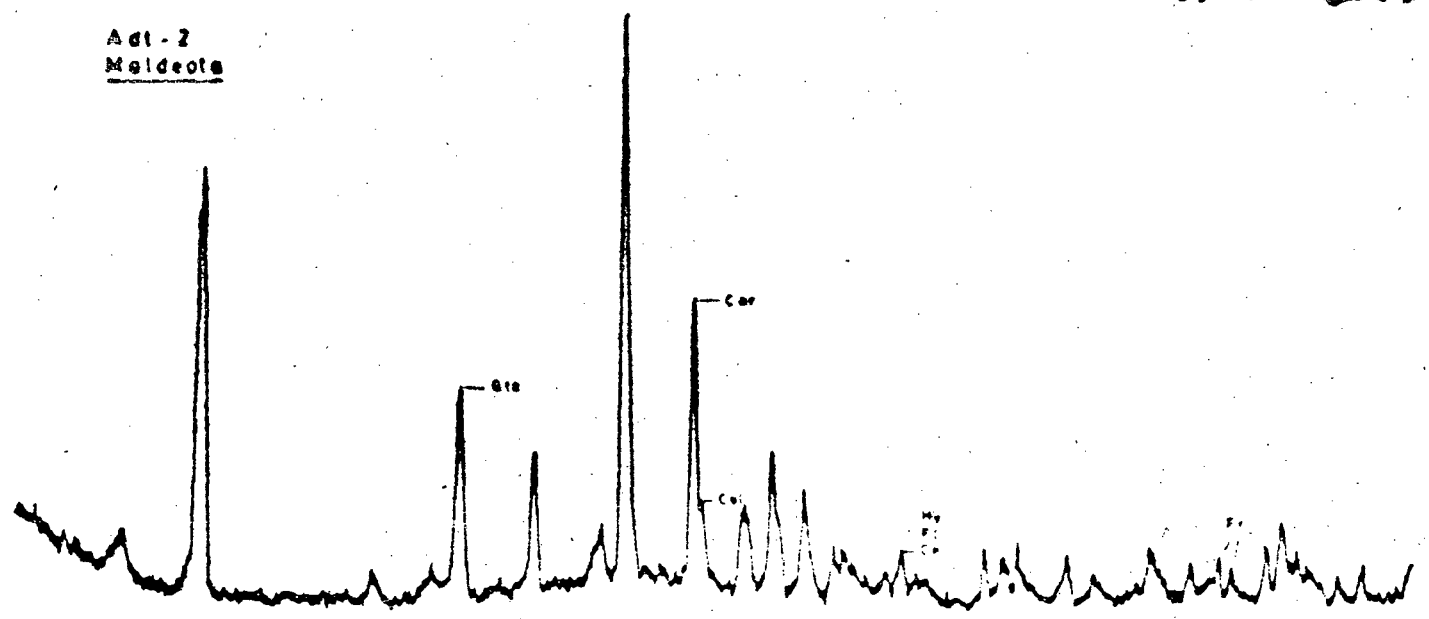
XRD of Bed Sediments

Cl=Chlorite, Qtz=Quartz, Fr=Francolite, P=Pyrite, Chl=Chlorapatite, D=Dolomite,
Fl=Fluorapatite, Cal=Calcite, Hy=Hydroxylapatite

Soil from the field
near song canal
(Maldeota)



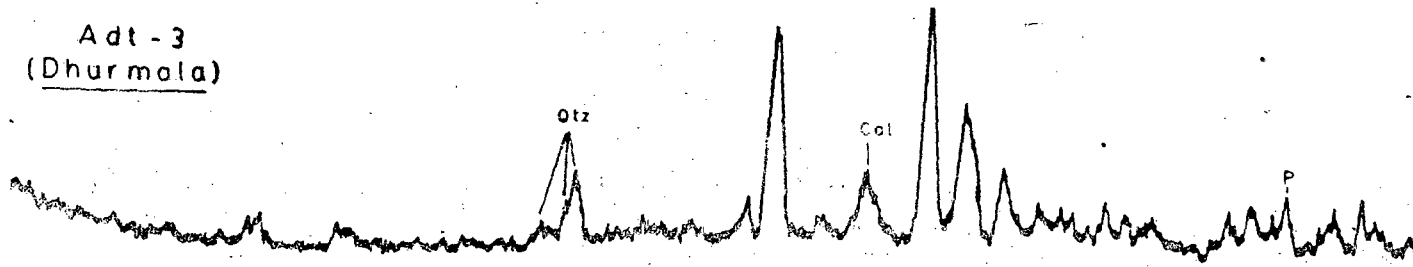
Adt - 2
Maldeota



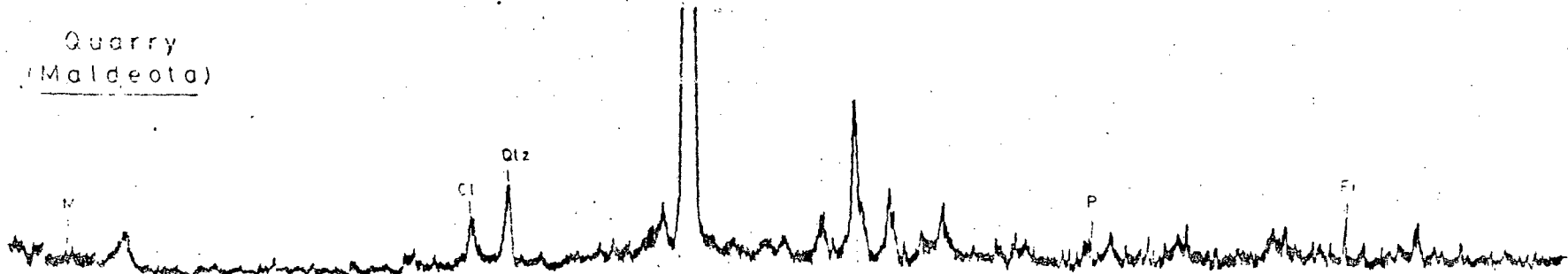
5 10 15 20 25 30 (2θ) 35 40 45 50 55
XRD of Bad Sediments

Qz - Quartz, Cc - Calcite, Csp - Chlorite, Ch - Chlorite, Fr - Francolite, K - Kaolinite, M - Muscovite, P - Pyrite, F - Feldspar, H - Hematite, S - Siderite, G - Gypsum, B - Biotite, E - Epidote, Hc - Hydroxide, Ff - Fluorite, Cc - Calcite, Ch - Chlorite, Fr - Francolite, K - Kaolinite, M - Muscovite, P - Pyrite, S - Siderite, G - Gypsum, B - Biotite, E - Epidote, Hc - Hydroxide, Ff - Fluorite

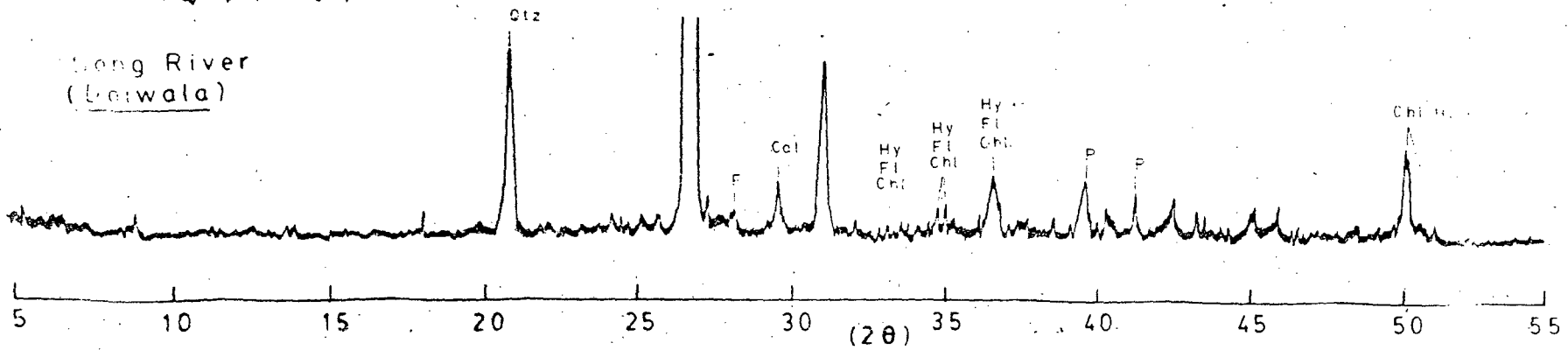
Adt-3
(Dhurmala)



Quarry
(Maldeota)



Long River
(Larwala)



XRD of Bed. Sediments

Il = Illite; Qtz = Quartz; F = Felspar; Col = Calcite; Chl = Chlor apatite; P = Pyrite; Cl = Chlorite;
M = Montmorillonite; Fr = Francolite; Hy = Hydroxyl apatite; Fl = Fluor apatite