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Study on the Relationship between Groundwater Flow System  
and Groundwater Quality in Dejima Area

by  
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## ABSTRACT

Groundwater quality evolution in groundwater flow system has been studied on microscale in a small valley head basin, located on an upland with multilayered geological formations. The study area has been chosen in Dejima upland area, Ibaraki Prefecture, Japan. The groundwater circulation is active and annual irrigation water is three times larger than precipitation in the study area. Comparing with the precipitation in which each of major elements is less than 2 mg/l, the irrigation water quality is  $\text{Cl}^-$ - $\text{SO}_4^{2-}$ - $\text{Na}^+$  type. It is found that groundwater is mainly recharged by irrigation water in quantity and quality.

Both piezometers and soil water samplers were used to collect water samples once in one or two weeks from April, 1985 to June, 1987. Water samples from wells were also collected at the same time. The chemical compositions of the samples were analyzed. Piezometers were also used to measure hydraulic potential. X-ray method was used to identify the clay mineral compositions of soils in study area. It was found that there are Joso Clay Bed and clay of Narita Formation in the study area, the clay minerals in the former being halloysite, vermiculite and mica, and that in the latter being montmorillonite. Moreover, the laboratory experiments were done to study the clay-water interaction in detail.

Hydraulic head distribution revealed that the groundwater flow system in the study area is composed of

local and intermediate groundwater flow systems. The clay of Narita Formation separates these two flow systems. The groundwater quality evolution processes occur both in local and intermediate groundwater flow systems.

Groundwater quality has its own characteristics with little change in each aquifer, but is different greatly from aquifer to aquifer, especially where clay exists. Therefore, distribution of groundwater quality is stratified in the study area.

On the other hand, structure and mineral compositions of clay control not only the concentrations of cations and silica in the groundwater, but also that of chloride ion. From the field observations and laboratory experiments, it was found that chloride ion is concentrated where the clay of Narita Formation exists. This phenomenon does not occur in the Joso Clay Bed.

Groundwater quality varies greatly and the movements of groundwater and chemicals in the groundwater are different from each other where clay exists. Therefore, clay layer in the groundwater flow system is one of the most important factors to control the groundwater quality evolution processes in the study area.

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## I INTRODUCTION

### 1.1 Review of previous studies

Study on the relationship of groundwater flow system and groundwater quality is an important topic in groundwater research. This relation may be very complex in general, depending on its geological and hydrological conditions. Many investigations have been done separately in groundwater flow system and groundwater quality, but there is only a few works in their relationship.

It is commonly believed that early studies of the water quality were concerned entirely with its classification and utilization. Laboratory experiments by Thompson and Way (reference in paper written by Renick, 1924) in the middle 1800's demonstrated that some properties of clay and other materials could change the composition of water passing them.

The process of cation exchange in groundwater bodies has been observed extensively since early studies by Renick (1924) who called attention to natural softening of groundwater by cation exchange in sediments underlying the northern Great Plains area of the United States.

During this period, the correlation and interpretation of the many variables associated with the chemical character of natural waters led to a need for suitable graphical techniques for data presentation. The three graphs most commonly used in north America were originally described by

Collins (1923) and Piper (1944).

Since 1960's, as environmental problems were getting more and more serious, contaminants migration in the groundwater became the most important topic on which hydrogeologists, soil scientists and environmental protectors have focused their attention.

In field situation, however, the aquifers through which contaminants migrate are invariably heterogeneous on the macroscopic scale, hence some hydrogeologists like to use advection-dispersion models for groundwater pollution assessment.

Various models have been developed in order to arrive at a mathematical description of the solute transport processes. Fried (1975) has classified these models into three groups: (1) geometric models, of which the work of Taylor (1953) is perhaps the best known example for solute migration in a single capillary; (2) probabilistic models, such as the random-walk model described by Scheidegger (1954); and (3) statistical geometric models, as described by Bear and Bachmat (1967) and Bear (1972). However, these models can only be used in the very simple groundwater system without considering complex chemical reactions that occur naturally in the system.

Development of the equilibrium approach gave a revolutionary impact on chemical hydrogeology. This approach had its beginning in the late 1940's, and brought the attention of the geologic profession to many of the concepts of chemical thermodynamics. The first of these concepts was

the Nernst equation which related electromotive force, pH, temperature, and dissolved species in the groundwater (Krumbein and Garrels, 1952).

Two of the most commonly used computer codes, known as WATEQ and SOLMNEQ, were developed by Turesdell and Jones (1974) and Kharaka and Barnes (1973), respectively, for interpreting concentrations of major ions. Ball, Jenne and Nordstrom (1979) modified WATEQ for analysis of equilibria involving minor and trace elements in water. Although models such as WATEQ and SOLMNEQ can be useful in interpreting the behavior of inorganic contaminants in groundwater, they are not designed for predictive purpose.

Predictive-equilibrium chemical models for aqueous systems, which have many of the ingredients of WATEQ, have been developed by Plummer, Parkhurst and Kosiur (1975) and Plummer, Parkhurst and Thorstenson (1983). Other models of this type were described by Westall, Achary and Morel (1976) and Mattigod and Sposito (1979). These models are predictive in the sense that they provide computed-equilibrium liquid-phase concentrations for inorganic species, provided that the solid phases (that is, minerals or amorphous compounds) with which the water reacts by way of precipitation or dissolution are assigned and the reaction sequence and thermodynamic data in the form of equilibrium constants or free energies are specified. Although the emphasis in these models is on solubility controls, other liquid-solid phase interactions such as oxidation-reduction and ion exchange can be included. These equilibrium models are not transport

models, in that they do not include velocity or dispersive terms.

On the other hand, soil scientists and mineralogists have focused their attention to the relationship between solid and liquid interface on micro-scale, without considering groundwater flow system.

Already in the early 1900's, Chapman (1913) derived an equation describing the ionic distribution in the diffuse layer founded on a charged planar surface. Schofield (1946) re-introduced the Gouy-Chapman theory for the calculation of the thickness of water films on mica surfaces. The work of Schofield (and collaborators) has contributed significantly towards the introduction of the Gouy-Chapman theory as a basic tool in soil chemistry. Bolt (1979) suggested to explain properties of the liquid layer adjacent to the solid phase with so called diffuse double layer theory. It is considered that the soil possesses a fairly constant surface charge density, and the concentration distribution of counterions in this layer follows the Boltzmann equation. By evaluating both the electrostatic and the chemical properties of solid surfaces, a substantial improvement in understanding specific adsorption effects should be possible. Rigorous application of electrical double layer (EDL) theory has thus far been limited to rather simple oxide surfaces, but application to more complex mineral systems should be feasible. An EDL model for computing properties of oxide surfaces and predicting behavior of sulfates was described by Davis, James and Leckie (1978). A

review by James and Parks (1982) described EDL concepts and their applicability to various liquid-solid systems.

Hydrogeologists, soil scientists and mineralogists are very interested in the evolution of water quality where clay exists. Experimental studies have shown that clay membranes give rise to electroosmosis (Srivastava and Avasthi, 1975), hyperfiltration (Kharaka and Smalley, 1976), and regular (chemical) osmosis (Young and Low, 1965; Kemper and Rollins, 1966; Olsen, 1969). Osmosis through clays has been invoked to explain such disparate phenomena in the subsurface as anomalous hydraulic heads (Marine, 1974), thrust faulting (Hanshaw and Zen, 1965), and breaching of clay liners of seepage ponds holding saline waste (Hudec, 1980).

A membrane is a semi-permeable barrier which permits the transport of some components of a solution and not others (Tuwiner, 1962). It rejects solutes on the basis of size and/or electrical restrictions (Gregor and Gregor, 1978). Geologic membranes have generally large enough pore sizes to accommodate the largest hydrated radii of ions commonly found in groundwater. Thus the salt-exclusionary behavior of clay membranes depends on electrical restrictions operating within the interstices of clay membrane structures.

The surfaces of clay minerals have a net negative charge which is mainly a result of substitution of lower-valence cations for higher-valence cations within the structure (Grim, 1968). This charge deficiency is manifested at the surface of the platelets where neutralization takes



place by absorption of cations in the vicinity of the negatively charged substrate. The charged surface of the clay and its cation-dominated absorption layer together define the Guoy double layer (Stumm and Morgan, 1970).

The salt-exclusionary properties of clays arise when the compaction of a clay slurry induces overlap of double layers of adjacent platelets. This overlap results in the pore space between clay platelets which have a negative electrical potential. Anions attempting to migrate through such pores are repelled because the cations must remain with their anionic counterparts to retain electrical neutrality in the outer, or "free" solution. Water, of course, is freely admitted to the membrane structure. All clays are non-ideal membranes, but the efficacy of their salt exclusion is greatest when a high CEC clay of low porosity separates dilute solutions (Marine and Fritz, 1981).

However, some other soil scientists have researched the miscible displacement in porous materials with loam and clay. The results both in field (Dyer, 1965) and laboratory (Dyer, 1965; Thomas and Swoboda, 1970; Smith, 1971) have shown that anions in some cases can move through soil faster than the average velocity of the water molecules present.

Most of the research works, as described above, were only concerned with one aspect about groundwater quality. Therefore, more studies need to be done in future.

In order to make clearly the characteristics of groundwater flow system and groundwater quality, some researchers (Ikegawa and Tase, 1984; Kurata and Tase, 1984;

Kurata, Tase and Kayane, 1984; Shindou and Ishikawa, 1985; Shindou and Tang, 1986; Tase and Mayila, 1986; Bae and Kayane, 1987) carried out their investigations in Dejima upland, Ibaraki Prefecture, Japan. The results of their research works show that the groundwater flow system is very complex, and the groundwater quality is influenced not only by the natural conditions but also by the agricultural activities. Since these influences obscure general hydrogeochemical relationships, more detailed information is required about the specific contributions of land use and the compositions of geological setting to the chemistry of groundwater.

## 1.2 Purpose of the present study

It is very important to interpret or predict the contaminants movement in groundwater. A study of this type is multidisciplinary in nature, but is primarily concerned with hydrogeology, mineralogy and geochemistry. From this point of view, the present paper, perhaps, is the first one to study in detail about the relationship between groundwater flow system, geological condition and behavior of chemicals in the system.

For the purpose of this study, following items were investigated.

(1) The characteristics of groundwater quality provided that the groundwater flow system and geological conditions have been well known.

(2) The behavior of major ions of groundwater where clays exist.

(3) The relationship between the groundwater flow system and groundwater quality on microscale.

In order to investigate these items, the following steps need to be carried out in present study.

(1) To make clear the groundwater flow system and geological conditions, which control the migrations of chemicals in groundwater;

(2) To make field observations and analyses of groundwater quality;

(3) To do laboratory experiments to evaluate the effect of clays on the groundwater quality; and

(4) To explain the relationship between the groundwater flow system and groundwater quality.

## II STUDY AREA AND PROCEDURE

### 2.1 Description of the study area

#### 2.1.1 Geographical position and topography

The area under investigation is situated at the central part of Dejima upland region in a peninsula of Kasumigaura Lake, and located in  $140^{\circ} 20'E$  and  $36^{\circ} 5'N$ , Ibaraki Prefecture, Japan; about 70 km northeast of Tokyo. This flat upland is surrounded by two small rivers, R. Ichinose and R. Hishiki (Figure 1).

The Dejima irrigation channel, supplied by the pumping station with water from Lake Kasumigaura, runs through the study area from east to west, irrigates paddy fields from May to August, and makes a notable impact on groundwater both in quality and quantity.

The total study area is about 140 ha. Its altitude is between 24 to 29 meters above sea level. The topographical features are flat in the central part along the irrigation channel and descend in northeast and southwest directions, forming two small valleys. From the hydrological system's point of view, the study area could be divided into two parts by the irrigation channel. Irrigation channel plays as a watershed. The north part is a relatively integrated basin with typical land use pattern. More strictly, it can be said that the study area is an artificial basin rather than a natural basin, because it is influenced significantly by the

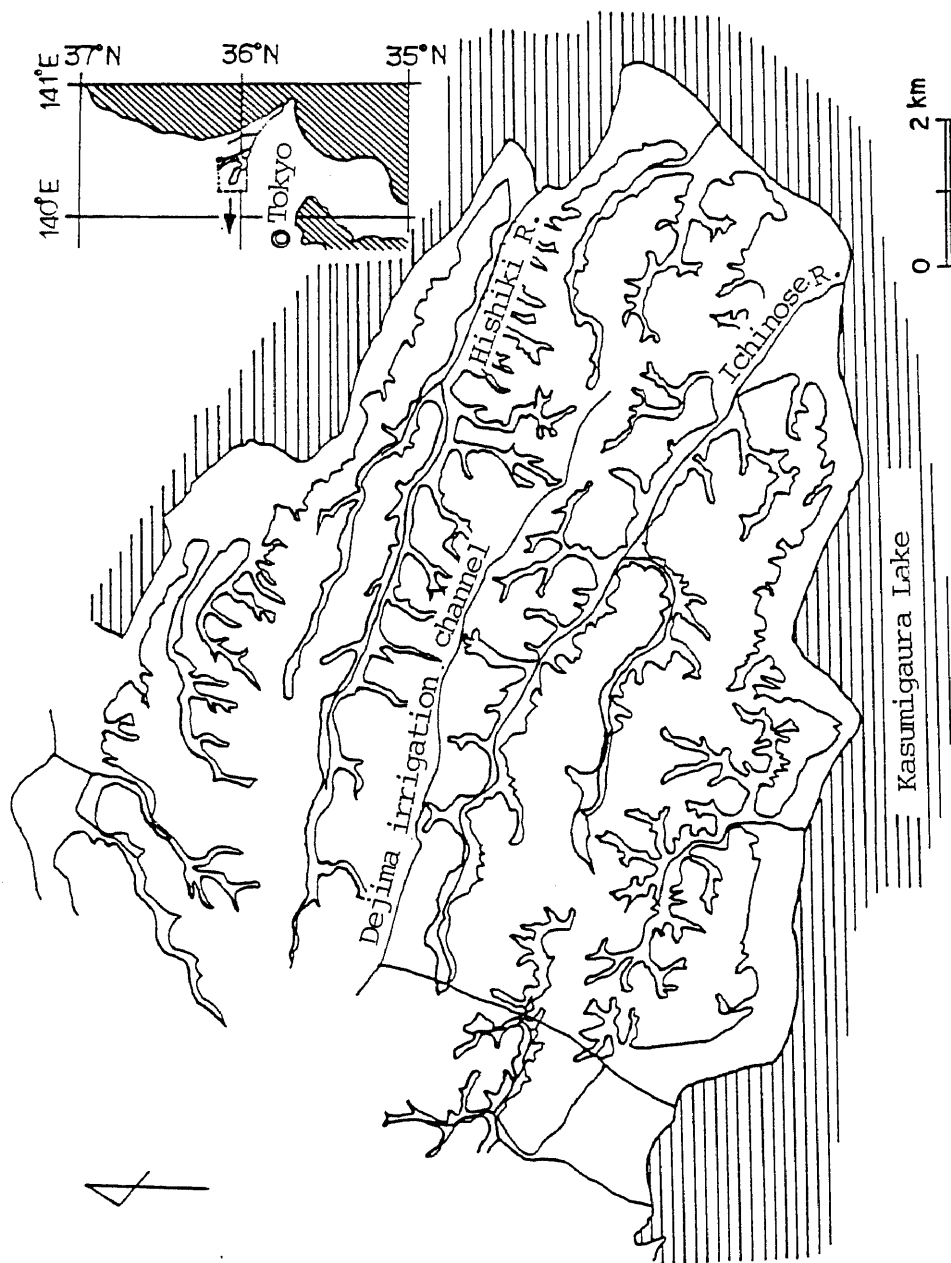


Figure 1 Locations of the study area.

irrigation water. This basin could be separated into three areas, considering both topography and land use. The first one is the recharge area near irrigation water channel, and is mainly composed of paddy fields. The second one is the discharge area in the valley, of which area is very small. The third one is the transmitting area between the areas described above, and is used for producing chestnut and planting wheat in autumn and corn in spring (Figure 2).

#### 2.1.2 Geology

Geological condition of the study area has been investigated by field survey and X-ray method in laboratory. Its geological structure can be represented by the A-B-C section shown in Figure 3 (reference to Figure 6).

As shown in Figure 3, the upland is composed of the volcanic ash layer (named Kanto loam Formation) of 2-3 m, clay or silt layer (Named Joso Clay Bed) of 1 m, sand layer (named Ryugasaki Formation) of 1-2 m, clay layer (upper part of Narita Formation) of 2 m, and sand layer (a member of Narita Formation) in a descending order. Therefore, the geological condition in the study area is too complex to study the groundwater quality by the models which we have known at present.

Masuda and Shindou (1986) described the geology of Kasumigaura region. According to their works, Joso Clay Bed is flooding sediment, sand in Ryugasaki Formation is fluvial

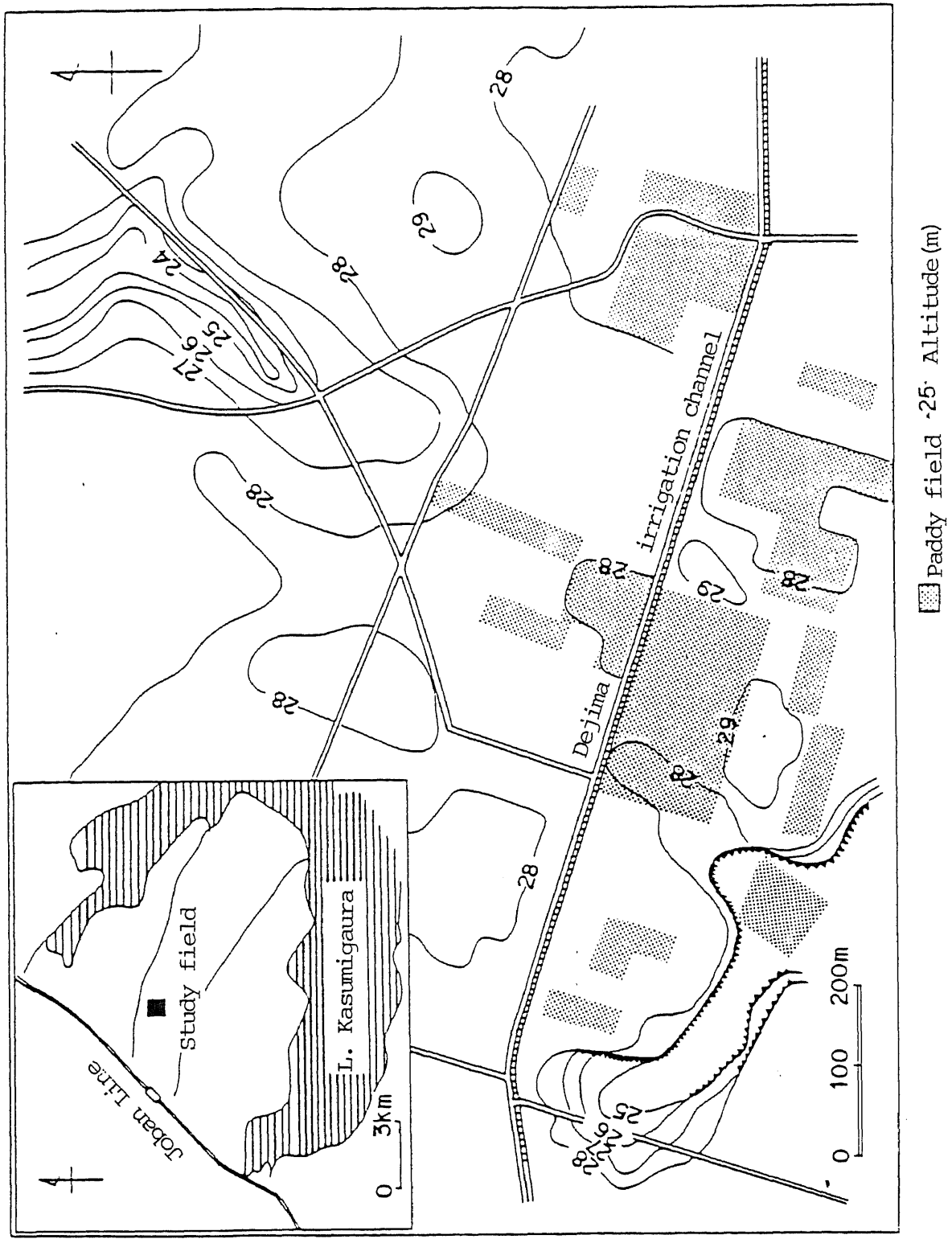


Figure 2 Topography and land use in the study area.

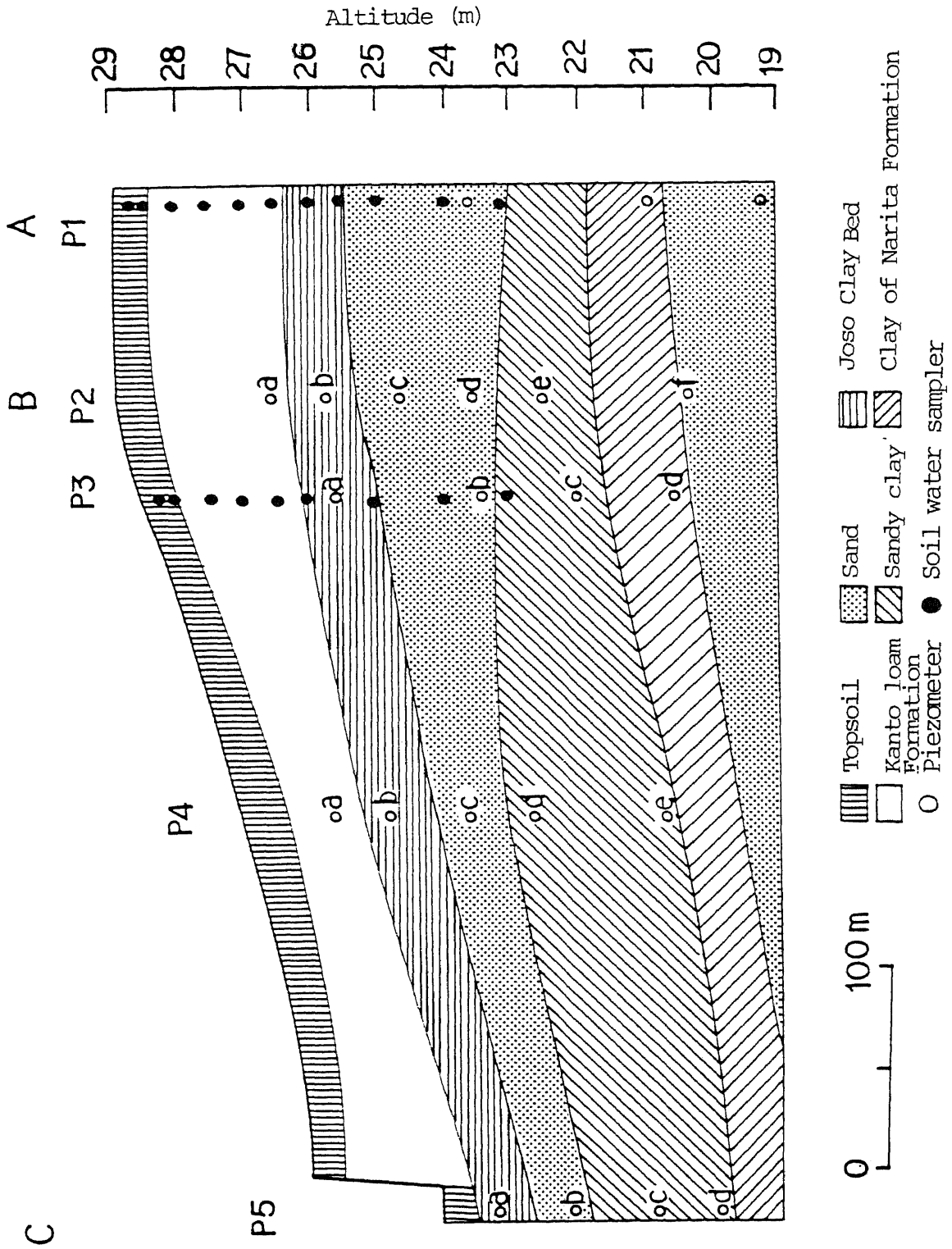


Figure 3 Geological cross section (A-B-C).  
(see Figure 6)



sediment and the clay in Narita Formation is swamp deposits. But the sand in Narita Formation is considered to be formed in estuary environment.

According to the hydraulic conductivity (Table 1), it could be considered that there are two aquifers in the study area, so-called upper aquifer and lower aquifer, which are divided by the clay layer of Narita Formation.

Moreover, X-ray analysis method was used to identify clay mineral compositions of soils in the study area. From Table 1, it can be found that there are mica and vermiculite in Kanto loam Formation, mica, vermiculite and halloysite in Joso Clay Bed, halloysite in sand layer of Ryugasaki Formation and montmorillonite and mica in Narita Formation.

Figure 4 shows some results of X-ray method for the soils in the study area.

### 2.1.3 Hydrology

In the study area, irrigation water is transported from Lake Kasumigaura through Dejima irrigation channel from the end of April or the beginning of May to the end of August or the middle of September every year, which make great influence on the groundwater flow system in the study area. Therefore, in this study, the period between the end of April to the middle of September is called the irrigation period, and the other months in the year is called the nonirrigation period.

The sources of groundwater in the study area are

Table 1. Geological succession with grain size, hydraulic conductivity and clay constituents

Formation	Thickness	Dominant grain size	Hydraulic conductivity (cm/sec)	Clay minerals in each formation
Kanto loam	2-3m	Silt-clay	$3.2 \times 10^{-3}$	Mica, V,
Joso clay	1m	Clay	$3.0 \times 10^{-3}$	Mica, V, H, A
Ryugasaki Formation	2-3m	Sand	$2.8 \times 10^{-2}$	H, A
Narita Formation	1-2m	Clay	$1.0 \times 10^{-7}$	M, Mica
		Sand	$7.3 \times 10^{-3}$	M, Mica

H: Halloysite                      V: Vermiculite  
M: Montmorillonite              A: Allophane

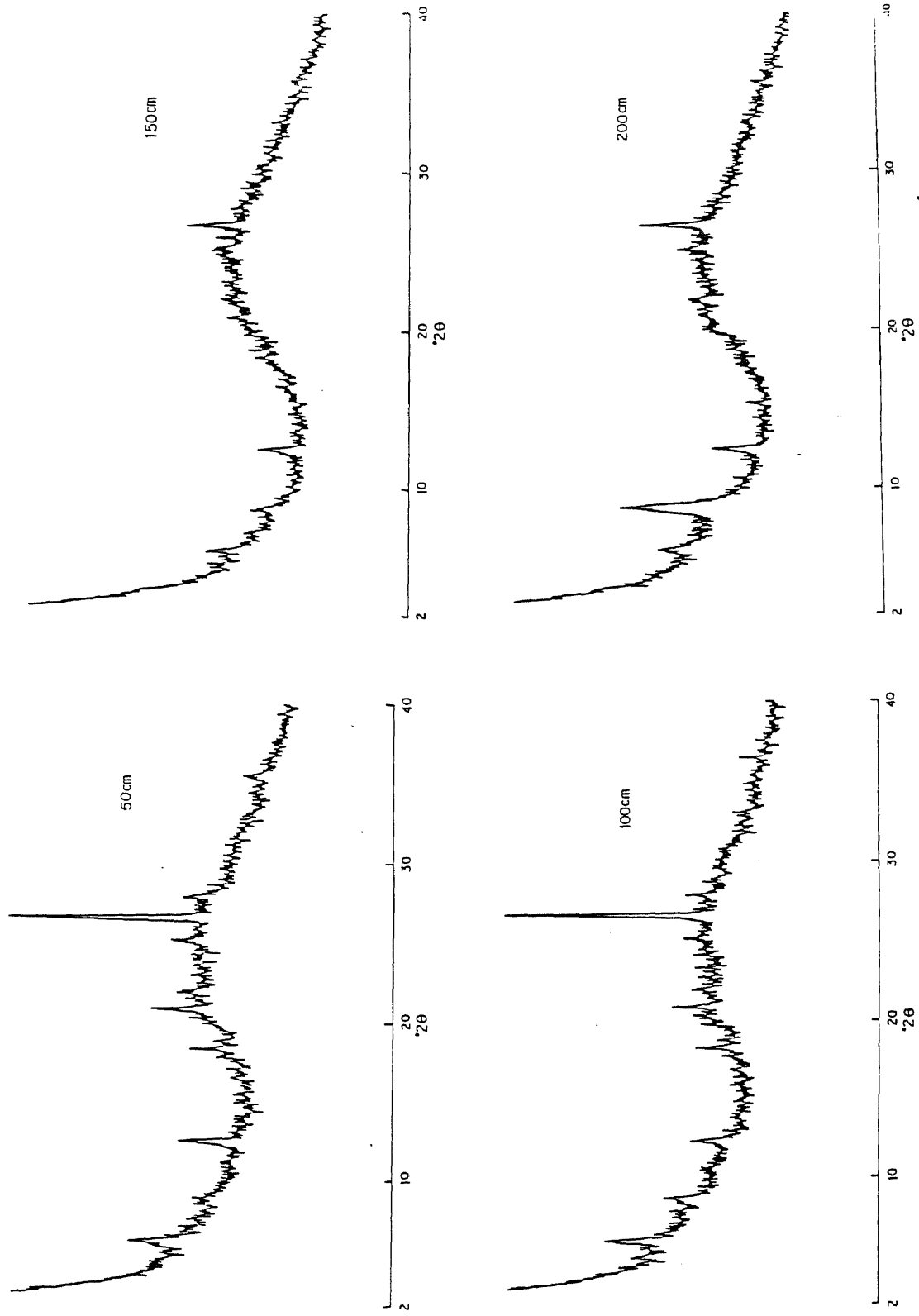


Figure 4-1 X-ray patterns of the clay mineral compositions in soils at 50 cm, 100 cm, 150 cm and 200 cm in depth (P2).

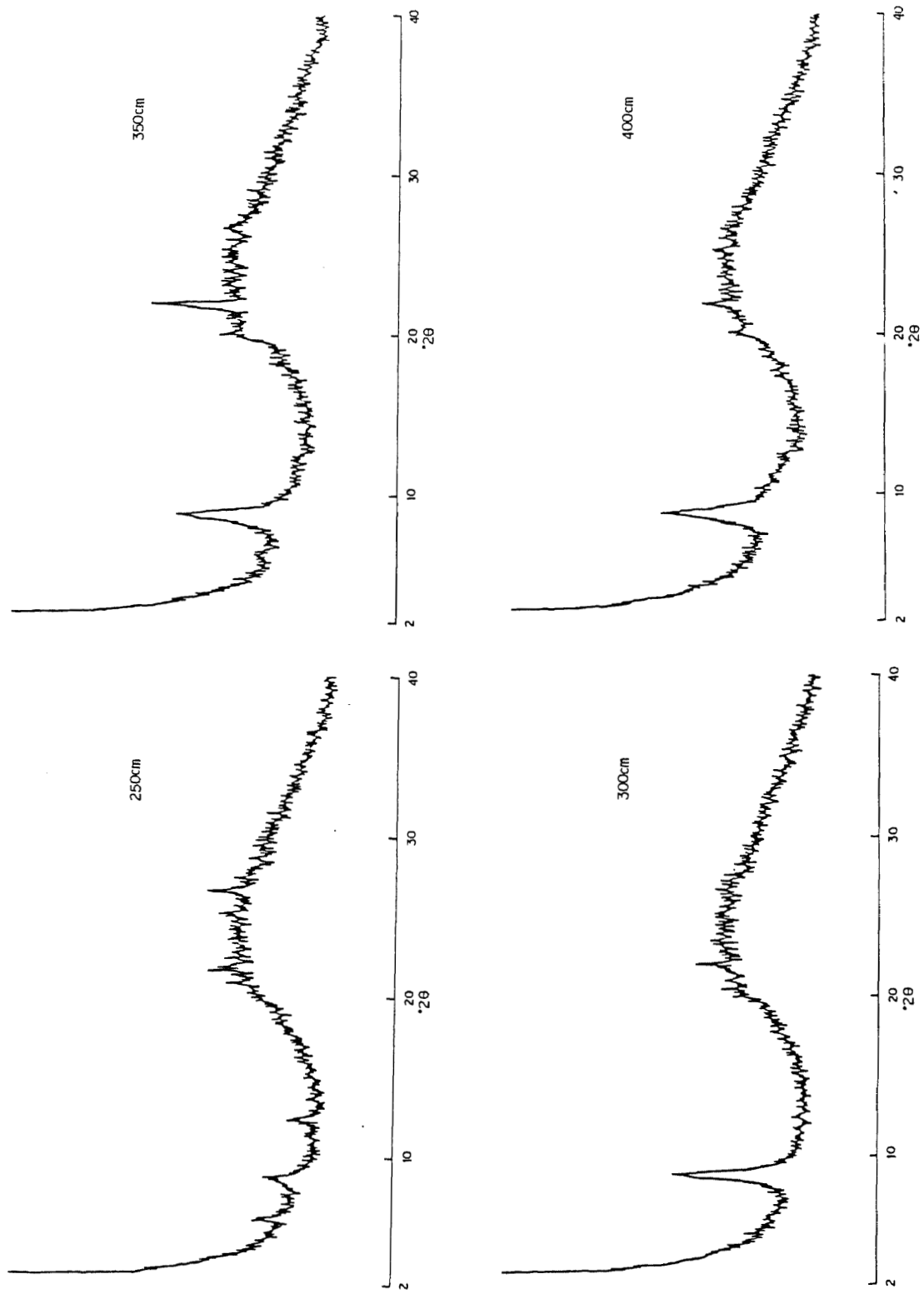


Figure 4-2 X-ray patterns of the clay mineral compositions in soils at 250 cm, 300 cm, 350 cm and 400 cm in depth (P2).

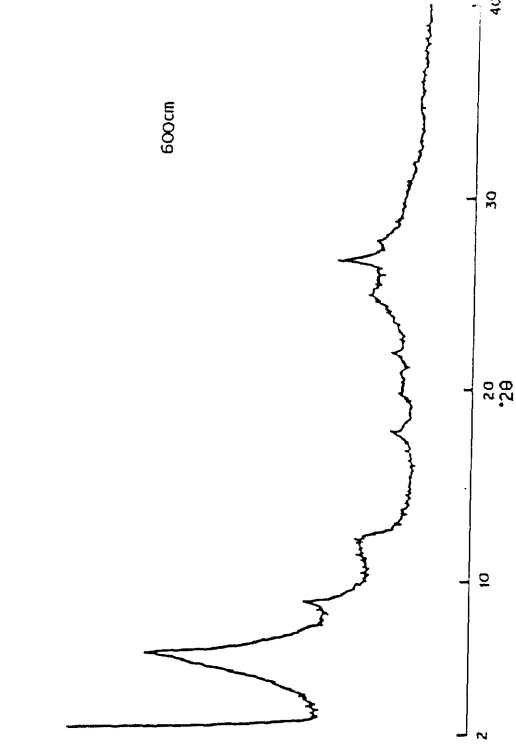
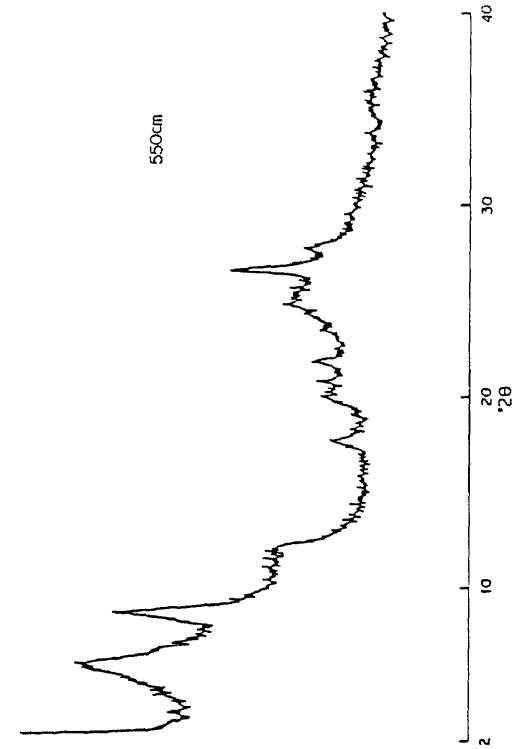
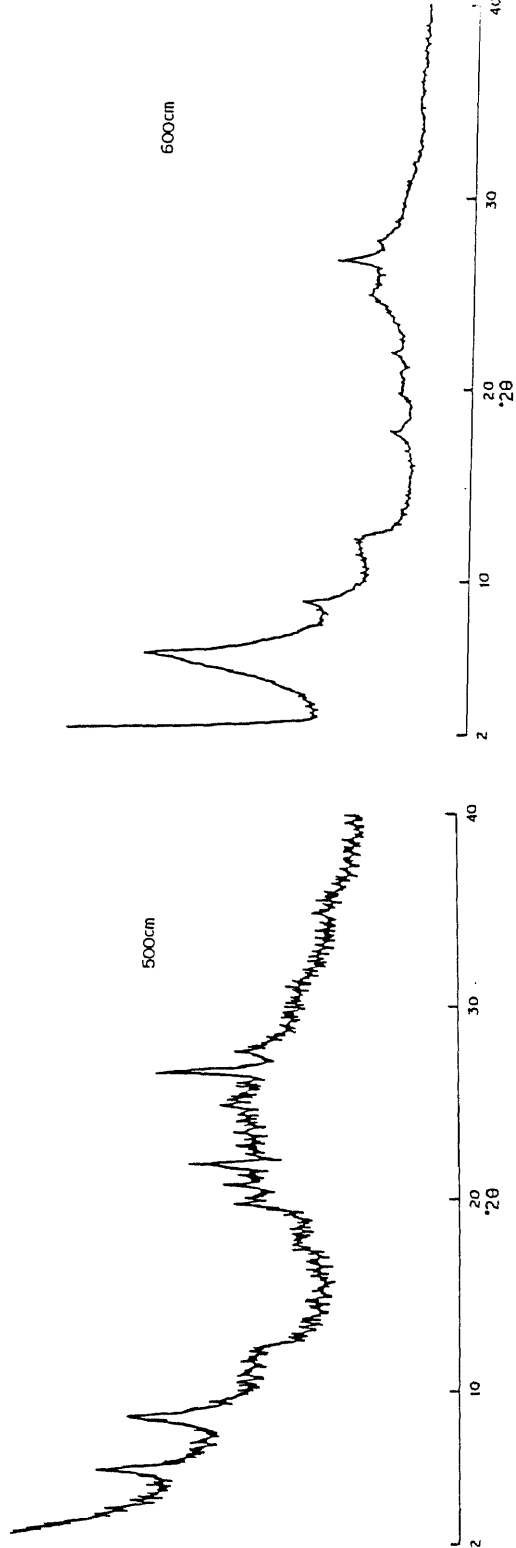
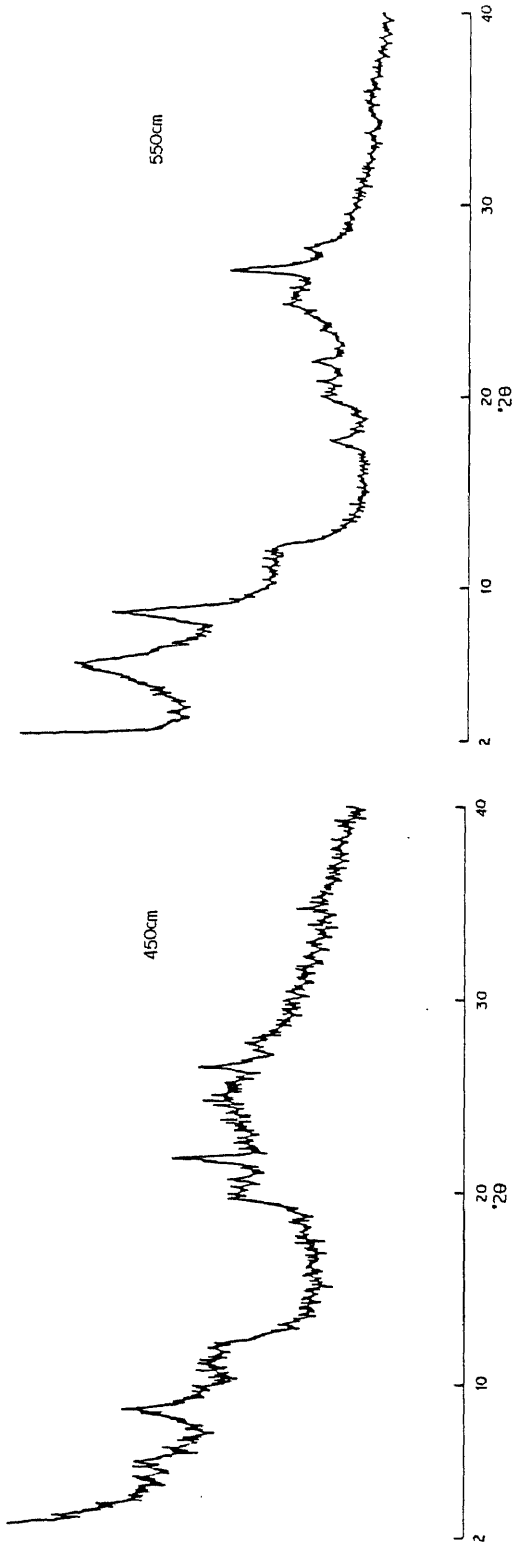


Figure 4-3 X-ray patterns of the clay mineral compositions in soils at 450 cm, 500 cm, 550 cm and 600 cm in depth (P2).

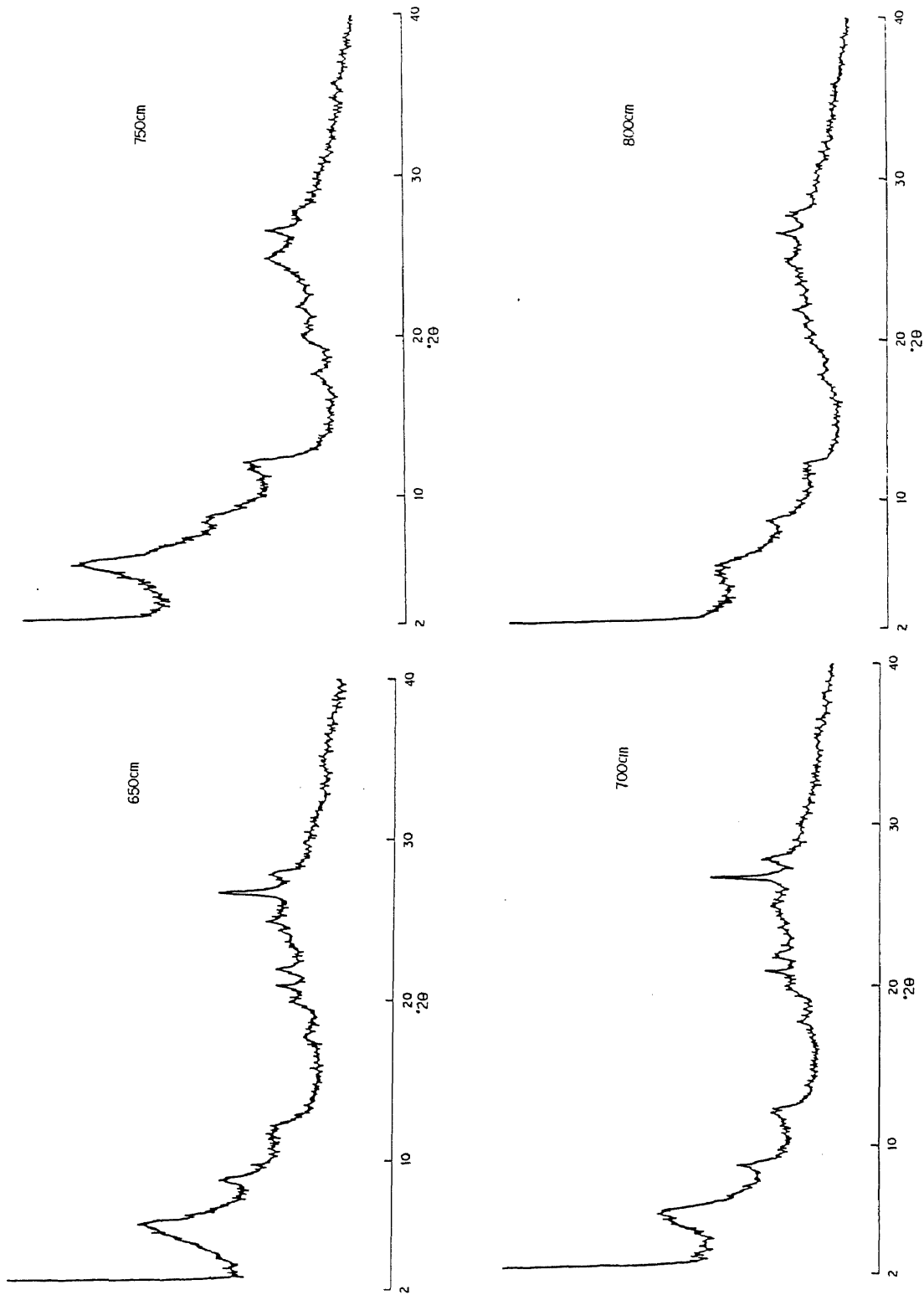


Figure 4-4 X-ray patterns of the clay mineral compositions in soils at 650 cm, 700 cm, 750 cm and 800 cm in depth (P2).

precipitation on the land surface that has worked its way downward by gravity through the soil and into the underlying layers, and irrigation water from paddy fields.

The local hydrologic cycle is explained by the following hydrologic budget equation:

$$P+I-E-R=\Delta S$$

where

P=precipitation

E=evapotranspiration

R=total runoff

I=irrigation water, and

$\Delta S$ =change in groundwater storage.

The nearest meteorological station with a suitable period of record is at Tsuchiura City, located about 10 km west of the study area. From 1956 to 1987, the average annual precipitation at Tsuchiura City was 1190.7 mm. Precipitation in the area occurs mainly during the rainy season in June, so called Bai-u season, and during the typhoon season from late summer to autumn.

Evapotranspiration has been calculated using the Penman's method. The potential evapotranspiration from the vegetated surface is estimated from the calculated open water evaporation by applying an empirical constant.

For the missing values of meteorological data at Tsuchiura City, meteorological data at Tsukuba Science City, which is located at about 16 km west of the study area, were used to calculate the evapotranspiration. The resultant estimate of average annual potential evapotranspiration is

610 mm. According to a previous study (Noguchi, 1973) of the water balance in this area, the direct runoff coefficient ranged from 10 to 20 %. Assuming on average direct runoff coefficient of 15 %, the average annual recharge in the area is estimated as 422 mm ( Bae and Kayane 1987).

From 1985 to 1987, precipitation was also recorded in the study area (Figure 5). During Bai-u season or typhoon season, the daily precipitation was large. During nonirrigation period, the precipitation in the study area was also small. From February to March every year, the precipitation was the least through the year.

As described above, irrigation activities influence the variation of water table. About  $1.1 \times 10^7$  cubic meter irrigation water is used for rice planting every year. It means that there is 28 mm water per day during the irrigation period in average (Shindou and Tang, 1986). During this period, water table shows several mounds in paddy fields. The groundwater is recharged by irrigation water, flows forward to valley, and part of which flows out the basin as spring water. On the other hand, groundwater is recharged only by the precipitation during nonirrigation period and the groundwater table in this period is too low that no spring water occurs at valley.

Table 2 shows monthly average precipitation and irrigation water in the study area. The annual average year



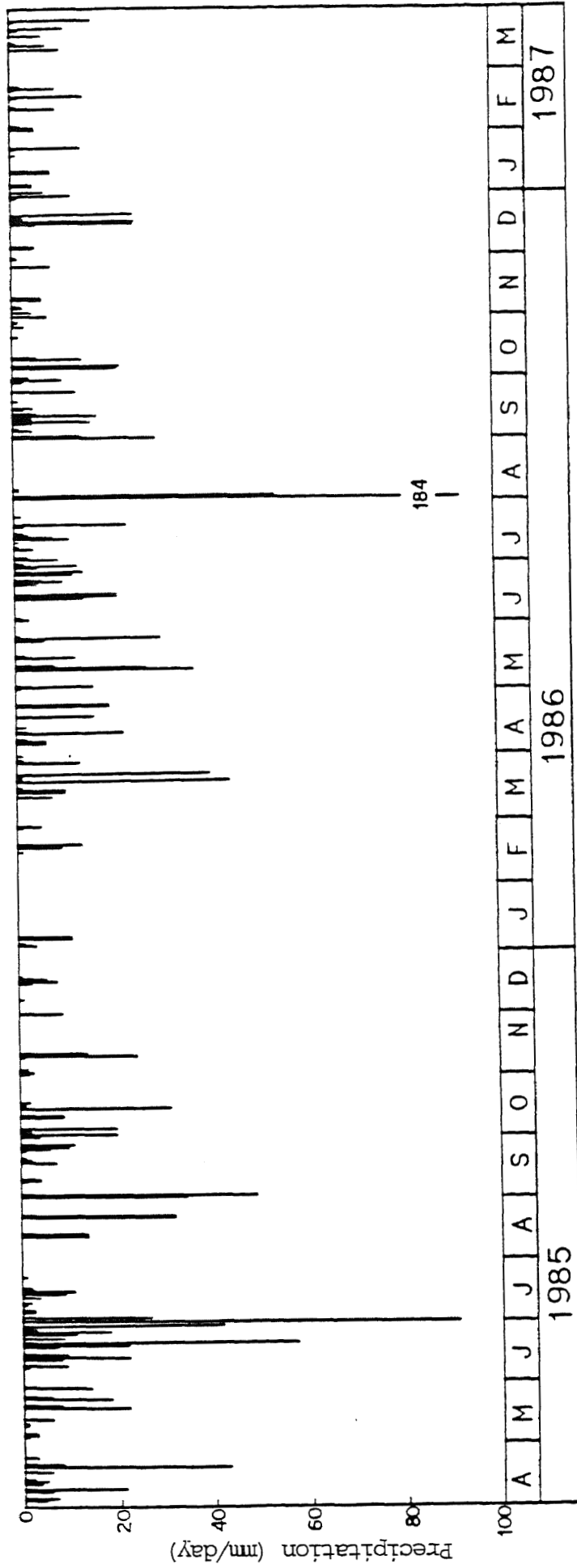


Figure 5 Daily precipitation at the study area (P2).

Table 2. Monthly average precipitation (from 1956 to 1987)  
and irrigation water (from 1985 to 1987)  
(mm/month)

	Jan.	Feb.	March	April	May	June
Precipitation	38.2 (3.2)	55 (4.6)	84.2 (7.1)	109.3 (9.2)	124.5 (10.5)	149.4 (12.6)
Irrigation water	0 (0.0)	0 (0.0)	0 (0.0)	140 (3.8)	868 (23.5)	840 (22.7)

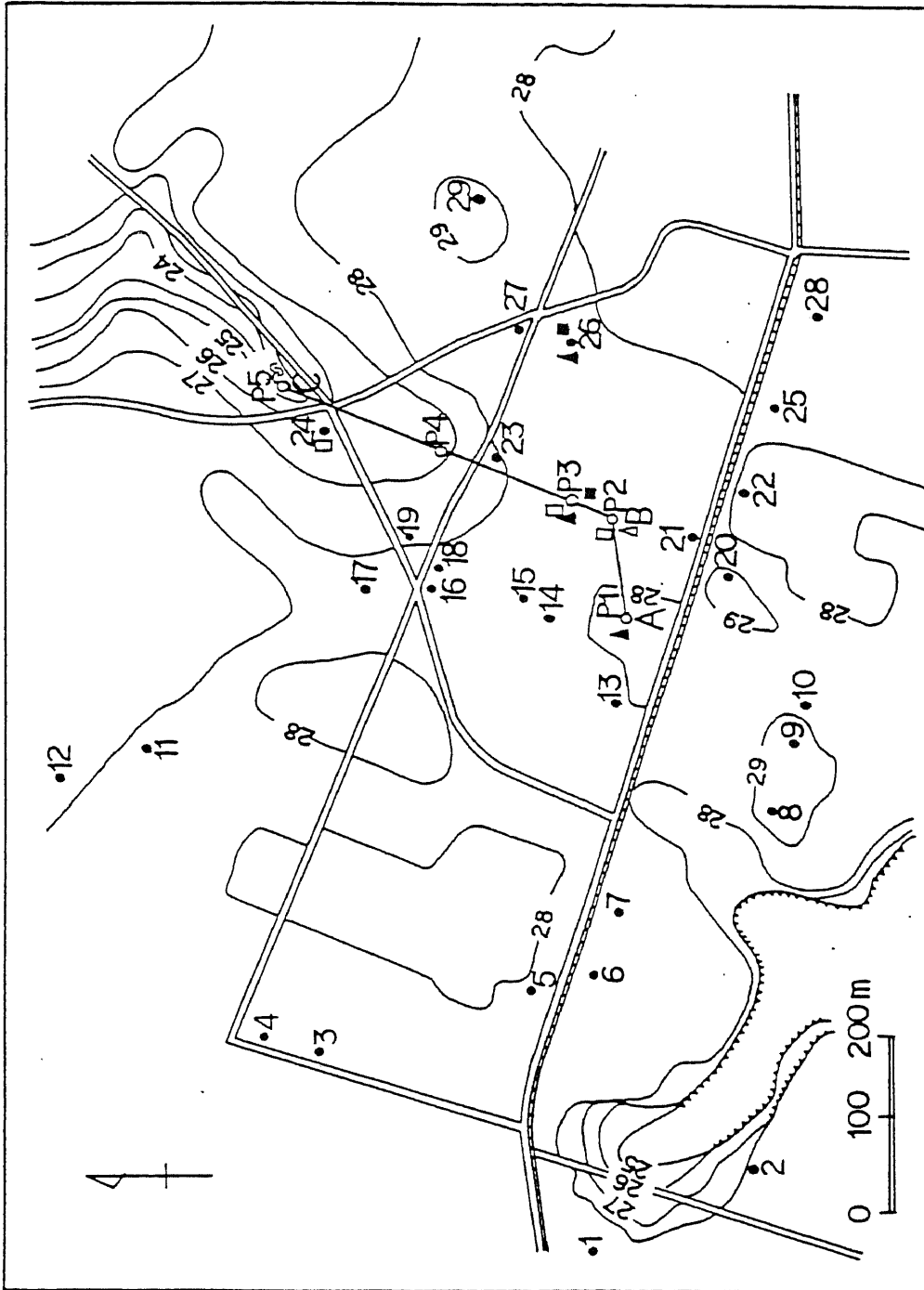
	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
Precipitation	112.6 (9.5)	112.4 (9.4)	165.2 (13.9)	129.5 (10.9)	68.3 (5.7)	42.1 (3.5)	1190.7
Irrigation water	868 (23.5)	868 (23.5)	112 (3.0)	0 (0.0)	0 (0.0)	0 (0.0)	3696

( ):percentage

precipitation is 1190.7 mm and annual total irrigation water is 3696mm. During irrigation period, monthly average irrigation water is one to six times of monthly precipitation. On the other hand, precipitation in nonirrigation period occupies only 35 percent of annual average precipitation.

## 2.2 Instrumentation

Figure 6 shows the observation points. A total of 30 observation wells were installed within the study area. Other than these wells, five sets of piezometers were also installed along the section A-B-C to monitor the potential variations of groundwater. Three sets of soil water samplers were sited at three points (P1, P3 and No.26), which represent different environmental conditions. There were 10 soil water samplers in each set and they were set at 30 cm, 50 cm, 100 cm, 150 cm, 200 cm, 250 cm, 300 cm, 400 cm, 500 cm and 600 cm in depth. At point P1, soil water samplers were set to gain the water in recharge area. Both of No.26 and P3 were chosen to monitor the water in the transmitting area. At P3, experiments were done to study the influence of soil water quality on to the groundwater quality and to compare the chemical analysis results of water samples taken from soil water samplers and piezometers. Two sets of tensiometers were set at No.26 and P3. At No.26, there were five tensiometers located at 40 cm, 80 cm, 120 cm, 160 cm and 200 cm in depth. At P3, tensiometers were set at 10 cm,



- ▲ Soil water sampler O Piezometer    ~27 ~ Altitude (m)
- ▲ Rain gauge    ● Well
- Water table recorder    ∩ Spring
- Tensiometer

Figure 6. Instrumentation in the study area.

20 cm, 40 cm, 60 cm, 80 cm, 100 cm, 120 cm, 140 cm, 160 cm, 200 cm, 250 cm and 300 cm in depth.

Water table was monitored by automatic water table recorders at both P3 and No.24 observation wells. Rain recorder was also set at P2.

### 2.3 Analysis methods

Water samples were obtained once in one or two weeks during study period directly from piezometers and observation wells, or from soil water samplers by vacuum suction technique. At the same time, water level, water temperature, pH, DO, ORP and electric conductivity were also measured.

The in situ groundwater temperature was measured at each depth after sampling. Measurements for pH were made with a combination electrode using the double buffer technique, with the estimated error about 0.05 pH unit.

Water samples were collected in pre-cleaned glass bottles. In laboratory, they were passed through 0.45  $\mu\text{m}$  filters and refrigerated at 4°C until the analyses were completed. Calcium, magnesium, sodium, potassium and silica were determined by Inductive Coupled Plasma Quantometer (ICPQ),  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  by Ion Chromatographic Analyzer (ICA) in the chemical analysis center, University of Tsukuba.

The reliability of these analyses was checked by means of charge balance control. Data analysis was not started

until 95% of the samples deviated by less than 10% from electroneutrality.

Besides, X-ray method was used to identify the minerals in the soils collected at different depth in the study area. X-ray analysis was performed on the samples after each of the following treatments: (1) air drying, (2) glycolation in an ethylene glycol atmosphere; and (3) heating at 550°C for 1 hour. The samples were x-rayed on a diffractometer using nickel filtered Cu K $\alpha$  radiation. The scanning rate was two degrees per minute.

Clay minerals were identified by observing changes of the basal reflections of treated and untreated samples.

Vermiculite can be tentatively identified by a poorly defined peak between 13.5 Å and 14.5 Å. This peak expands upon glycolation to about 15 Å and produces a broad to sharp peak that collapses to about 10 Å after heating to 550°C for 1 hour.

Montmorillonite is identified by a broad peak between 13.39 Å and 15.53 Å. This peak expands to about 17 Å upon glycolation and subsequently collapses to 10 Å after heating to 550°C for 1 hour.

Kaolin minerals display a sharp, first order peak between 7.14 Å and 7.25 Å, and a second order peak between 3.58 Å and 3.59 Å. These peaks are unaffected by glycolation but disappear after heating to 550°C for 1 hour.

Chlorite is identified by a sharp, symmetric peak between 13.31 Å and 14.28 Å. Second order at 7 Å and reflections at 3.5 Å disappear or undergo partial collapse

after heating.

Other minerals in the  $<2\mu\text{m}$  fraction of the soils include quartz and mica, which has two sharp peaks, a minor peak at  $4.23 \text{ \AA}$  and major peak between  $3.3 \text{ \AA}$  and  $3.42 \text{ \AA}$ .

### III SUBSURFACE WATER FLOW SYSTEM

#### 3.1 Variation of groundwater flow

The continuity pattern of the flow system is demonstrated by the distribution of hydraulic heads measured from the wells and piezometers.

The principal groundwater flow direction in the study area is in north direction. The hydraulic gradient in the principal direction of flow is the greatest. This yields a specific flux of 0.7 m/day in upper aquifer (Shindou and Ishikawa, 1985).

##### 3.1.1 Groundwater flow during nonirrigation period

Figure 7 shows contour map of water table during the nonirrigation period (Feb. 6, 1986). The undulation of water table was coincided with that of topography. In Figure 8, equipotential lines were drawn along the B-C cross section based on the water table contour map and topography map. The equipotential lines were distributed densely in clay layer of Narita Formation. According to the distribution of equipotential lines, water in lower aquifer was supplied from upper aquifer. During this period, the water table was too low that there was no groundwater flowing out from the study area as the spring water. It is considered that the morphological features control the groundwater flow system, since there is no influences of irrigation from paddy fields



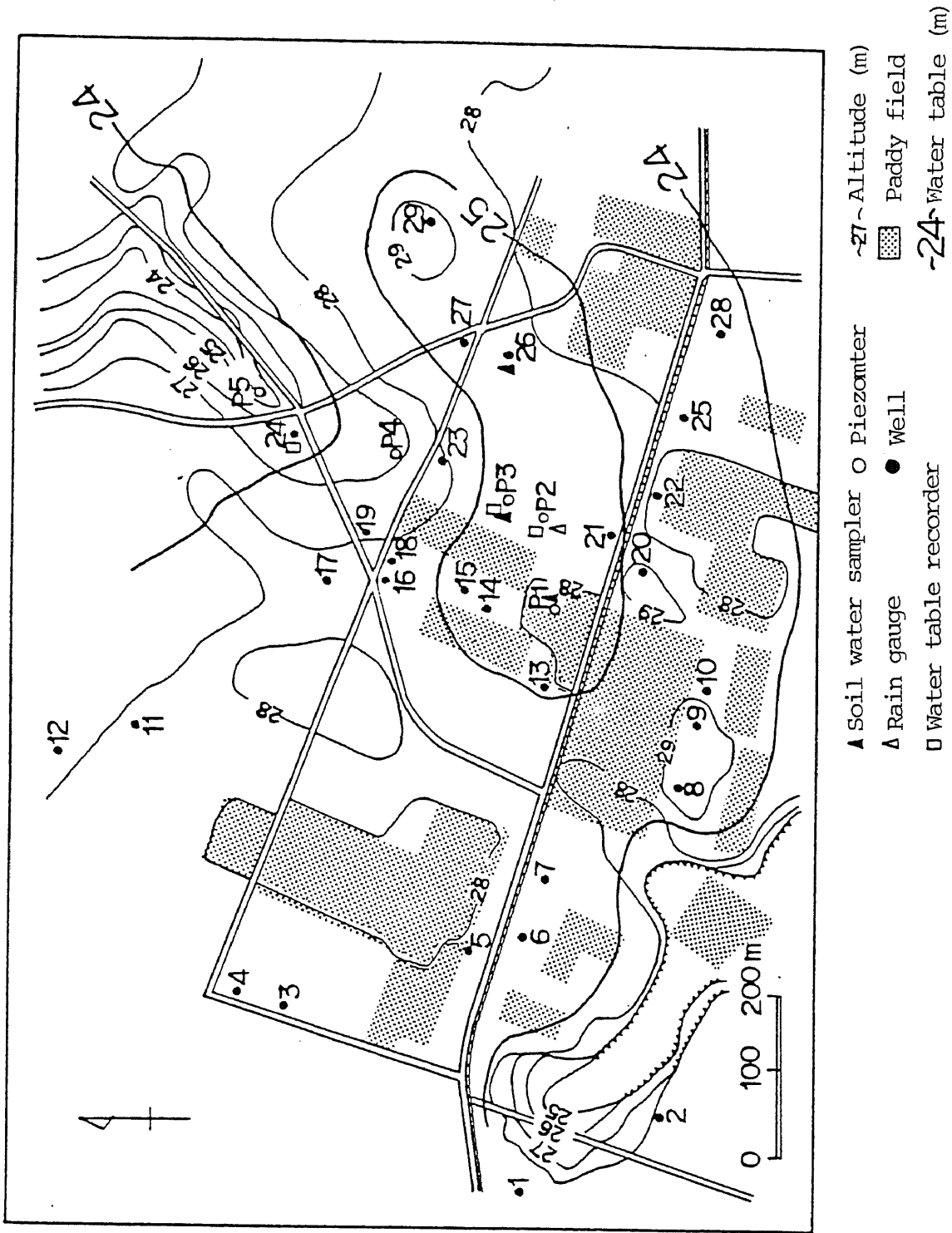


Figure 7 Contour map of water table during nonirrigation period (Feb.6, 1986).

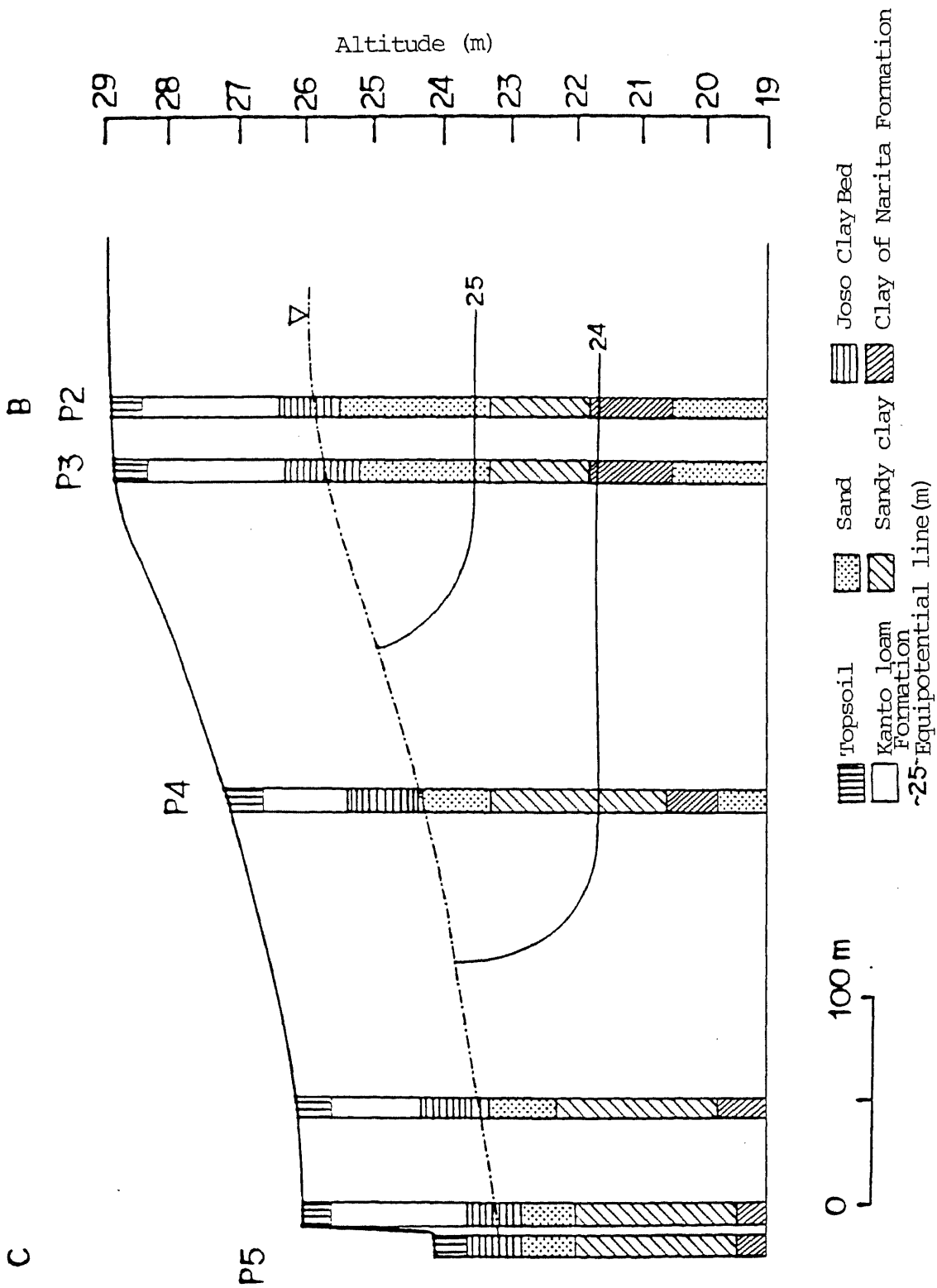


Figure 8 Distribution of equipotential lines during nonirrigation period (Feb.6, 1986).

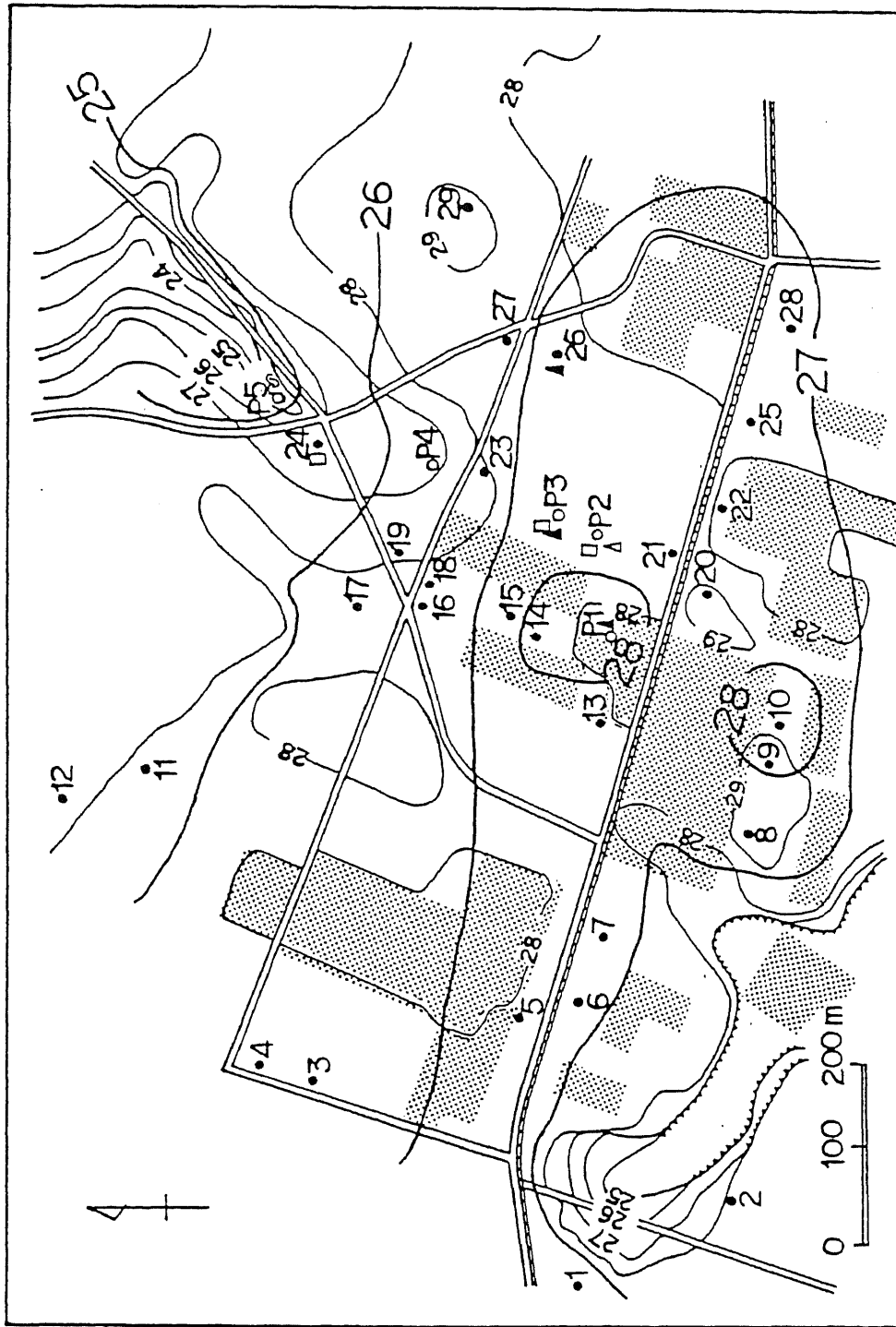
during this period. Because of no irrigation and less precipitation, the water table fell down to 25.6 meters in height at the recharge area and 23.3 meters at the discharge area.

### 3.1.2 Groundwater flow during irrigation period

Figure 9 shows the water table contour map during the irrigation period (May 31, 1985). The pattern of groundwater flow was controlled by the irrigation water, and coincided with the distribution pattern of paddy field. In Figure 10, equipotential lines were also drawn along the B-C cross section. As described above, groundwater flowed horizontally towards the valley in upper aquifer, because hydraulic conductivity of the clay layer in Narita Formation is very small compared with other layers. However, comparing with the nonirrigation period, more water in upper aquifer leaked down to the sand layer in Narita Formation, especially at recharge area. At the valley, the potential of groundwater was so high that some part of groundwater flowed out as spring water.

Because of irrigation activities, the water table rose to 28 meters in height in the recharge area and 24.7 meters in the discharge area.

By comparing the distribution of equipotential lines during the irrigation period with that of the nonirrigation period, it was found that the rising of water table in the recharge area was the largest, and decreased downstream.



- ▲ Soil water sampler O Piezometer
- △ Rain gauge
- Water table recorder
- Well
- ∩ Spring
- ▨ Paddy field
- ~25~ Water table (m)
- ~27~ Altitude (m)

Figure 9 Contour map of water table during irrigation period (May 31, 1985).

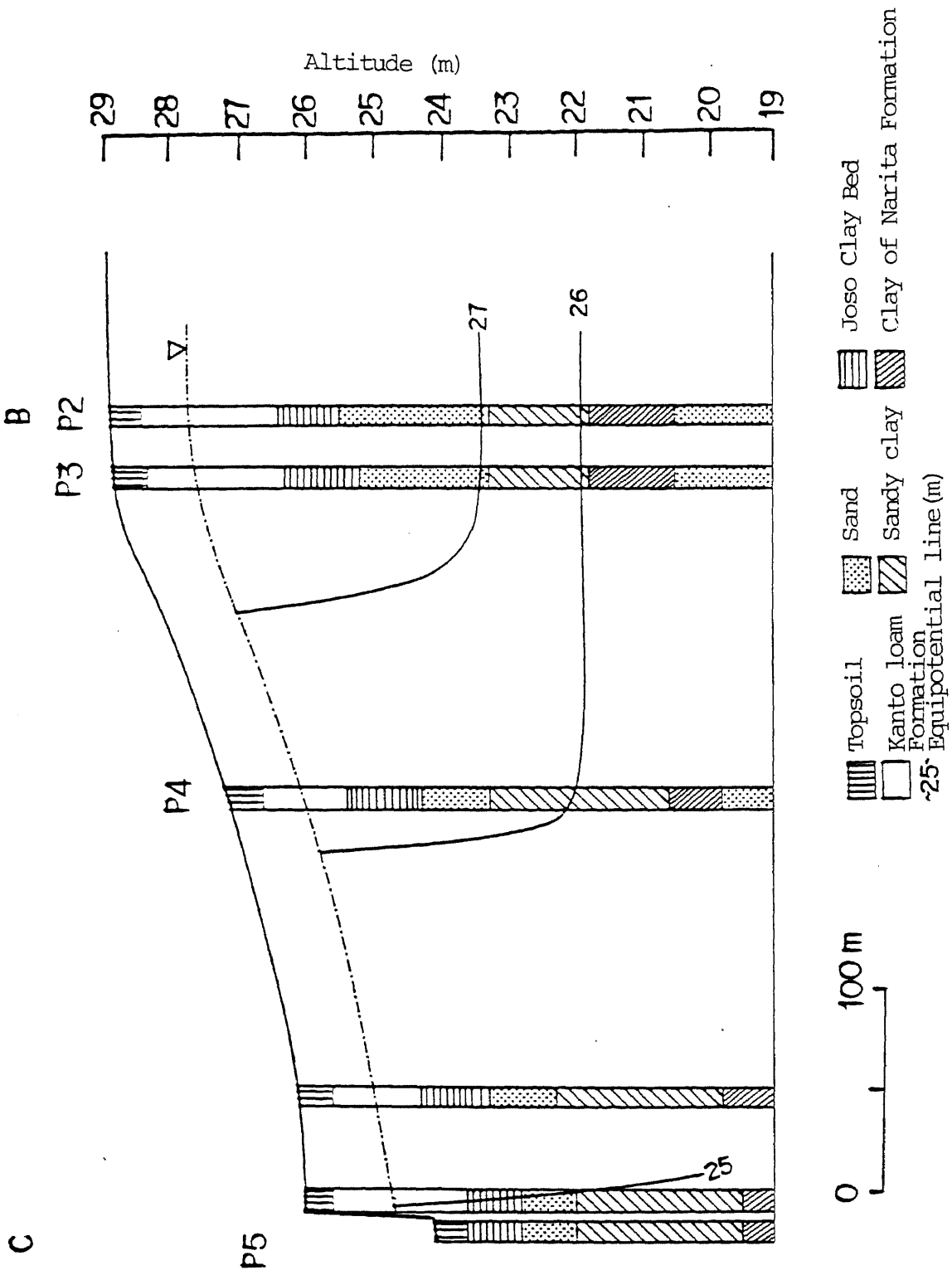


Figure 10 Distribution of equipotential lines before a heavy rain during irrigation period (May 31, 1985).

Therefore, it can be said that the irrigation water is the greatest recharge source in the study area.

3.1.3 Response of hydraulic heads to rainfall in different aquifers and different periods.

As described in section 2.1.2, the upper and lower aquifers are divided by the clay layer in Narita Formation. So the responses of the hydraulic head in these aquifers to the rainfall and irrigation are different.

At the beginning of irrigation period, when the irrigation water had been put into paddy fields, the hydraulic head increased rapidly. The variations of hydraulic heads in the piezometers in the upper aquifer were the same. However, the variations of hydraulic heads in clay layer and the lower aquifers were too small, therefore hydraulic head differences between the upper aquifer and lower aquifer became large. About one month later, the hydraulic heads in the clay layer of Narita Formation and the lower aquifer increased, whereas the large hydraulic head difference between the upper aquifer and lower aquifer remained. During the nonirrigation period, the hydraulic heads in piezometers in the study area decreased. It was found that the decrease rate of hydraulic head in the upper aquifer was larger than that in the lower aquifer.

On the other hand, the response of water table to rainfall during irrigation period was more rapidly than of during nonirrigation period. As reported by Tang, Tase,

Shindou, Tanaka and Kurata (1987), there existed a converging zero flux plane for soil water in the unsaturated zone, thus the rapid response of water level to the rainfall during irrigation period was caused by transmitting pressure from paddy fields. However, during the nonirrigation period, the response of water level to the rainfall was slow, because there was no transmitting pressure from paddy field in the study area.

#### 3.1.4 Seasonal variation of groundwater flow.

Figure 8 presents the typical distribution of equipotential line during nonirrigation period, whereas Figure 10 presents the typical distribution of equipotential line during irrigation period, and Figure 11 presents the typical distribution of equipotential line after a heavy rain (over 50 mm/day) during the irrigation period. Comparing with these figures, it was found that the irrigation activities caused the variation of whole groundwater flow system, and the precipitation caused the local groundwater flow in the valley (discharge area) during the irrigation period.

Figure 12 shows variations of hydraulic head in piezometers along the B-C section from April, 1985 to June, 1987. The recharge pattern in the study area was very different in irrigation period and the nonirrigation period. As a whole, the hydraulic heads remained high during the irrigation period and low during nonirrigation period. There

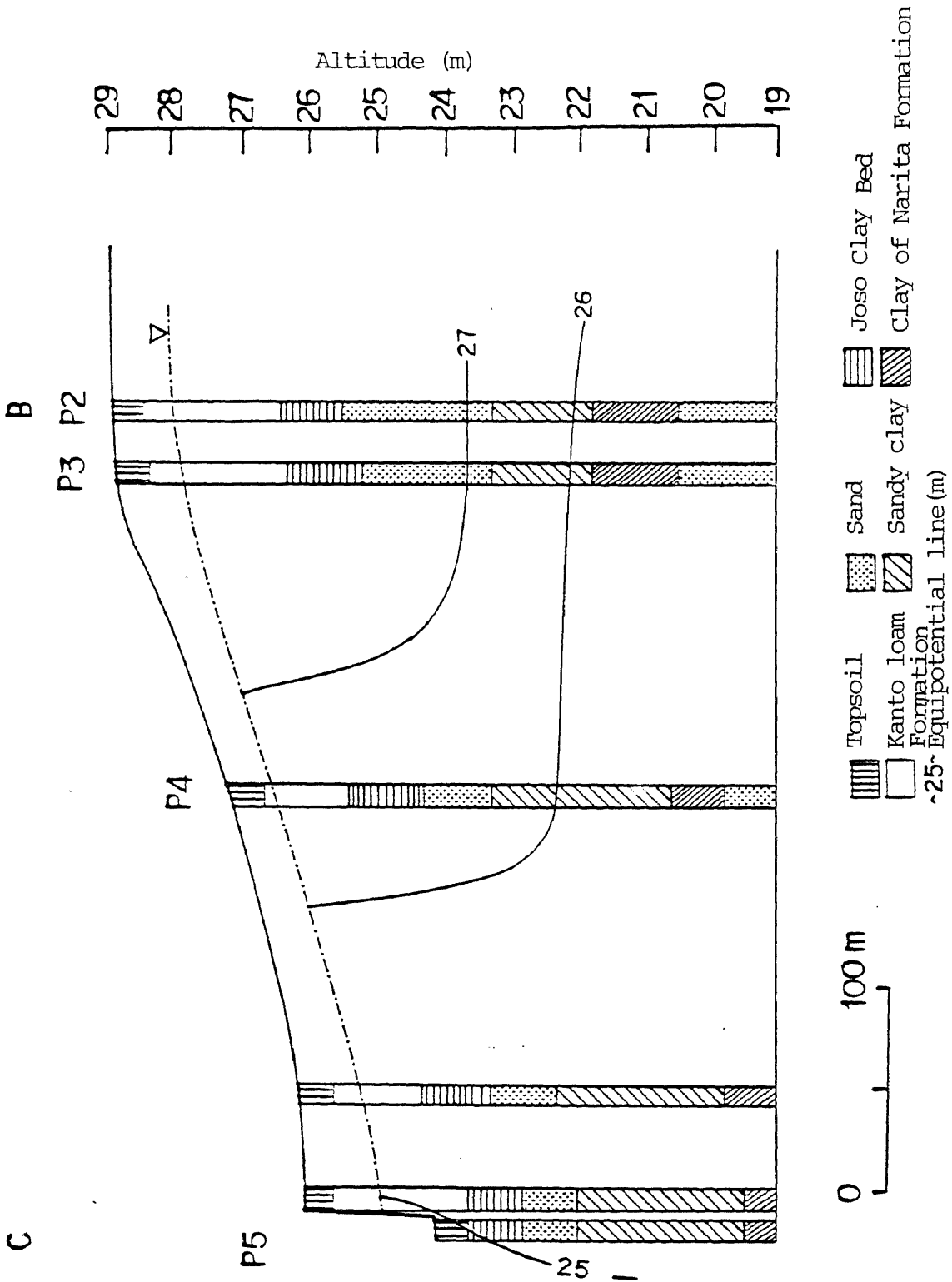


Figure 11 Distribution of equipotential lines after a heavy rain during irrigation period (Aug.13, 1985).



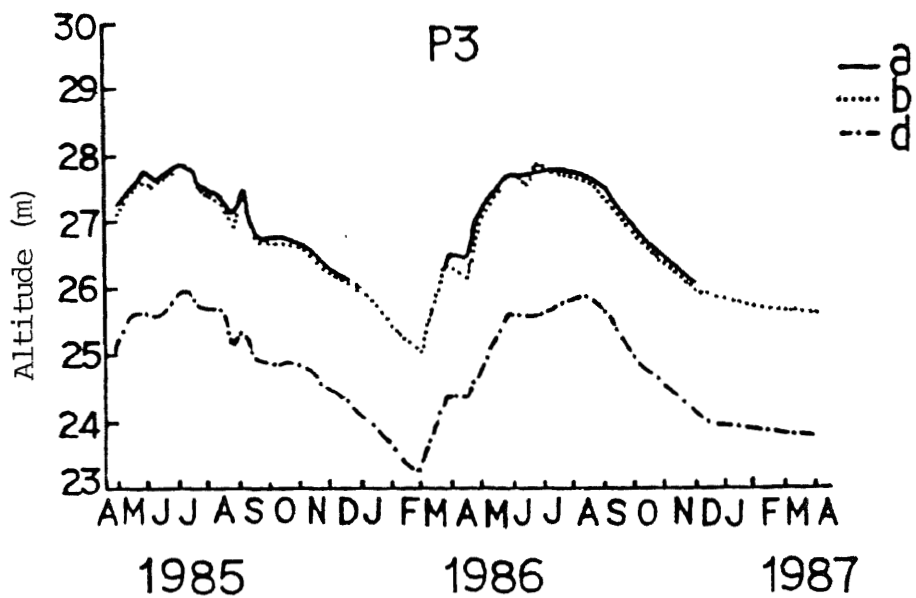
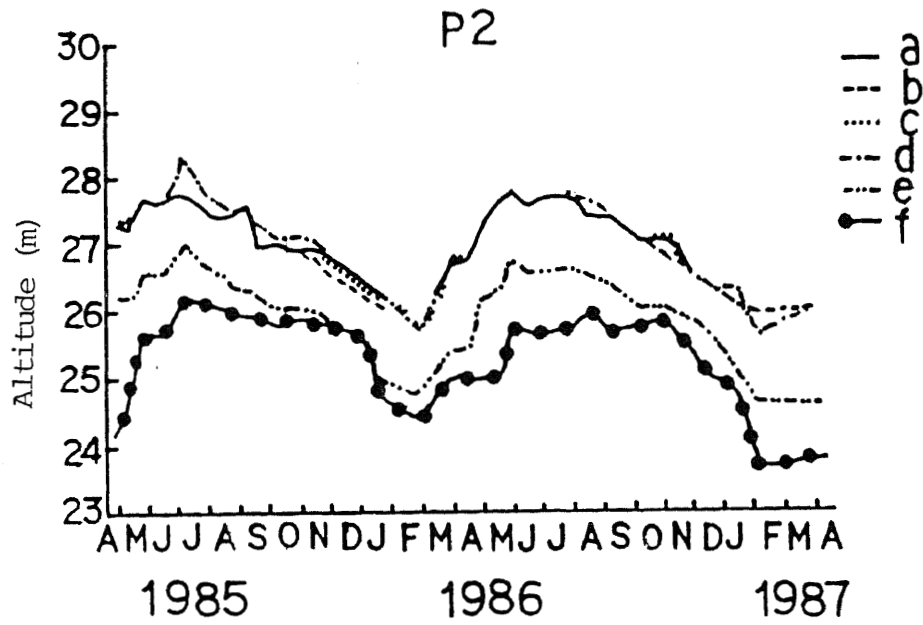


Figure 12-1 Variation of hydraulic head in piezometers P2 and P3 during April, 1985 to April, 1987

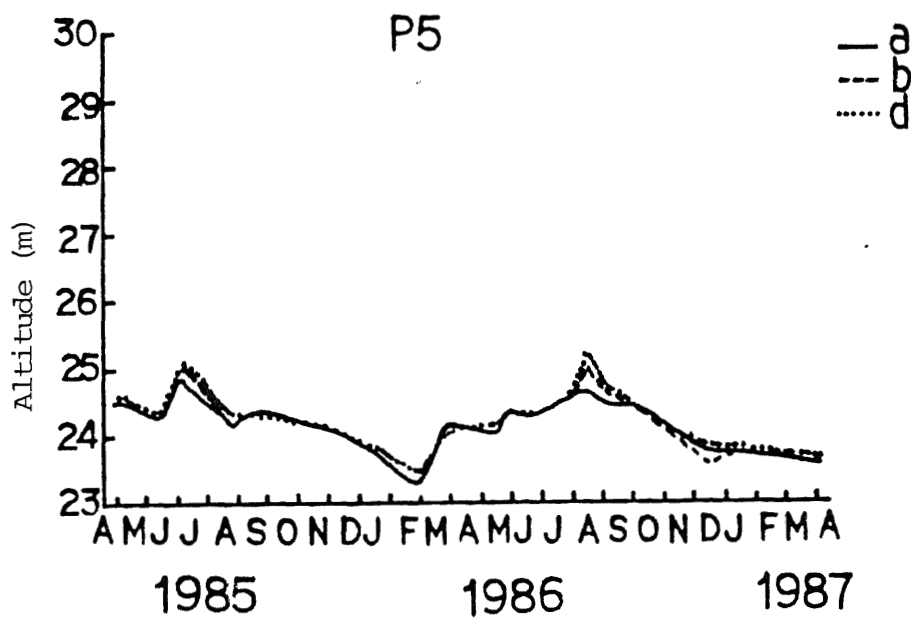
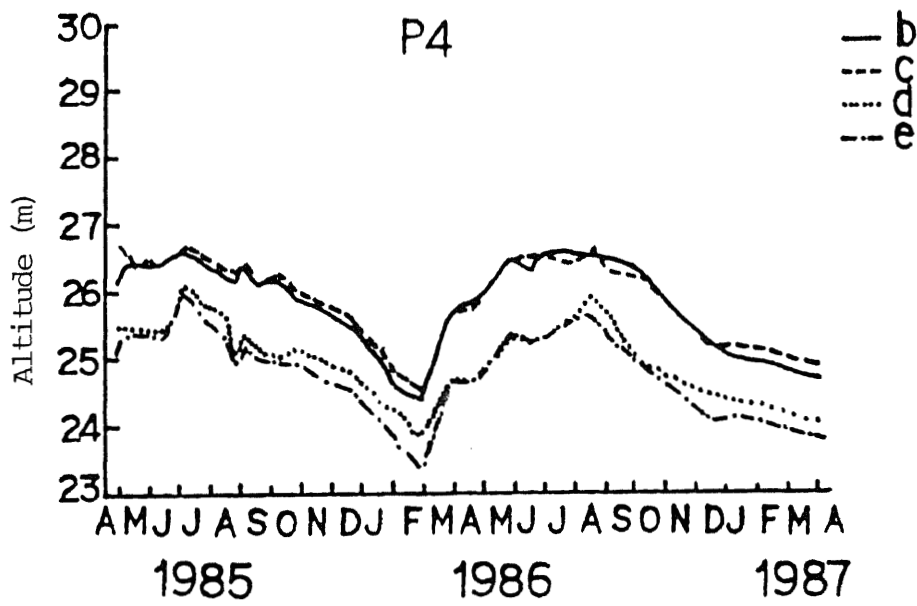


Figure 12-2 Variation of hydraulic head in piezometers P4 and P5 during April, 1985 to April, 1987.

existed a one-year period cycle for the groundwater flow. The differences between the hydraulic heads in the irrigation period and that in the nonirrigation period were about 2.5-3 meters in the upper aquifer and 1.5-2.5 meters in the lower aquifer. The difference between the upper aquifer and lower aquifer also varied in space and time. In general, the difference during irrigation period was larger than that of nonirrigation period, especially in recharge area. On the other hand, the differences in each sub-area were as follows: about 2 meters in recharge area, about 1 meter in transmitting area and a few centimeters in discharge area. In other words, the vertical flux of groundwater was the greatest in recharge area, getting less in transmitting area and the least in discharge area. After a heavy rain during Bai-u season or typhoon season, however, the distribution of hydraulic heads in valley (P5) shows an occurrence of the upward flux in the lower aquifer. Therefore, the spring water was recharged mainly by upper aquifer before a heavy rainfall, and only part of spring water was supplied from lower aquifer after the rainfall.

### 3.2 Soil water movement

Figure 13 shows the mean profile of hydraulic potential during irrigation period and nonirrigation period in No.26. It can be said that the soil water flux in unsaturated zone is upward during irrigation period, and downward during

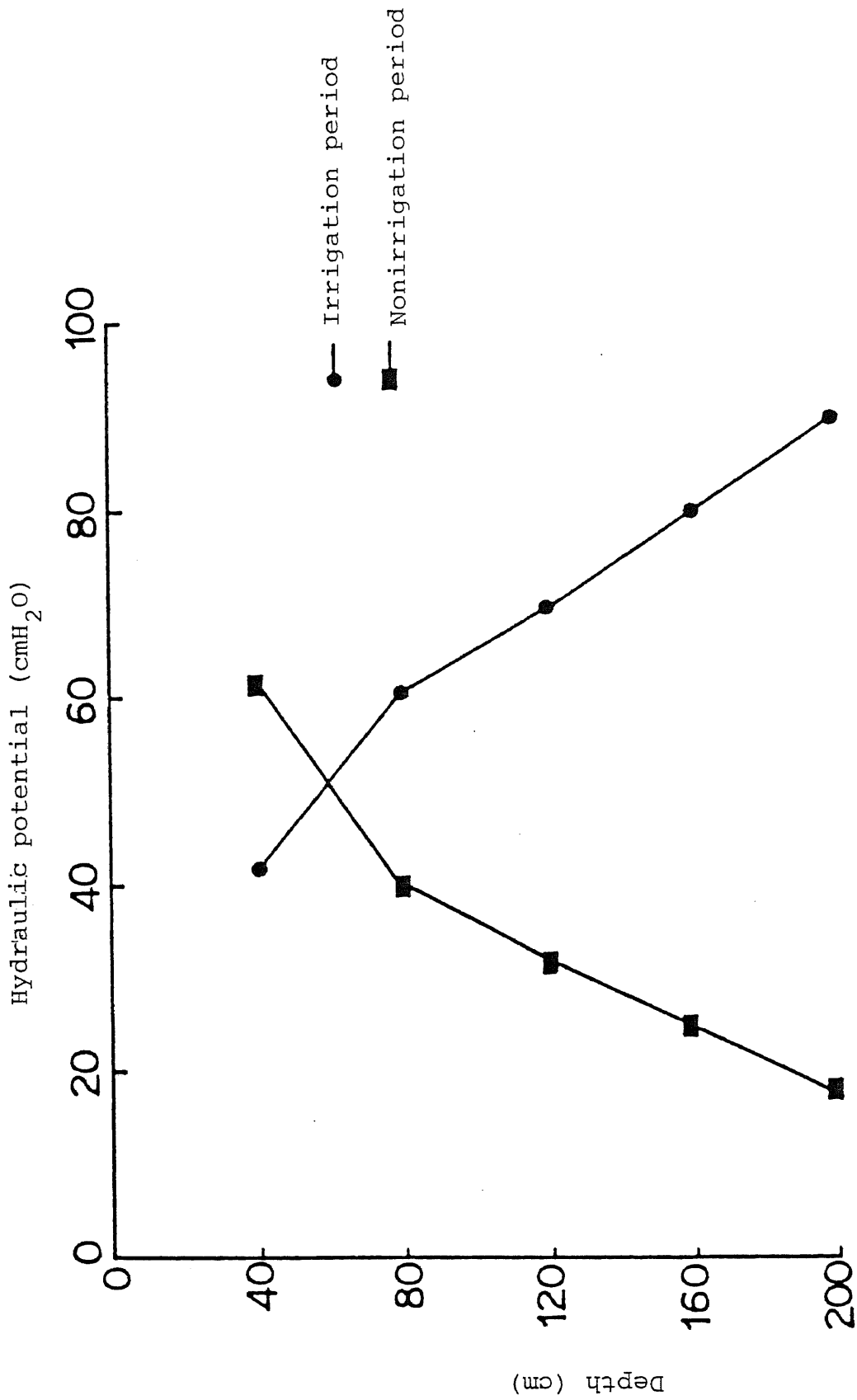


Figure 13 Mean profile of hydraulic potential during irrigation period and nonirrigation period in No.26.

nonirrigation period. This means that it would take a long time for the water in unsaturated zone to move into groundwater. Permitted that the average precipitation be 1191 mm per year, the half of which would be lost by evapotranspiration and no runoff occurs, so it would take more than 2 or 3 years for the rain water infiltrating into groundwater by water balance method.

Tang, Tase, Shindou, Tanaka and Kurata (1987) observed the behavior of soil water in a crop field (No.26), which was affected by irrigation to surrounded paddy fields in the study area. It was found that the behavior of soil water in a crop field near paddy fields is significantly affected by fluctuation of water table, rainfall, and evaporation. The flux of soil water is generally downward in surface zone and upward in and above capillary zone and convergent zero flux plane is formed in and after rainfall during the irrigation period. But during the nonirrigation period, the convergent zero flux plane disappears.

### 3.3 Estimation of groundwater flow system

Figure 14 shows a schematic diagram of subsurface water system in the study area. According to the results described in section 3.1, the groundwater in upper aquifer is mainly supplied by the irrigation water. The groundwater in the lower aquifer is only supplied by the upper aquifer, since

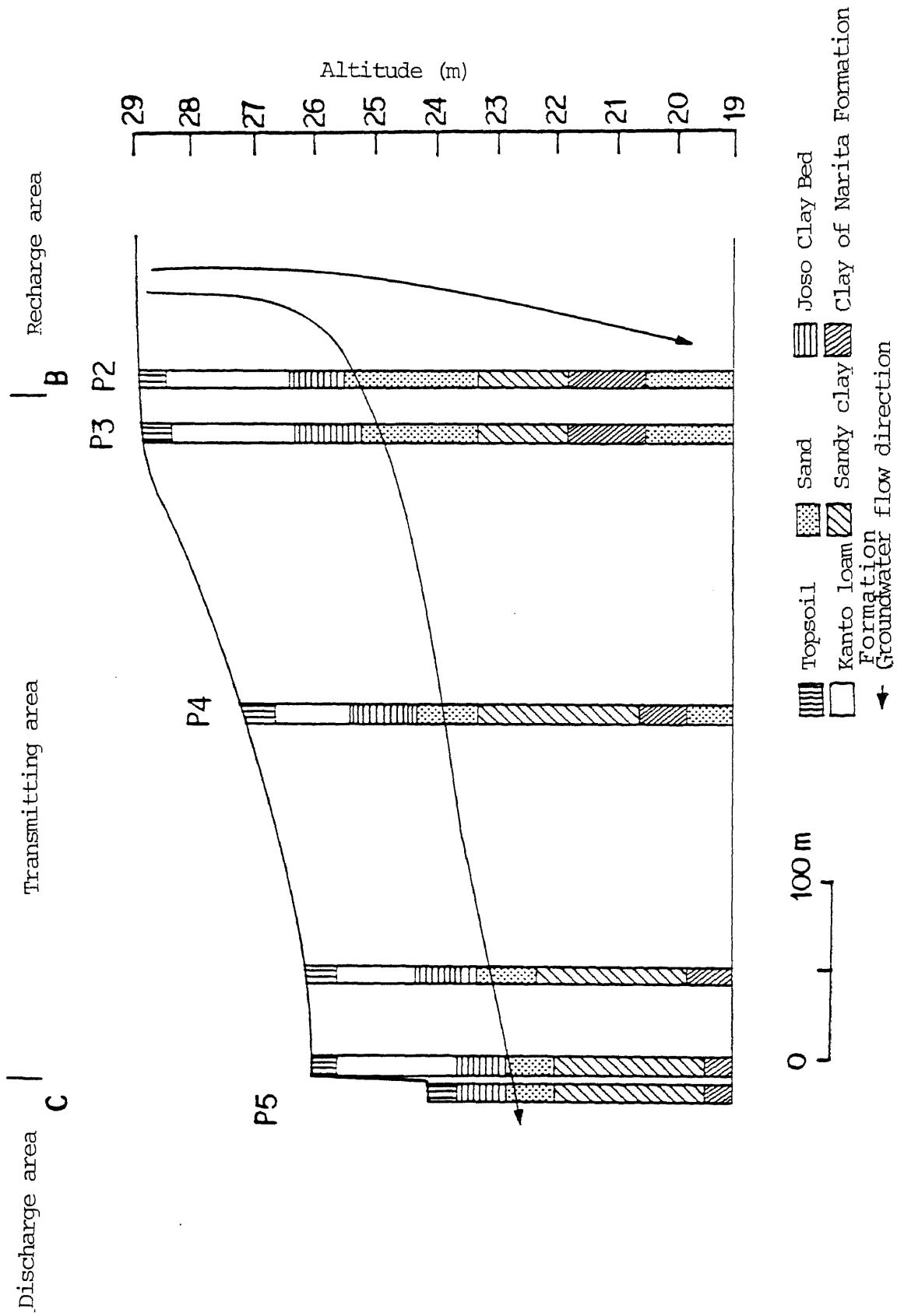


Figure 14 Schematic diagram of groundwater flow system in the study area.

there is a high hydraulic head difference between these aquifers through the year. However, after a heavy rain in Bai-u season and typhoon season, there exists a flux from the lower aquifer to upper aquifer in valley, considering distribution of the hydraulic heads.

On the other hand, Bae and Kayane (1987) showed that groundwater age in lower aquifer of the study area is about 7 or 10 years. The groundwater in upper aquifer flows faster than that in the lower aquifer. It can be considered that the upper aquifer forms a local groundwater flow system and the lower aquifer belongs to a larger groundwater flow system in the Dejima upland.

#### IV SUBSURFACE WATER QUALITY

##### 4.1 Characteristics of water quality in irrigation water and precipitation

The irrigation water was carried from Lake Kasumigaura into the study area for paddy cultivation from April to September every year. As a whole, the irrigation water quality was sodium-chloride type. The analyses of irrigation water are shown in Table 3. The characteristics of irrigation water could be summarized as follows:

- (1) The dominated cation was sodium and the dominated anions were chloride and sulfate.
- (2) The concentration of silica was less than 2 mg/l.

Another major natural source of solutes to groundwater is rain falling in the study area. The average chemical composition of precipitation shown in Table 3 was derived from 23 reliable analyses of rain water collected by rain collector at P3 over the research period from April, 1985 to June, 1987. The following conclusions could be drawn:

- (1) The chemical composition of all rainfall samples was uniform.
- (2) The water quality variation in precipitation was small. The concentrations of each major elements were less than 2 mg/l.
- (3) Comparing with the chemical composition in the irrigation water, precipitation contributed little chemicals for the groundwater system in the study area.



Table 3. Average concentrations of major ions in precipitation and irrigation water during April, 1985 to June, 1987 (mg/l).

	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SiO <sub>2</sub>
Precipitation	2.55 (0.74)	0.6 (0.74)	0.8 (0.4)	1.7 (0.34)	1.63 (1.73)	1.38 (0.53)	0.48 (0.18)	0.45 (0.34)
Irrigation water	34.13 (7.64)	3.53 (3.82)	36.13 (3.87)	23.62 (5.12)	18.55 (8.77)	16.65 (2.62)	5.7 (1.48)	2.58 (1.99)

( ): the standard deviation

## 4.2 Characteristics of groundwater quality

### 4.2.1 The Seasonal variation of groundwater quality

#### (1) Electrical conductivity and water temperature

During the irrigation period, electrical conductivity and temperature of the groundwater were high along the irrigation channel and around the paddy fields. In transmitting area and discharge area, the temperature and electrical conductivity were lower than that in recharge area.

On the other hand, the distribution of groundwater temperature and electrical conductivity during the nonirrigation period were very different from that of the irrigation period.

Figures 15 and 16 show seasonal variation of groundwater temperature and electrical conductivity in the aquifers in P2, respectively.

From Figure 15, it can be found that the groundwater temperature in the upper aquifer varied greatly, especially during irrigation period. During this period, the groundwater temperature in Kanto loam Formation varied from 12 °C to 18.2° C. Some time-lags in the groundwater temperature were found in the other parts of the aquifer, where the variations of groundwater temperature were also smaller than that in Kanto loam Formation.

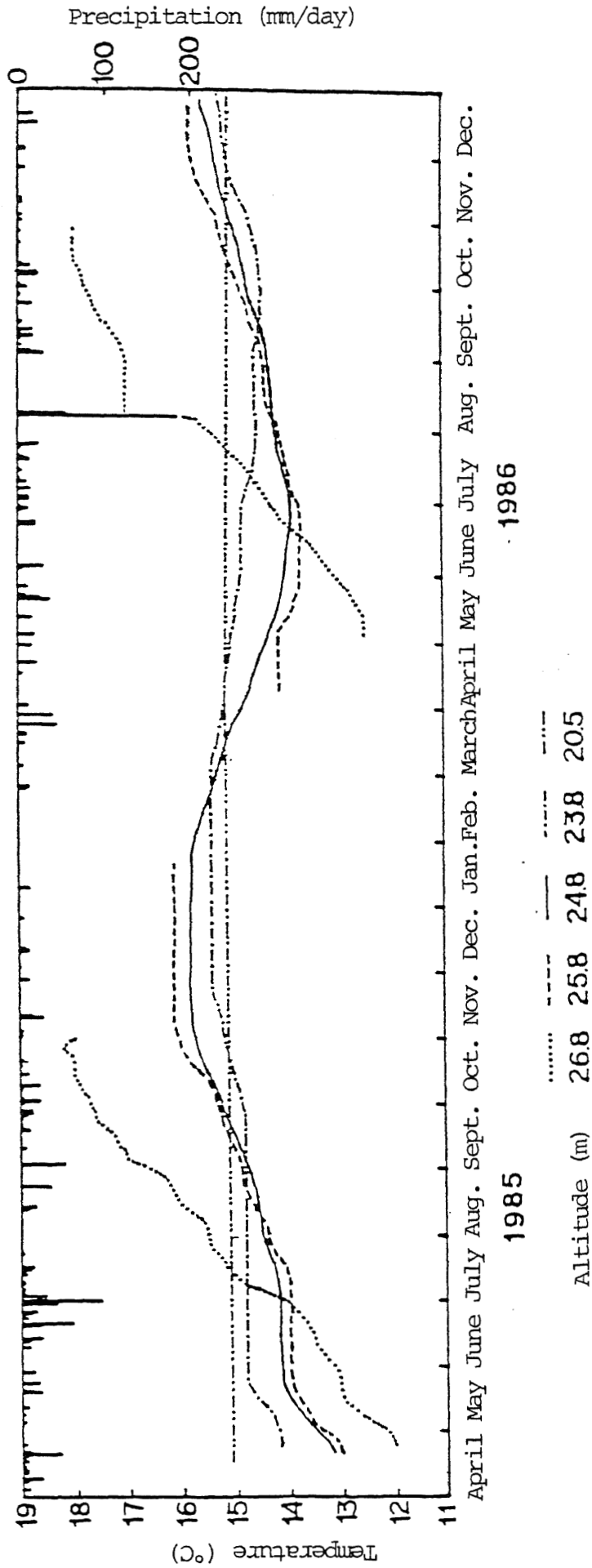


Figure 15 Variations of groundwater temperature in piezometers (P2).

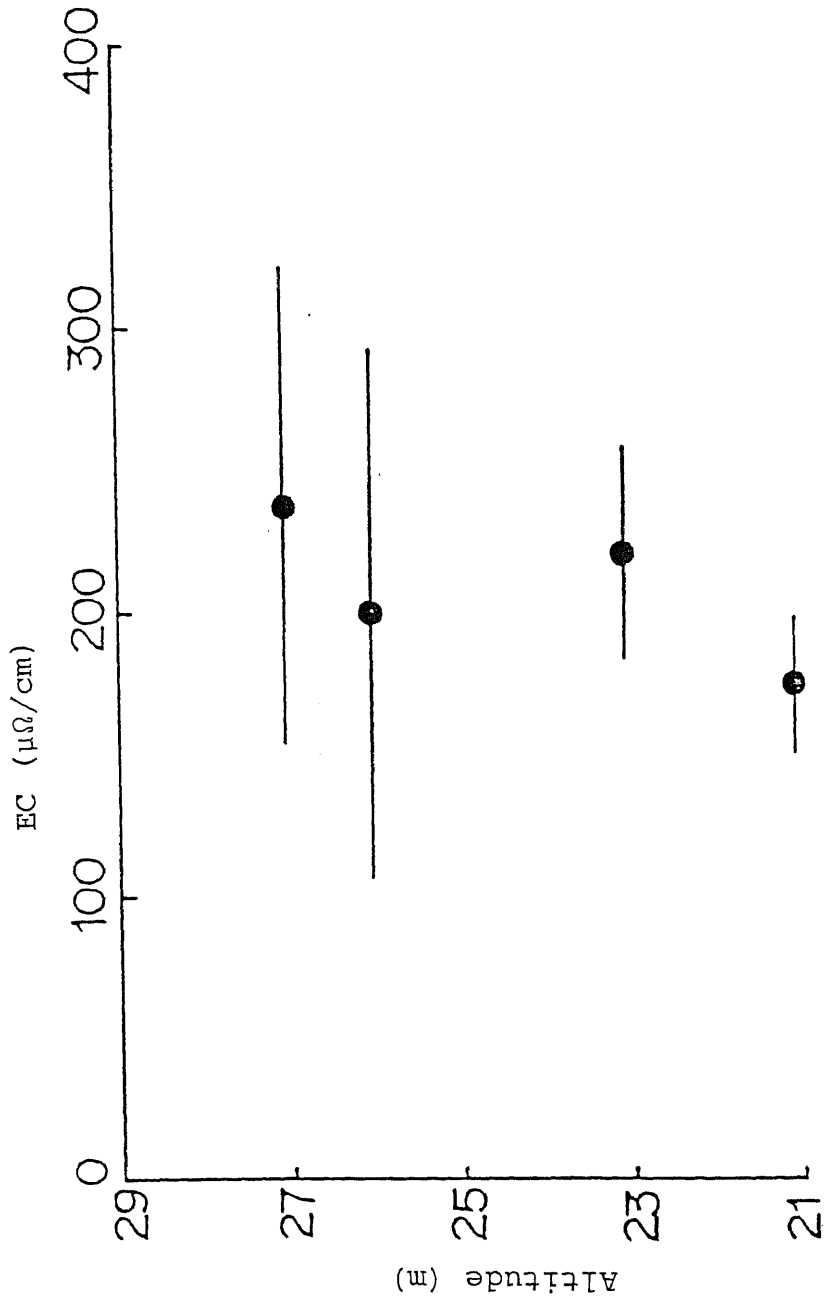


Figure 16 Mean profile of electrical conductivity in piezometers (P2).

In the upper aquifer, electrical conductivity of groundwater was the highest in the Kanto loam Formation, and decreased to  $200 \mu\Omega / \text{cm}$  in the sand layer of Ryugasaki Formation.

As a whole, both of groundwater temperature and electrical conductivity in the upper aquifer had a sharp variation at beginning of irrigation period. This variation is considered as the result of irrigation activity. At the beginning of irrigation period, the groundwater temperature is lower than irrigation water temperature. It can be considered that the water stored in soil during winter is pushed down into groundwater by the water recharged from paddy fields.

On the other hand, in the lower aquifer, both of groundwater temperature and electrical conductivity had lower values and changed little through the year.

## (2) Cations and Anions

Soils can act as a buffer to reduce the range to which the major ions vary in the groundwater. It was found that the concentration of major ions varied greatly in the recharge area, and less in other area.

In the upper aquifer, concentration of sodium was about 30 mg/l in the irrigation period and about 20 mg/l in the nonirrigation period. The concentrations of calcium and magnesium were high in irrigation period and low in the nonirrigation period. The seasonal variations of cations concentration were greater in the upper aquifer than that in

the lower aquifer. Concentration of silica in groundwater varied little in upper and lower aquifers.

The concentration of sulfate acid was up to 40 mg/l only in the upper aquifer of the recharge area, but was less than 10 mg/l in the upper aquifer of other area and lower aquifer.

The high concentration of nitrate was found only in the upper aquifer effected by livestock activities. In the lower aquifer, it was less than 5mg/l in concentration.

Figure 17 shows that chloride ion had a high concentration zone in and above the clay layer of Narita Formation where its concentration was more than 50 mg/l.

#### 4.2.2 Vertical distribution of major elements

Figure 18 shows the vertical distribution of chloride, silica, calcium and sodium ions in groundwater (P2).

It was found that the concentration of chloride had two peaks in altitude of 27 meters and 23 meters. The former was located at boundary between Kanto loam Formation and Joso Clay Bed, and the latter between sand layer of Ryugasaki Formation and clay of Narita Formation.

Concentration of silica increased with depth. Below the altitude 23 meters (in Narita Formation), the concentration of silica raised up to above 20 mg/l.

The vertical distribution of calcium and sodium ions showed a symmetrical relationship to each other. The changing points located exactly at the clay layer in Narita

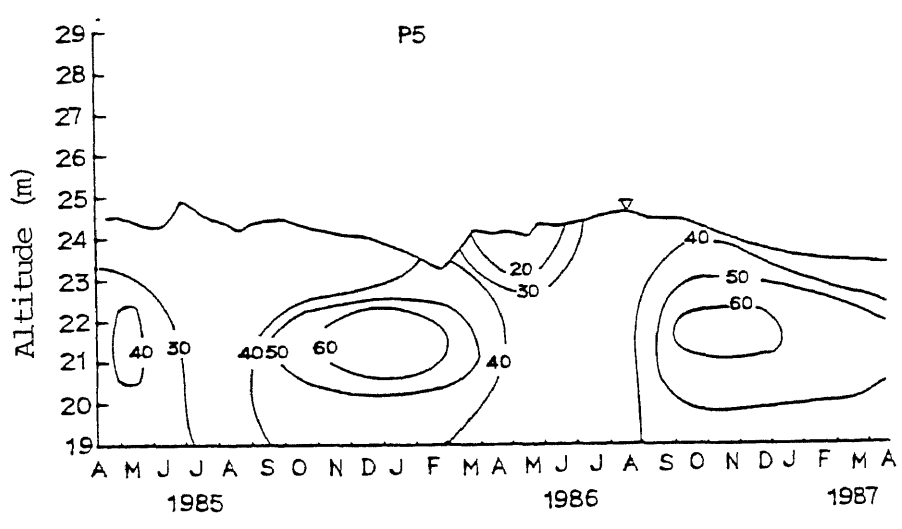
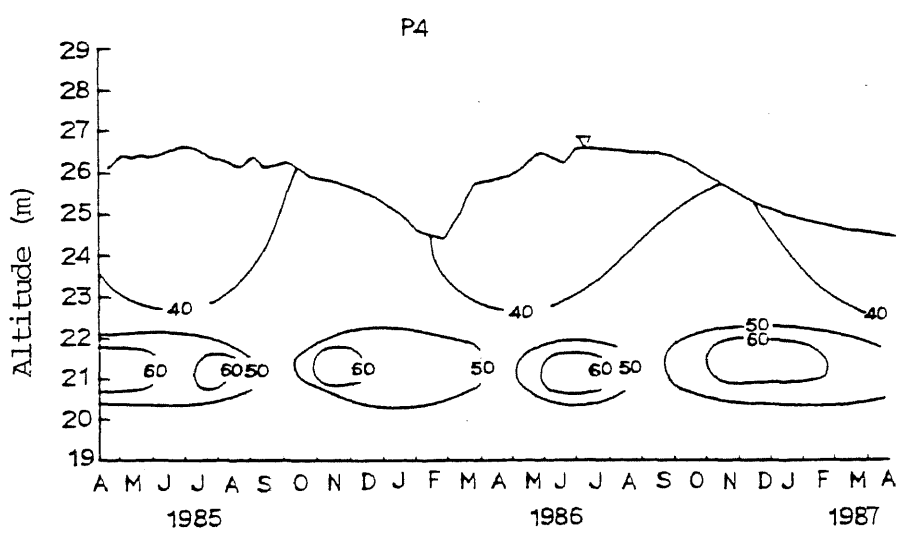
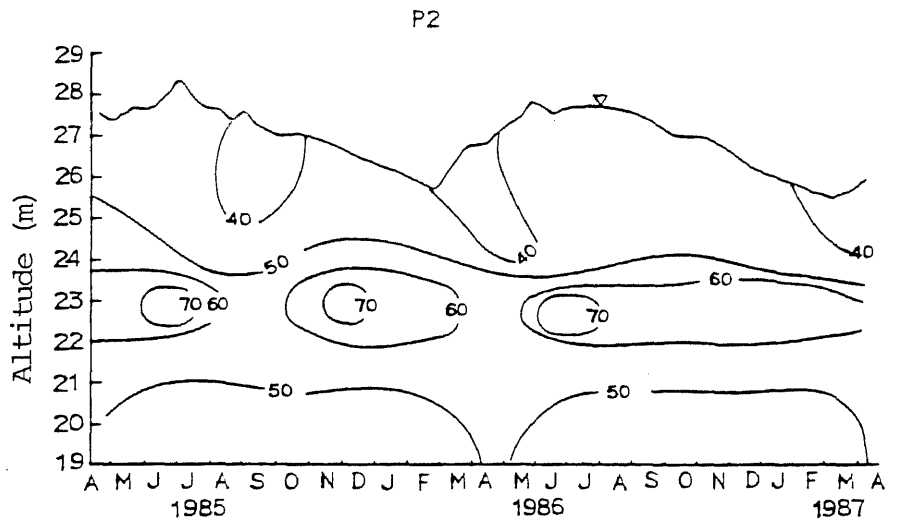


Figure 17 Variation of  $\text{Cl}^-$  concentration in typical piezometers.

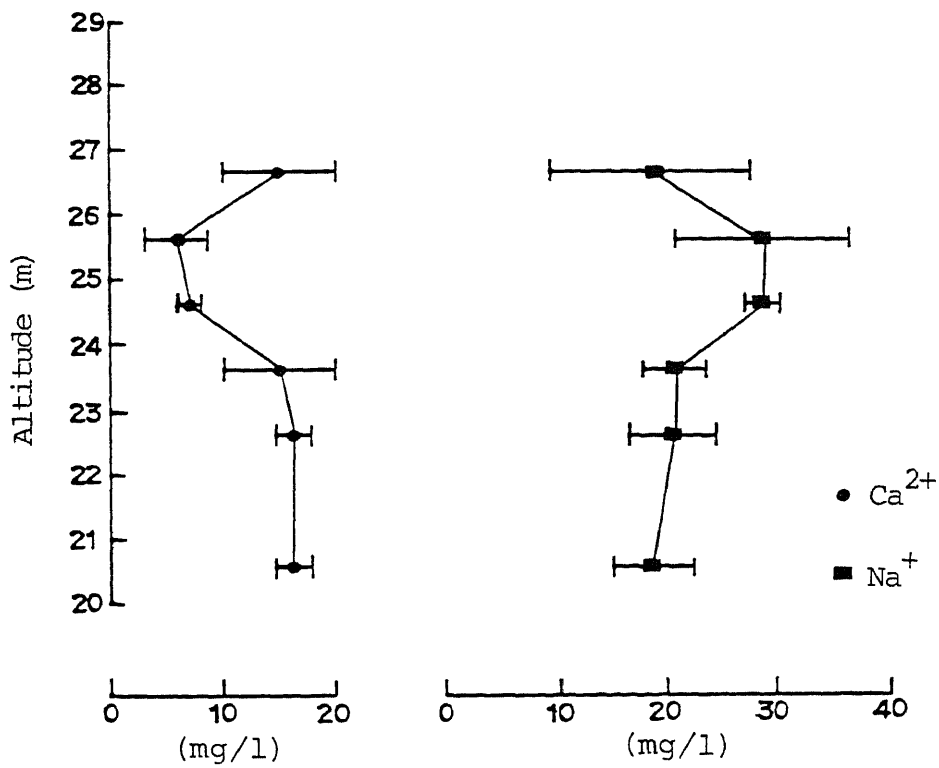
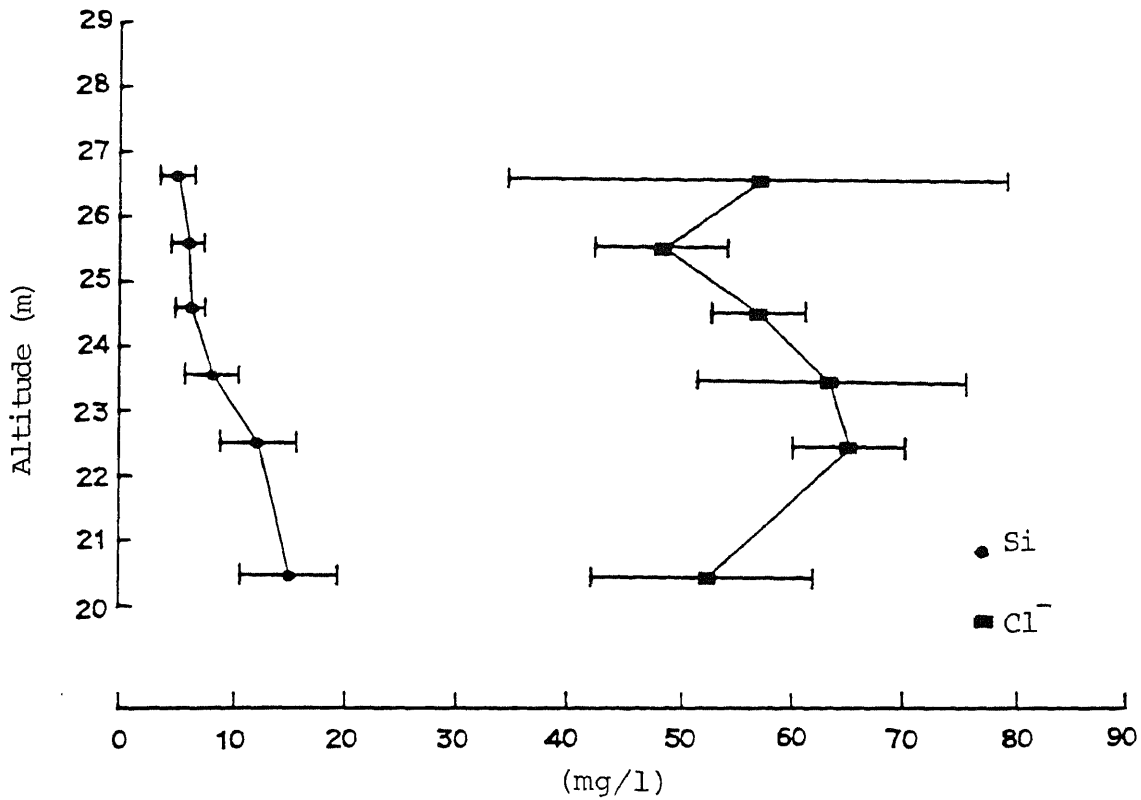


Figure 18 Distribution of SiO<sub>2</sub>, Cl<sup>-</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> in piezometers (P2).



Formation where the high concentration of chloride ion existed.

It was apparent that the groundwater quality changed greatly across the clay layer.

#### 4.2.3 The three-dimensional distribution of groundwater quality

Figure 19 shows the groundwater quality pattern diagram in the B-C section. Considering the characteristics of groundwater quality described above, the distribution of groundwater quality in three dimensional space can be classified as follows.

(1) The first group -- water with  $\text{Na}^+\text{K}^+\text{Cl}^-\text{NO}_3^-$  type in Kanto loam Formation: It was directly effected by the precipitation and irrigation water.

(2) The second group -- water with  $\text{Na}^+\text{K}^+\text{Cl}^-$  type in Joso Clay Bed: It was the first clay that the groundwater from recharge area flowed through.

(3) The third group -- water with  $\text{Na}^+\text{Ca}^{2+}\text{Cl}^-$  type in sand layer in Ryugasaki Formation: The standard deviations of major ions' concentration were the least compared with that in other layers, which means that the groundwater quality compositions in that layer were stable;

(4) The fourth group -- water with  $\text{Ca}^{2+}\text{Cl}^-$  type in the boundary zone between the sand layer of Ryugasaki Formation and the clay layer of Narita Formation: Groundwater quality compositions varied greatly; and

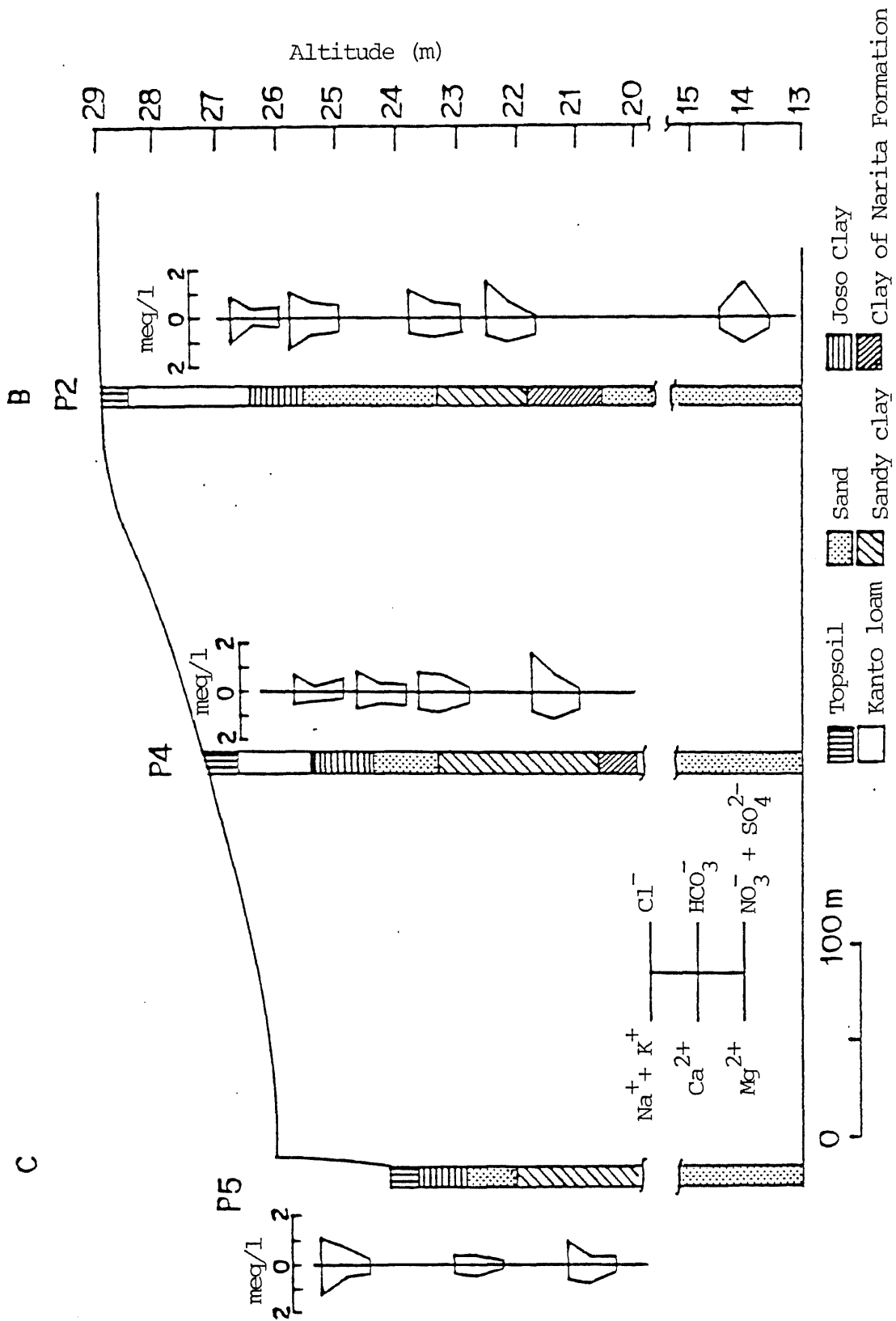


Figure 19 Groundwater quality pattern diagrams in vertical section (B-C).

(5) The fifth group -- water with  $\text{Ca}^{2+}+\text{HCO}_3^-$  type in Narita Formation: There, groundwater quality compositions varied little.

On the other hand, from recharge area to discharge area, the chemical composition of groundwaters in the same aquifer varied little, but very different from aquifers. In other words, the groundwater quality are distributed in stratification along the aquifers.

Opposite to the water in the lower aquifer where the water quality had the same characteristics everywhere, the water in the upper aquifer was different in water quality due to the influence of land use types.

In most parts of the study area, the concentrations of the dissolved solutes were similar to those of the irrigation water with  $\text{Na}^++\text{Cl}^-+\text{SO}_4^{2-}$  type. The concentrations of major ions did not show any significant trends with increased distance from the irrigation channel.

Livestock greatly effected in the compositions of nearby groundwater in which high concentrations of  $\text{NO}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  were found. In general, the groundwater quality was  $\text{Na}^++\text{Cl}^-+\text{HNO}_3^-$  type.

In the area far from the recharge area and without the influences of livestock activities, the water quality remained  $\text{Na}^++\text{Cl}^-+\text{NO}_3^-+\text{SO}_4^{2-}$  type, but the concentration of each ion was not more than 10 mg/l.

The concentration variations of major elements in piezometers from April, 1985 to June, 1987 were shown in Table 4.

Table 4. Average concentration of major ions in piezometers during April, 1985 to June, 1987.

Piezo meter	Altitude (m)	Cl <sup>-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	HCO <sub>3</sub> <sup>-</sup> (mg/l)	Ca <sub>2</sub> <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Na <sup>+</sup> (mg/l)	SiO <sub>2</sub> (mg/l)
P2	26.8	46.75 (25.5)	41.26 (42.7)	5.43 (3.94)	48.19 (15.1)	13.77 (5.48)	30.81 (18.9)	9.39 (4.87)	15.72 (8.14)	4.87 (1.85)
P2	25.8	47.09 (7.19)	14.61 (22.8)	3.7 (2.68)	0.32 (0.4)	6.2 (1.99)	4.81 (4.81)	4.25 (1.56)	28.09 (7.55)	6.53 (5.18)
P2	24.8	49.34 (12.1)	2.18 (6.23)	1.19 (1.21)	27.45 (16.5)	6.8 (1.23)	4.66 (3.66)	4.86 (0.99)	24.88 (5.19)	5.92 (1.48)
P2	23.8	66.18 (7.87)	1.66 (4.78)	1.95 (3.01)	39.04 (22.6)	17.58 (2.13)	5.23 (4.26)	10.04 (1.23)	19.01 (2.94)	8.98 (1.58)
P2	22.8	61.91 (9.77)	0.82 (1.56)	2.07 (3.45)	43.31 (21.4)	15.88 (2.77)	5.79 (4.37)	8.73 (1.55)	20.9 (4.45)	10.73 (3.24)
P2	20.8	48.51 (8.24)	0.33 (0.4)	3.78 (9.9)	50.02 (19.5)	16.02 (1.64)	4.88 (3.99)	8.56 (1.23)	16.51 (3.91)	15.47 (2.54)
P2	13.8	17.45 (4.07)	0.03 (0.04)	5.46 (3.59)	100.7 (4.88)	23.34 (1.2)	5.97 (2.47)	6.74 (0.36)	11.27 (0.56)	19.49 (0.65)
P3	25.5	47.14 (14.2)	41.19 (24.1)	2.87 (0.96)	25.01 (18.9)	12.74 (3.78)	8.94 (6.08)	7.0 (2.79)	24.38 (6.67)	5.08 (1.58)
P3	23.5	15.21 (13.0)	30.98 (9.04)	2.78 (1.16)	32.33 (15.3)	16.63 (3.02)	8.33 (5.23)	9.48 (2.64)	13.18 (3.68)	12.06 (9.87)
P3	22.0	52.91 (8.61)	6.22 (2.65)	1.89 (1.03)	43.92 (15.9)	18.2 (2.35)	12.82 (8.49)	7.79 (1.36)	11.0 (11.3)	15.5 (3.25)
P3	20.5	54.9 (2.98)	10.84 (8.63)	2.22 (0.55)	64.66 (14.6)	18.09 (0.58)	4.68 (7.30)	10.03 (0.76)	22.89 (1.22)	7.87 (0.50)
P4	25.5	35.63 (5.73)	14.08 (3.88)	2.47 (0.73)	19.52 (9.76)	9.61 (0.99)	3.5 (3.98)	5.74 (0.83)	13.02 (2.04)	7.69 (1.39)
P4	24.8	33.47 (9.19)	30.91 (9.57)	2.97 (0.84)	4.7 (15.9)	9.66 (1.57)	6.11 (6.11)	5.43 (1.51)	11.85 (3.14)	9.86 (2.41)
P4	23.5	36.0 (4.58)	14.54 (5.77)	2.22 (0.95)	37.82 (16.5)	14.21 (2.13)	5.97 (4.67)	6.12 (6.14)	12.8 (1.54)	7.7 (1.36)
P4	22.5	58.50 (7.12)	9.62 (4.05)	2.78 (0.69)	32.33 (19.5)	19.97 (2.4)	8.43 (4.95)	7.63 (1.62)	12.83 (1.3)	21.96 (3.37)
P4	20.8	60.92 (7.02)	0.37 (0.25)	4.09 (3.26)	64.05 (15.3)	27.19 (2.76)	6.45 (5.62)	8.55 (1.13)	14.68 (1.43)	20.62 (2.18)
P5	23.2	37.8 (4.55)	12.65 (2.81)	1.58 (0.62)	48.19 (13.4)	16.25 (1.87)	6.27 (4.52)	7.58 (1.15)	11.54 (0.89)	16.0 (2.08)
P5	22.0	41.67 (19.3)	4.93 (2.45)	2.44 (0.73)	14.03 (15.3)	10.37 (1.94)	11.66 (9.15)	4.51 (1.80)	8.2 (2.66)	11.5 (4.26)
P5	21.0	44.5 (15.9)	10.79 (6.74)	1.76 (0.69)	36.6 (27.5)	13.8 (2.13)	12.14 (9.69)	6.56 (0.97)	12.32 (5.4)	18.41 (1.89)
P5	20.0	30.5 (4.62)	4.66 (3.81)	2.27 (0.47)	18.3 (14.6)	8.26 (2.34)	3.42 (3.72)	4.05 (1.00)	10.51 (1.04)	18.35 (2.58)

( ): the standard deviation

Sodium concentration was the highest in paddy area and the lowest in discharge area and lower aquifer.

The concentration of potassium in groundwater was less than 5 mg/l everywhere in the study area.

The concentrations of calcium and magnesium were high in the lower aquifer and low in the upper aquifer.

Silica analyses of groundwater from various aquifers in the study area have been carried out. The results indicate that the range of silica concentration is relatively narrow, between 5 and 30 mg/l  $\text{SiO}_2$ , and the majority of values were less than 10 mg/l in the upper aquifer and more than 20 mg/l in the lower aquifer. From the chemical equilibrium point of view, the range of observed silica concentrations suggests that variations of a few milligrams per liter may be regarded as importance although the significance of any variation cannot be assessed in this study. In addition, hydrogeological processes, such as groundwater mixing, leakage of groundwater between formations, may contribute to the variation of silica in the groundwater.

4.2.4 The evolution of groundwater quality explained by stability diagrams

From the hydrochemical point of view, the reaction between groundwater and rock can be monitored by the changed chemical composition of the groundwater. Recharge water is

chemically aggressive towards the silicates and this aggressiveness will decrease as the groundwater reacts with the minerals. Its process can be illustrated by stability diagrams.

The important sources of silica in the aquifer are montmorillonite and kaolin minerals. Using the reactions in Table 5 and revised thermodynamic data, stability diagrams for the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  and  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  systems have been constructed. The method of construction is given by Garrels and Christ (1965).

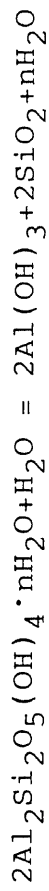
In the following example, the stability diagrams are used to indicate the change in chemical composition of the groundwaters which will control the breakdown of the silicates and in turn the level of silica released to solution.

The groundwaters have been plotted on the stability diagrams using activity ratios. The activities of the different species were calculated using the extended Debye-Huckel equation. From the plots, clear trends of the groundwater quality evolution can be deduced.

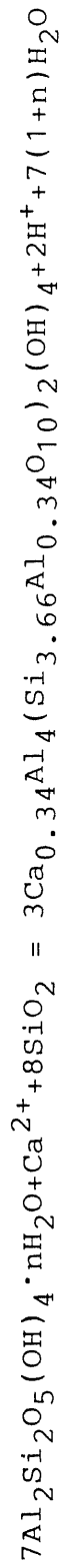
The groundwaters in the upper aquifer have been between 3-10 mg/l  $\text{SiO}_2$  and show a scattered points (Figure 20). The scattered of points may be attributed to variations in the carbonate chemistry, which commonly comes from recharge waters and can be thought to be derived predominantly from the soil zone. Comparable silica levels were measured in solutions equilibrated with soils from the discharge area.

In this sand layer of Ryugasaki Formation, silica

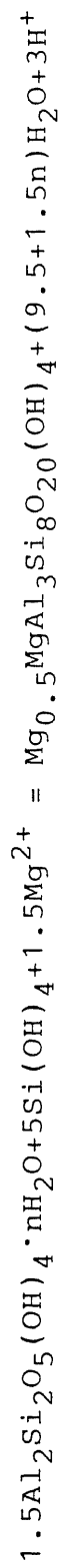
Table 5. Incongruent dissolution reactions for silicates used  
in the construction of stability diagrams



Kaolin minerals                      Gibbsite

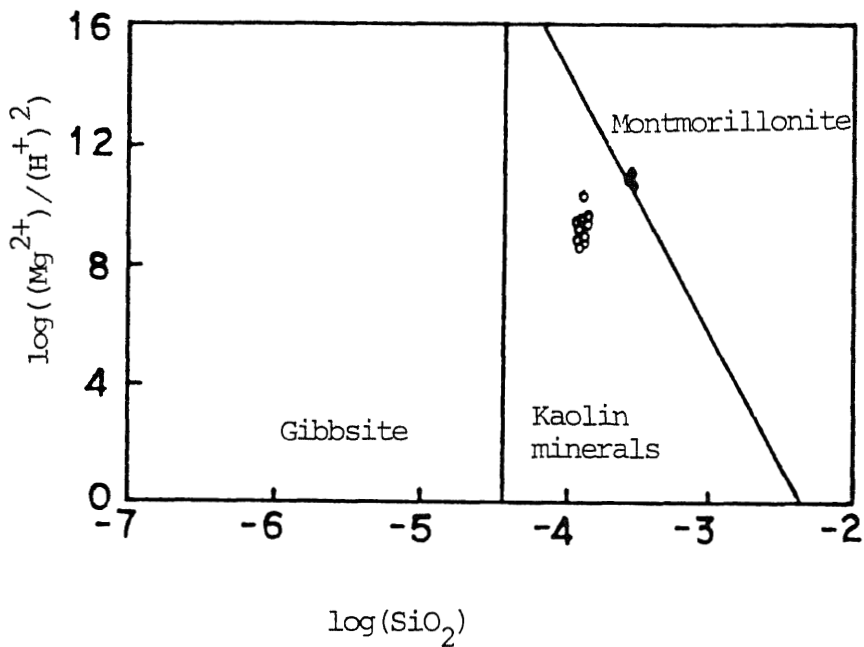
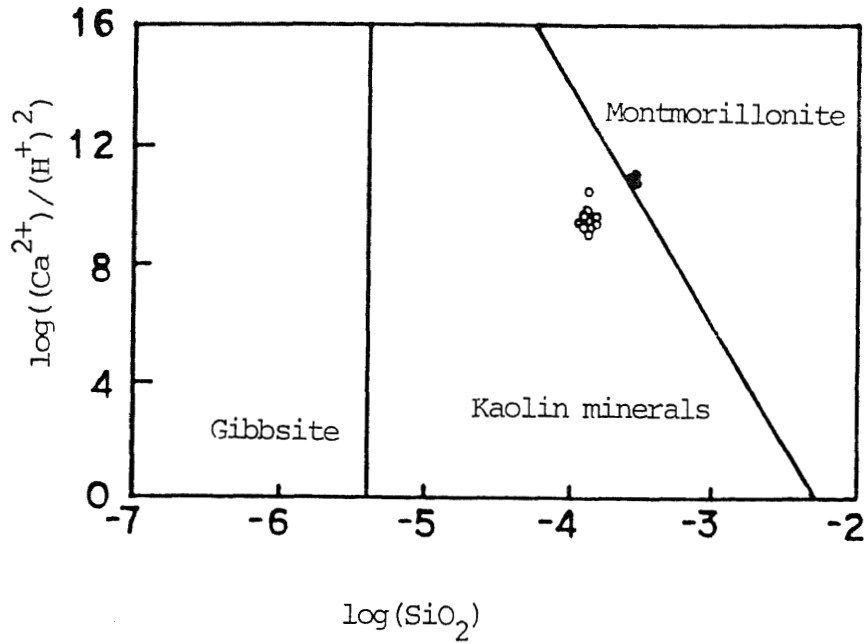


Kaolin minerals                      Ca-Montmorillonite



Kaolin minerals                      Mg-Montmorillonite

$$n = 0, 1, 2$$



- The groundwater in Narita Formation
- The groundwater in strata above Narita Formation

Figure 20 Gibbsite-Kaolin minerals-Montmorillonite stability fields expressed in term of  $\log((\text{Ca}^{2+})/(\text{H}^+)^2) - \log(\text{SiO}_2)$  and  $\log((\text{Mg}^{2+})/(\text{H}^+)^2) - \log(\text{SiO}_2)$  for groundwater in the study area.



concentration in waters shows an increase to 10 mg/l  $\text{SiO}_2$  and these groundwaters fall mostly in the kaolinite stability field. They are lying adjacent to the stability fields of the higher order silicates. This fact indicates that these waters have lost some of their chemical aggressiveness as a result of increased reaction with the silicates within the aquifer due to increased residence time. In some cases, equilibrium with the kaolin mineral phase has been established, suggesting that any further increase of silica can only come from the breakdown of montmorillonite.

Many chemical features of waters in the lower aquifer indicate that they are significantly older than that of the other groundwaters and this is confirmed by tritium date of up to 10 years (Bae and Kayane 1987).

Silica concentrations of these waters have increased value, often exceeding 20 mg/l. The majority plots fall in the stability fields of the least stable silicates (Figure 20), indicating equilibrium between these groundwater and the matrix minerals. From the chemical composition of these groundwaters, it is clear that continued reaction with the silicate minerals present in the aquifer can not occur, preventing any further increase in silica concentrations.

The development of equilibrium between the groundwater and the silicate minerals is indicated by a series of hydrochemical sections. The lines of the sections are shown in Figure 20, and the groundwaters are plotted on the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  and  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  stability diagrams.

Geochemical studies have shown that montmorillonite would be quantitatively the most important silicate in the clay of Narita Formation. The results of the present study show that the extent to which this mineral undergoes chemical reactions with the groundwater is a major control on the level of silica concentration in the groundwaters. Silica will continue to be added to solution while disequilibrium exists between the groundwater and the smectite minerals. The development of equilibrium between the groundwater in Narita Formation and silicates is favored, as the montmorillonite is most stable in environments of limited groundwater flow and breakdown by diffusion processes, which will be reduced in areas of low flow.

Solution of siliceous minerals is not thought to significantly contribute silica to solution as the groundwaters rapidly become saturated with respect to quartz. Although the solubility of amorphous silica is not exceeded, its concentration in the clay suggests that it is an unimportant source of silica.

The final concentrations of silica in groundwater reflect the extent to which the groundwaters have reacted with silicate minerals within the aquifer. This is controlled by many factors including kinetic rate controls, the nature and chemistry of the mineral phases, the groundwater chemistry, and the surface area of the minerals exposed to circulating groundwaters, which is influenced by porosity, permeability and pore size. In addition, the

flushing rate controls the removal of soluble phases (open or closed conditions), the presence or absence of more reactive phases, time, and the history of the groundwater including hydrogeological processes such as groundwater mixing. Many of these influences are specific to individual aquifer system and cannot be determined without detailed investigation. Careful interpretation of the reactions, occurred between the groundwater and the aquifer matrix, such as demonstration by using stability diagrams, may allow silica concentration to be used to indicate relative groundwater residence times and to help chronicle groundwater evolution.

#### 4.3 Characteristics of spring water quality

The groundwater flowed out from the study area in two ways -- spring water and groundwater. The water quality varied greatly in the former and little in the latter. As described in Chapter 3, during irrigation period, some part of groundwater discharge from the study area (P5). The spring water samples were analyzed. Its pH and water temperature were also obtained.

Figure 21 shows the concentration variations of calcium and sodium in spring water from June, 1985 to August, 1986, where the data was not available from October, 1985 to March, 1986, because no spring water existed. It is very interesting that sodium and calcium in spring water varied

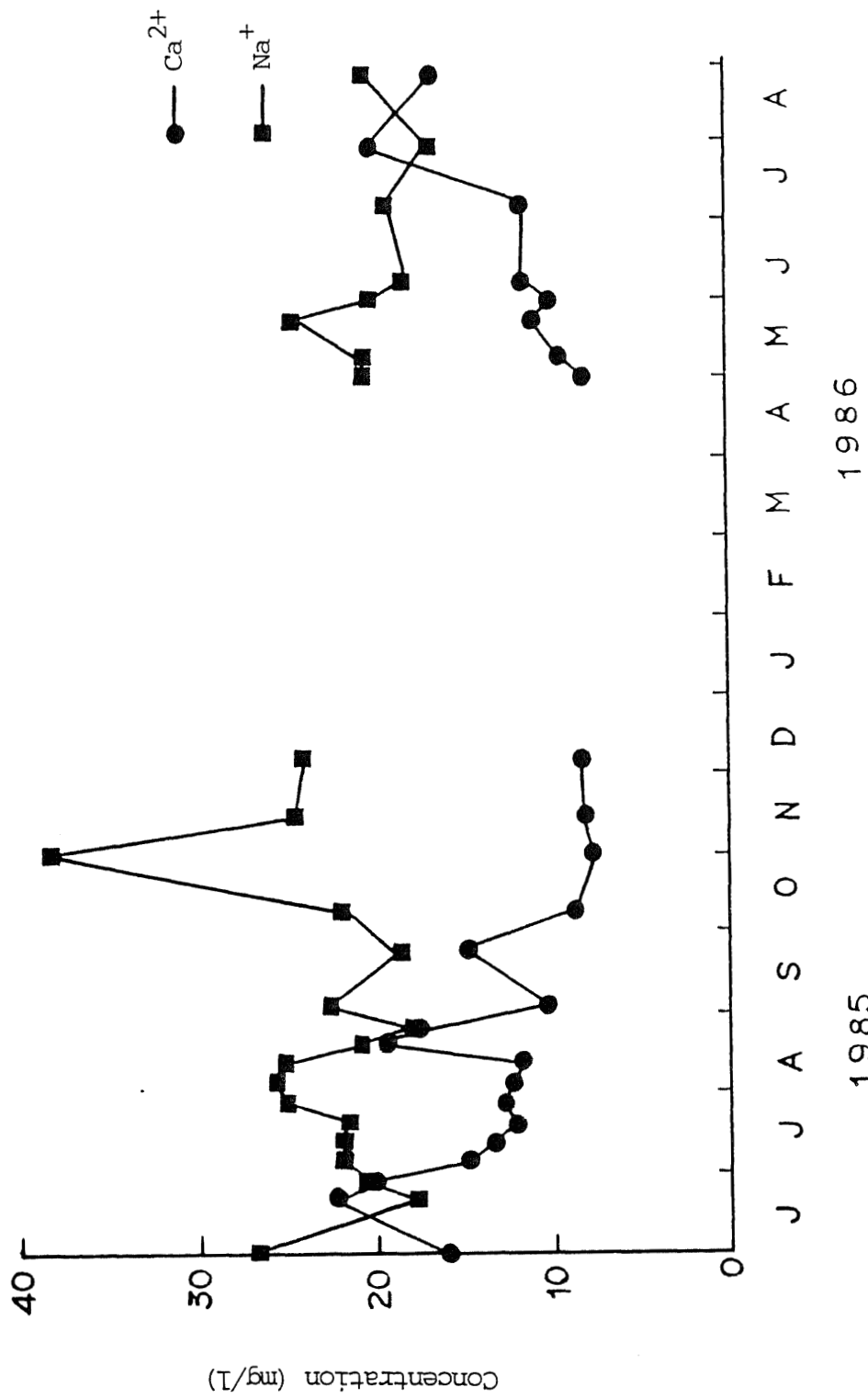


Figure 21 Variation of Ca<sup>2+</sup> and Na<sup>+</sup> in spring water (P5).

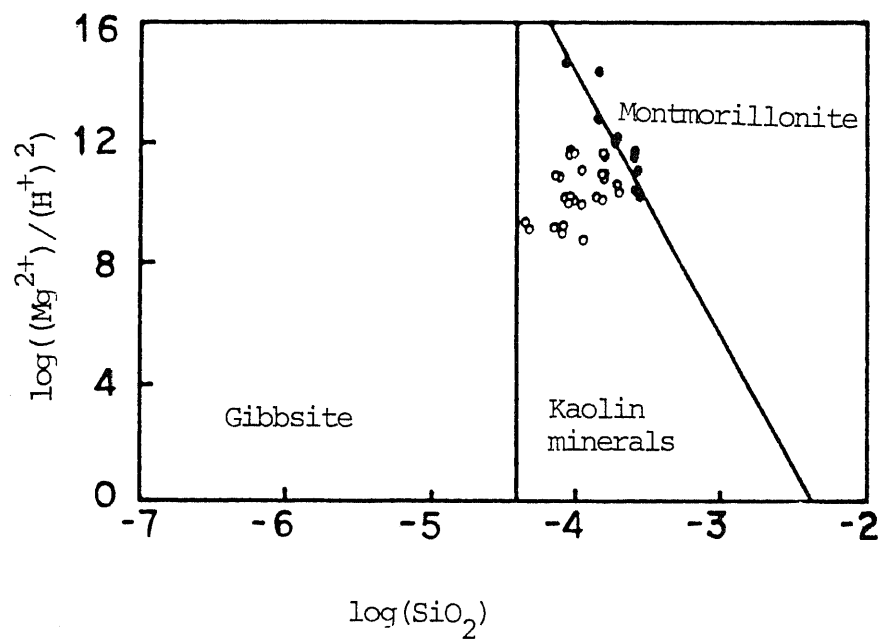
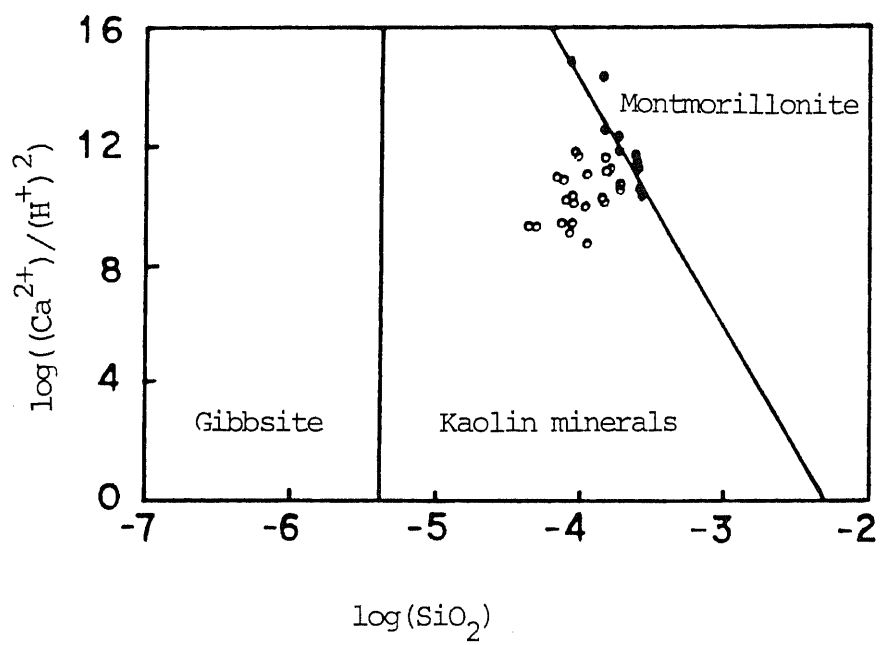
with time.

Referring to Figure 12, it was found that the variations of sodium and calcium in concentration responded well to the heavy rain. Before the heavy rain, the concentration of calcium was low and that of sodium was high. But after heavy rain, the concentration of calcium increased whereas sodium decreased. Moreover, the concentration of silica after rain was higher than that of before rain.

Spring water acts as the groundwater "outcrop". It can help us more clearly to know the groundwater flow system. The stability diagrams are also used here to indicate the change in chemical composition of spring waters. All spring waters fall in the Gibbsite-kaolin minerals-montmorillonite stability fields and are indicated on the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  and  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  stability diagram (Figure 22).

Before a heavy rain, the spring waters occupy the part of kaolin minerals stability field. On the other hand, they fall mostly in the montmorillonites stability field after the heavy rain. Comparing with figure 20, it is notable that the spring waters before and after a heavy rainfall in the same stability fields as the waters in upper aquifer and lower aquifer, respectively.

Figures 10 and 11 show the equipotential lines distribution in the valley where there was a spring. Before the rain, the equipotential lines were distributed vertically in the aquifer, thus, only the water in upper aquifer was considered to be available for the spring water.



- Spring water after heavy rain
- Spring water before heavy rain

Figure 22 Gibbsite-Kaolin minerals-Montmorillonite stability fields expressed in term of  $\log((\text{Ca}^{2+})/(\text{H}^+)^2) - \log(\text{SiO}_2)$  and  $\log((\text{Mg}^{2+})/(\text{H}^+)^2) - \log(\text{SiO}_2)$  for the spring water.

However, after the rain , the equipotential lines were distributed closely at the valley. Therefore, the spring water was recharged by waters from the upper and lower aquifers.

From the observed data, the response of groundwater flow system to the rain events contributes the variation of spring water quality. It can be considered that the spring water is supplied only by the groundwater from the upper aquifer before a heavy rain, and by the mixing of groundwaters from upper aquifer and lower aquifer after a heavy rain.

## V LABORATORY AND FIELD EXPERIMENTS

Two experiments, water-rock interaction experiment and column experiment, have been done in laboratory to study the effects of soils on the groundwater quality. As described in Chapter 4, the groundwater quality in field changes dramatically when clays exist. Therefore, the attention has been focused on clays in laboratory experiments.

On the other hand, in order to study mass flux in unsaturated zone, tracer experiment was done in the field.

### 5.1 Water-rock interaction experiments with clay

The soil samples were taken from the Narita Formation, from which clays were collected by standard method (Starkey, Blackmon and Hauff, 1984). The clay constituents were identified by X-ray method. This experiment has carried out for 14 days. The experiments began by putting 0.5 g dry clay into the test tube in which there was 5ml NaCl solution (24 mg/l of sodium ion). Then, samples were taken after 0 hour, 1 hour, 2 hours, 4 hours, 8 hours, 16 hours, 1 day, 2 days, 7 days and 14 days.

Figure 23 shows the result of the experiment with the clay in Narita Formation. During the first 16 hours, the concentration of major ions in the solution varied greatly. Two days after the experiment began, the water-clay interaction seemed to approach equilibrium state and the concentration of major ions in the water showed only a



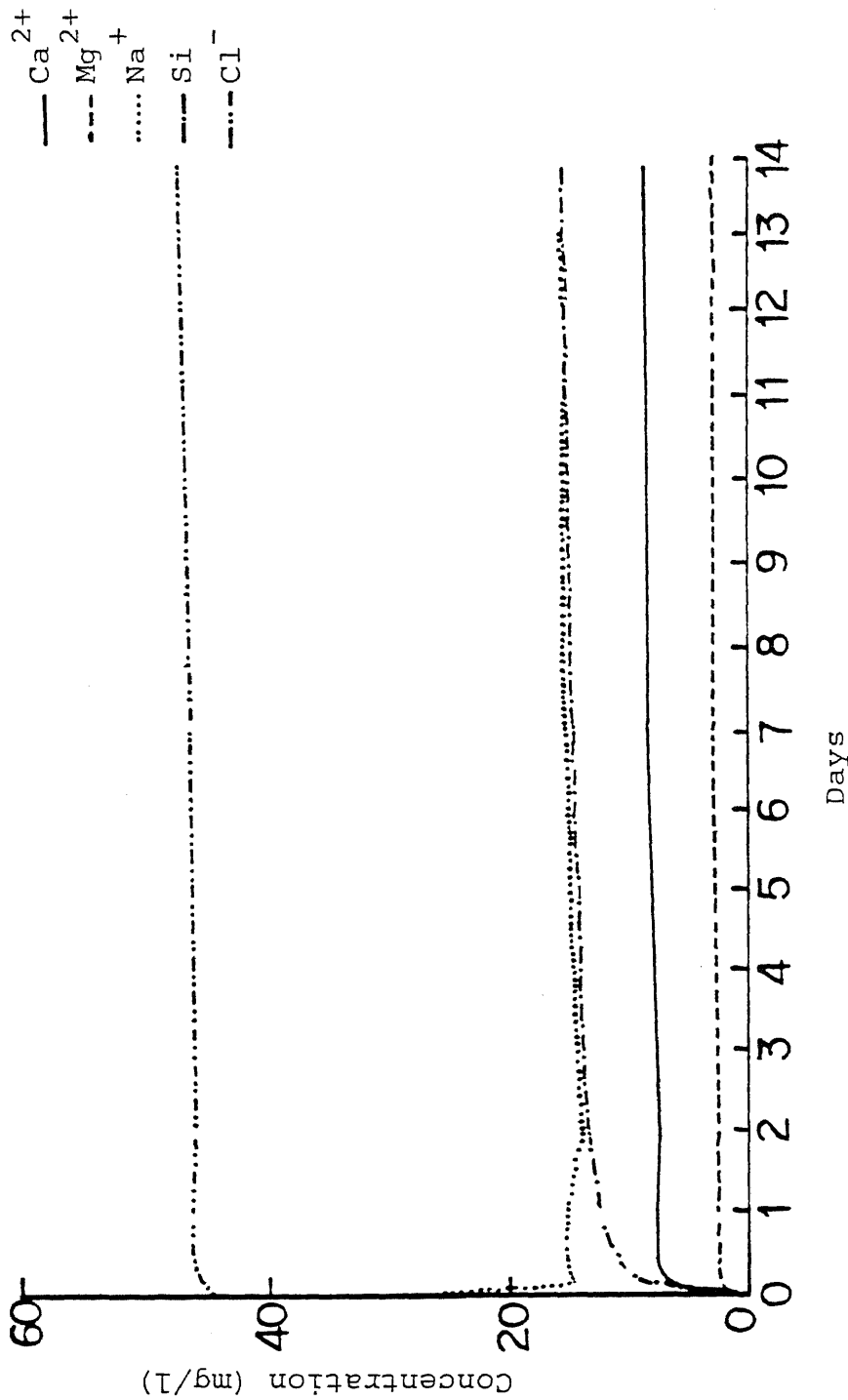


Figure 23 Variations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Si, Cl<sup>-</sup> concentrations in the water-clay interaction experiment with the clay in Narita Formation.

little variation.

In the experiment, the concentration of chloride ion in solution increased only 2 percent in comparison with that in original solution, and it was hardly to be considered that it was a meaningful variation because of the instrumental error. The concentration of sodium decreased, whereas calcium and magnesium increased. The reliability of these analyses was checked by means of charge balance control. It may be considered that the ion-exchange reaction between one value ions and two value ions occurred. The concentration of the silica also increased from 0 mg/l at the beginning of the experiment to about 10 mg/l at the end of the experiment. It was inferred that the increase of silica concentration in water might be caused by the silicate solution reaction in the clay.

Therefore, the nature and behavior of silica in the groundwater can be considered as following:

Silica exists in solution as the form of  $\text{Si(OH)}_4$  and is known as stable species and chemically unreactive under normal groundwater conditions. Silica concentration in the study area ranged up to 30mg/l  $\text{SiO}_2$  with an input level from less 1 mg/l in rainfall to about 2-3 mg/l in the irrigation water. The output concentration was derived from hydrolysis of silicates and the solution of siliceous minerals within soil zone.

Detailed investigations of silica in the aquifers of the study area have shown that the development of observed silica levels reflected the degree to which reactions

between groundwater and silicate minerals in the matrix could take place. The final concentration was attained when the groundwater reached equilibrium with the least stable silicate.

Silica concentrations are conservative and may be as a diagnostic of groundwater bodies, so variations of a few mg/l may be regarded as significant in interpretation of the water-rock reactions and the final equilibrium between the groundwater and silicate minerals.

The variation of observed silica concentrations reflects the extent to which silica is added to solution by the breakdown of silicate minerals. The solutions of siliceous minerals such as quartz and opal are less significant.

The breakdown and weathering of silicate minerals in aqueous environments are complex and controlled by many processes including kinetic rate laws, the composition of the attacking solution, and the nature and habit of the mineral phase. The extent of the weathering is also dependent on the time, the flushing rate and the presence of more reactive phases. Essentially, the release of silica to solution will depend on the degree of contact between the groundwater and suitable silicate minerals and the chemical ability of the groundwater to cause the mineral to breakdown.

As described in Chapter 4, the concentrations of all major elements in precipitation are less than 2mg/l. Therefore, rainwater rapidly attacks the minerals including silicates. The release of silica in the soil zone can be

examined by the silica level difference between recharge waters and the waters that have passed through the soil zone. Measured silica concentration in rainwater in the study area is negligible. The data shown in Table 6 indicate a rapid and significant release of silica to recharge waters from the soil zone. The level released from soils in Narita Formation is higher than that in other formations, which suggests that the presence of clay of Narita Formation is significant in increasing the level of silica released.

The experimental results are supported by the recorded background level of 4-5 mg/l  $\text{SiO}_2$  present in the groundwater of upper aquifer area, suggesting that this concentration is the minimum derived from the soil zone, although locally higher levels may be released from the soil.

Increase in silica concentrations during groundwater movement through the aquifer depends on the continued breakdown of silicate minerals present in the rock matrix. With continuing reaction between the groundwater and the aquifer matrix, it is possible that the groundwater may show an evolutionary sequence, that is, from these waters that show a high degree of disequilibrium with respect to the matrix minerals, to waters that have achieved chemical equilibrium with the appropriate silicates.

From the results of field and laboratory works, it can be found that cations exchange occur where clay exists.

The irrigation water is the source of recharge for the groundwater. As described in Chapter 4, the irrigation water in the study area came originally from the Kasumigaura Lake.

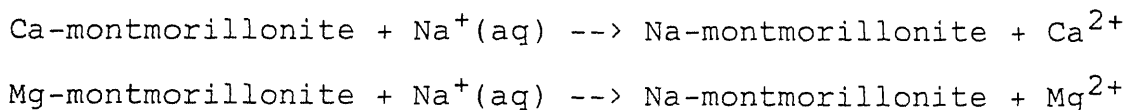
Table 6. Silica concentrations (mg/l) and pH levels measured in solutions of distilled water equilibrated with clays for a period of 14 days

Clay	pH of final solution	SiO <sub>2</sub> concentration in final solution
Joso clay	7.10	8.9
Clay in Narita Formation	6.98	25.8

Its composition is represented by Table 3. However, ion-exchange reactions in aquifers have changed the relative concentrations of cations in solution.

From the field observations, it is known that cations compositions of groundwater vary greatly when it flows through the clay of Narita Formation from the upper aquifer. Montmorillonite, which is the major clay mineral of Narita Formation, is a layered mineral acquiring negative charges, because of substitution of ions in the lattice. At the same time, these negative charges are neutralized by cations on the surface. These cations are also free to move in a diffuse swarm at the surface.

When sodium passes through the clay in Narita Formation with the groundwater, the sodium ion will then replace calcium ion or magnesium ion as shown below:



Clay as an exchanger is a reservoir for various ions. If a solution of constant ionic composition is passed through a clay, the ion exchanger in the clay will attain a certain composition of cations. During the transient state, i.e. when the ion exchanger is adjusting itself to the composition of the solution passed through it, the percolating solution is also changing in composition. As soon as the ion exchanger attains its final composition, no change in the percolating solution will be seen. It can explain not only why cation composition changes little in the upper and lower aquifers, but also great when

groundwater flows from upper aquifer to lower one. Because the ion exchange substances act as reservoirs, the upper and lower aquifers will damp time fluctuations in the ionic composition of water passing through a soil.

It was found that the variations of all elements in the experiment, excluding chloride ion, have the same tendency as that observed in the study area.

## 5.2 Column experiments of chloride ion migrating through clay

In the water-rock interaction experiment described above, the results can not explain the variation of chloride ions observed in study area, because it was only concerned with the chemical reaction between water and clay. Thus the column experiments had been done in order to investigate both physical and chemical roles of clay in water quality formation.

Figure 24 shows the column apparatus. The undisturbed core soil samples taken from the piezometers set up in the study area were used in the experiments. Before the experiments began, the soil samples were washed by NaCl solution until the concentration of chloride in effluent was invariable and approached that of input solution. During the experiments, the difference of hydraulic potential between the upper and lower sides of the soil sample was controlled by the manometer and vacuum pump. When 60 ml NaCl solution

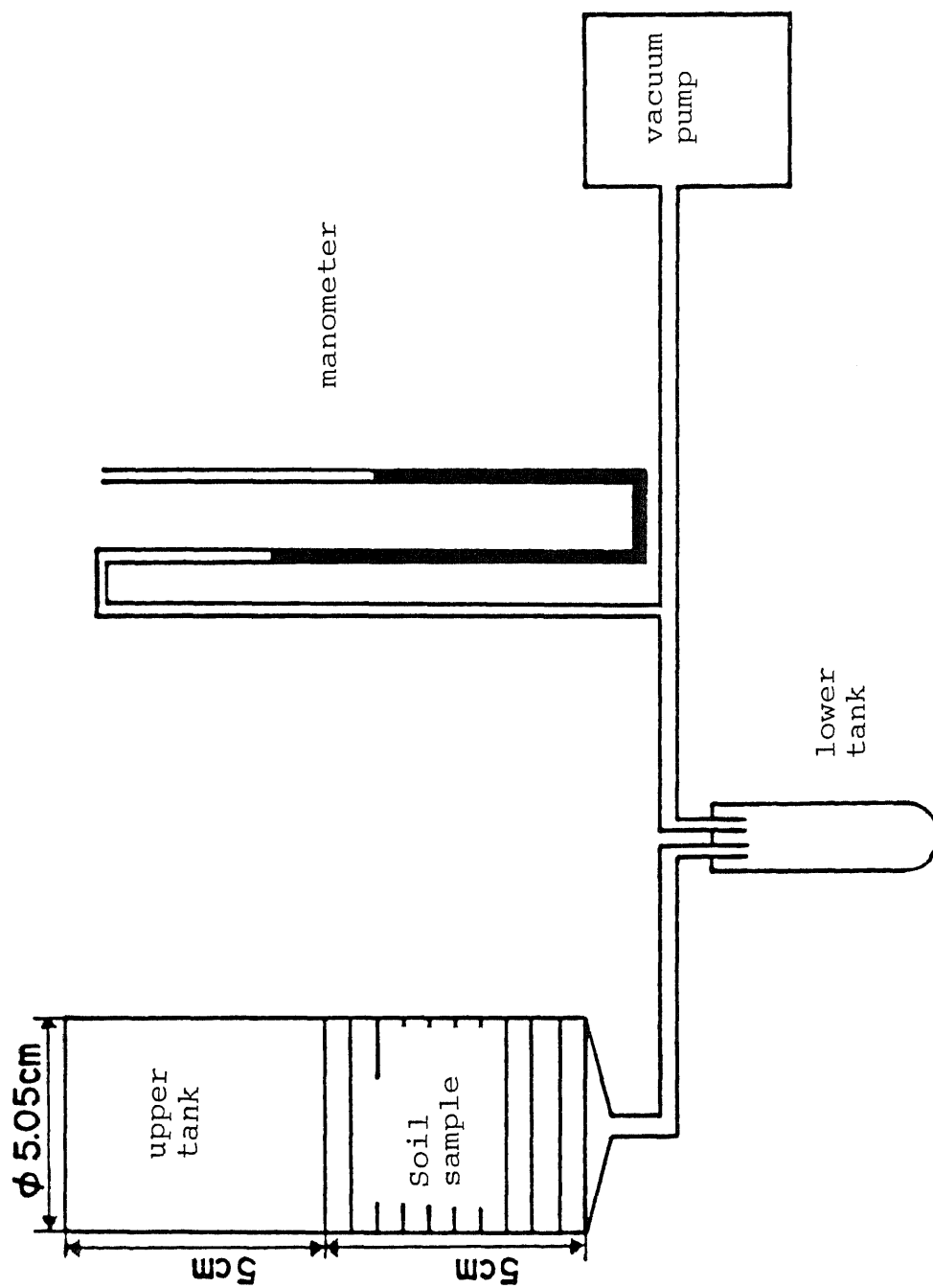


Figure 24 Schematic diagram of column apparatus.



was put into the upper tank, the water samples were taken from both upper and lower tanks at the same time. Another 60 ml NaCl solution was put into the upper tank again when there was not enough NaCl solution in the upper tank for the experiment.

Figure 25 shows the result of column experiment with the clay in Narita Formation. Before the experiment, the soil sample was washed by NaCl solution (32mg/l of chloride ion) and the concentration of chloride in the input NaCl solution during the experiment was 64mg/l. During the experiment, the concentration of one-value ions were higher in the upper tank than that in the lower tank. The concentration of two-value ions increased greatly after solution flowed through the soil sample. The concentration of silica was up to 20 mg/l in effluent. The most interesting result was the variations of chloride ion concentration in the upper and lower tanks.

The variations of chloride concentration ratios with time in both of upper tank and lower tank were shown in Figure 26. The concentration ratio in the lower tank increased until it reached about 1 and after that it changed little. On the other hand, the concentration ratio in the upper tank was always larger than 1. The result means that chloride ion was concentrated only in the upper tank.

The same experiment also has been carried out with soil in Joso Clay Bed. In this experiment, the soil sample was washed by NaCl solution (64mg/l of chloride ion), and the concentration of chloride in the input NaCl solution was

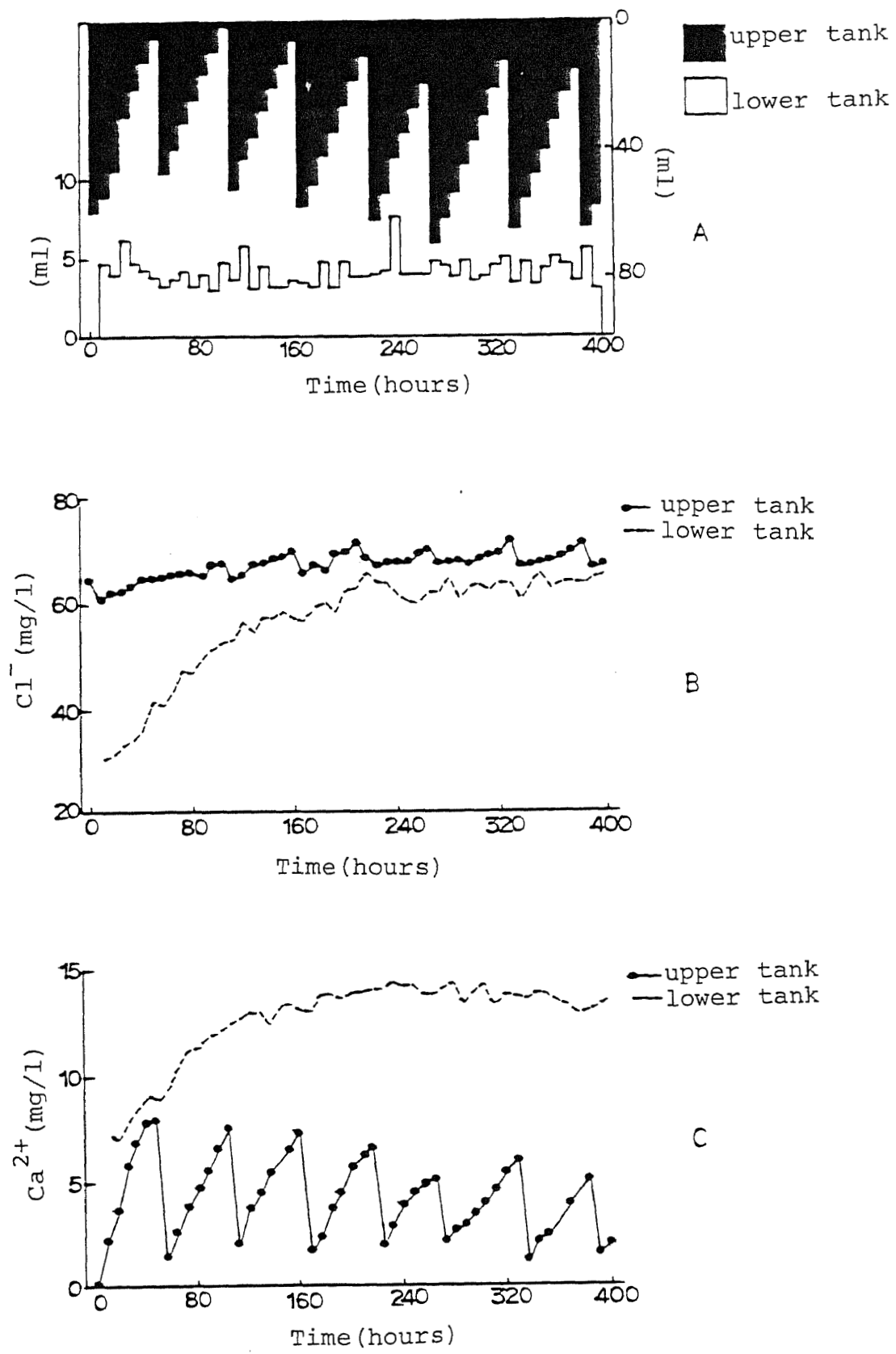


Figure 25-1 Variations of solution volume,  $Cl^-$  and  $Ca^{2+}$  concentrations in upper and lower tank during the column experiment with the clay in Narita Formation.

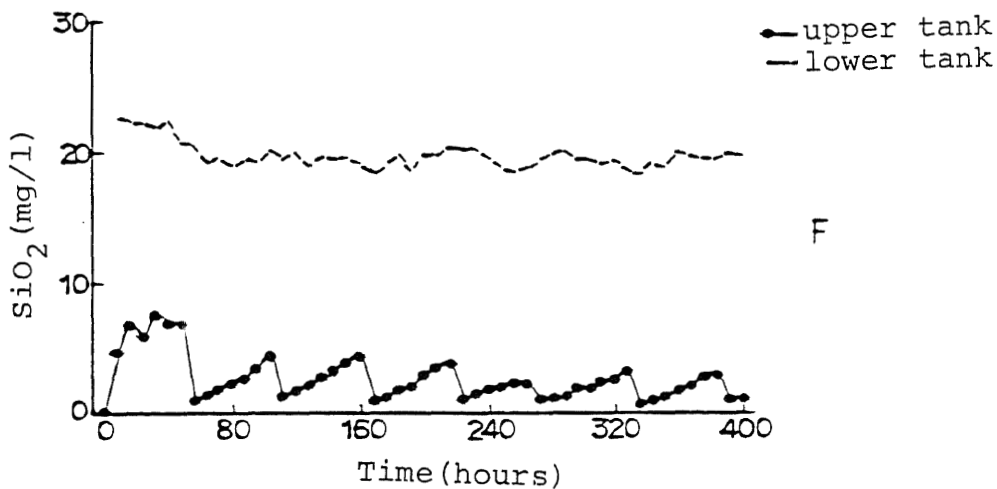
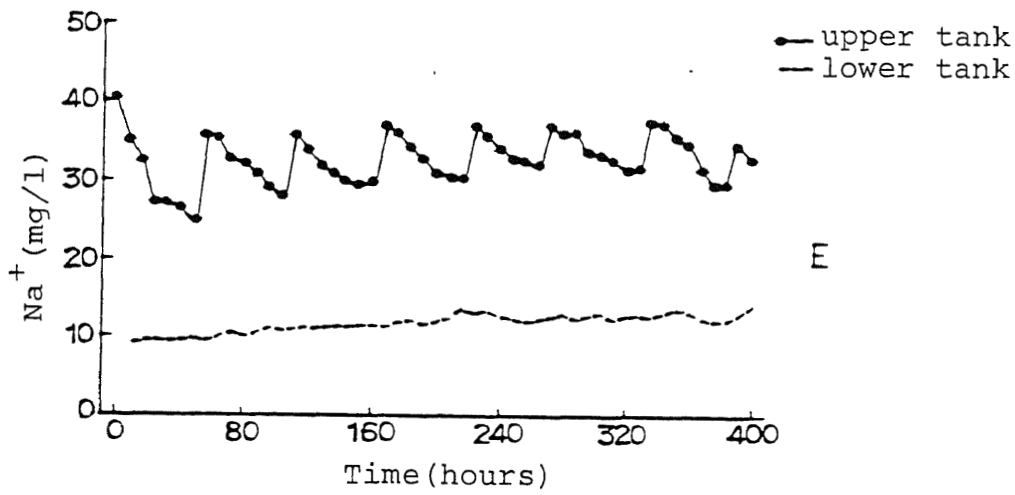
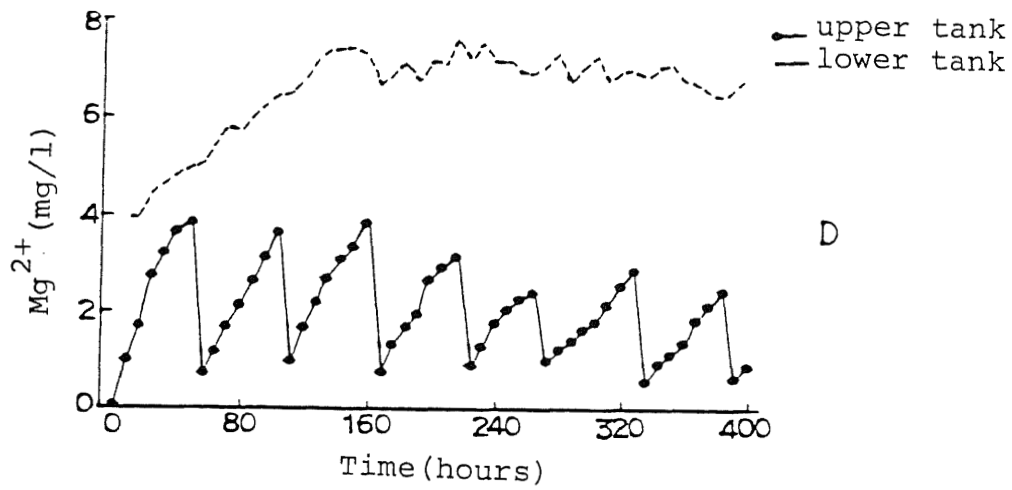


Figure 25-2 Variations of  $Mg^{2+}$ ,  $Na^+$  and  $SiO_2$  concentrations in upper and lower tank during the column experiment with the clay in Narita Formation.

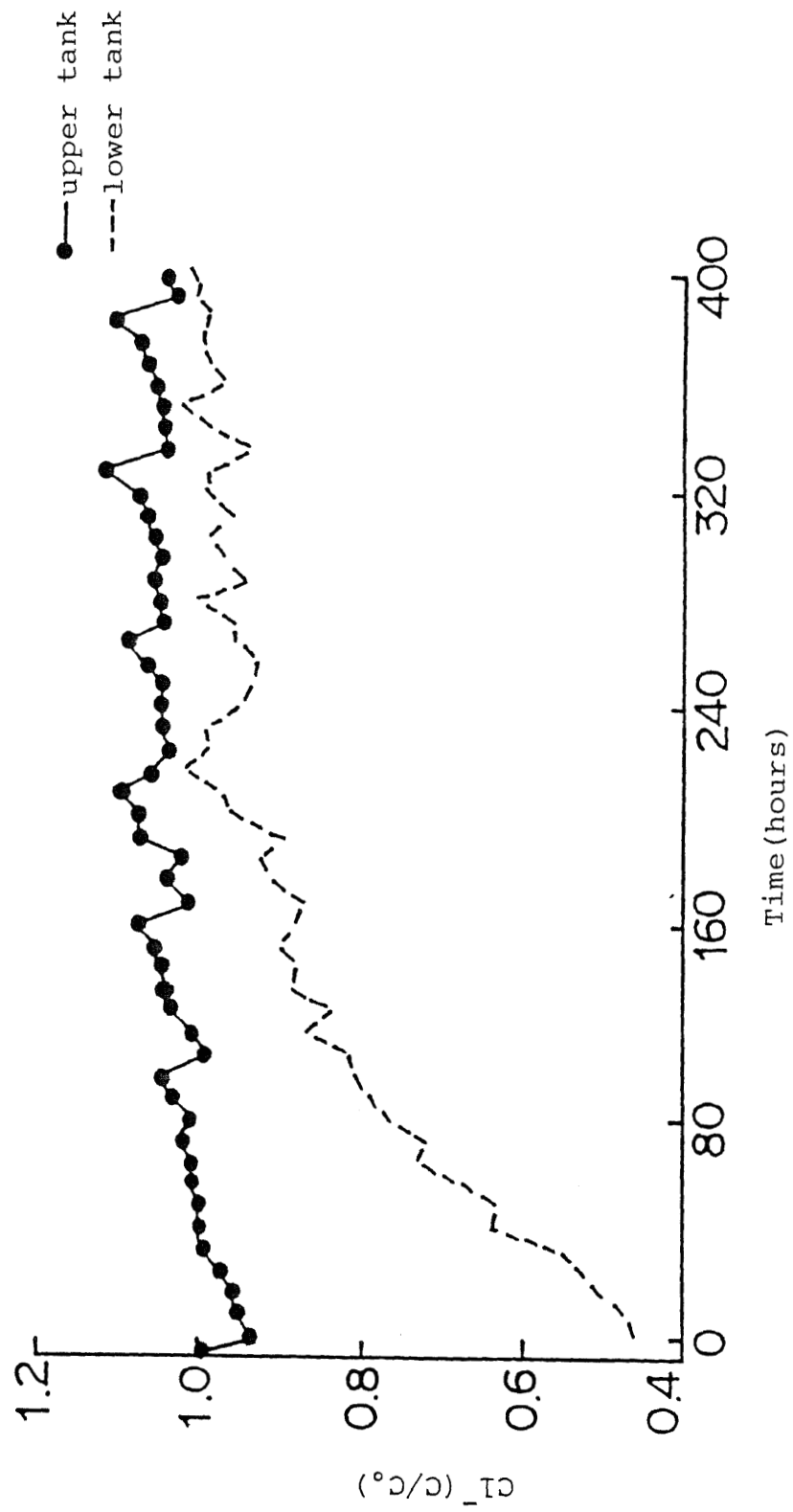


Figure 26 Variation of  $Cl^-$  concentration ratio ( $C/C_0$ ).

32 mg/l. The compositions of the water in the upper tank and that in the lower tank were the same, and the concentration of major elements showed less changes. Especially, in this case, no chloride ion was concentrated in the upper tank (Figure 27).

A theoretical model of the cation adsorption process can be developed from electrostatic considerations (Bolt, 1979). As noted earlier, the surface of a mineral solid immersed in a solution normally has a net negative electrostatic charge that attracts cations from the solution to maintain electroneutrality. The charge tends to immobilize a "fixed layer" of cations at the solid surface. At greater distances from the surface the charge intensity is lower, but ions of charge opposite to that of the surface will be present in larger concentrations than in the bulk solution. This "diffuse layer" of ions extends outward until the distance from the surface is great enough that the surface potential no longer affects the solution properties. The concept of layer of charge near the interface is broadly termed as the "electrical double-layer" (EDL) theory.

Because the surface of clay has negative charges, the anions can not move into clay until they have connected with other cations to form an electronuclear combination. On the other hand, the water can move into clay easier than anions do. In the column experiment, the concentration of anions in the upper tank would get higher and higher when the solution flows through clay of Narita Formation. Among cations that move into clay with anions, some of them take part in ion

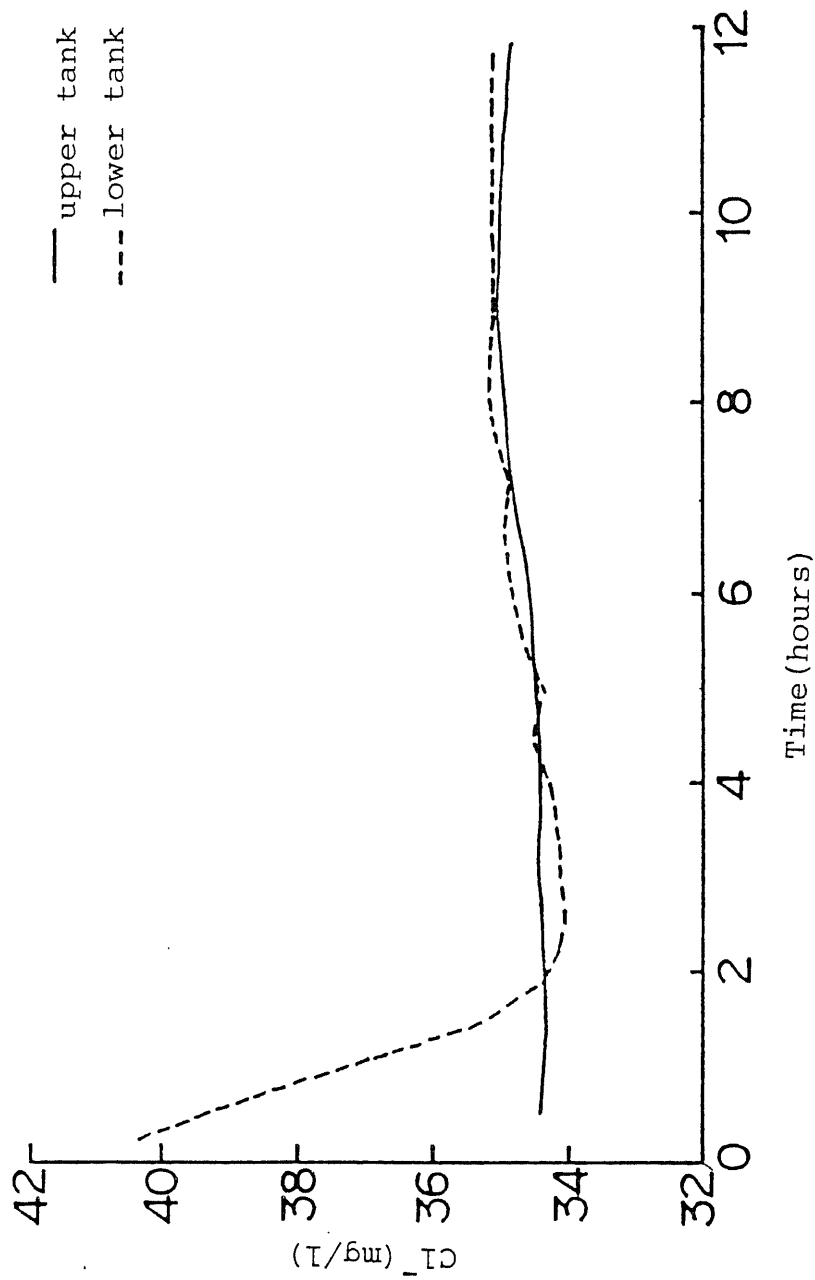


Figure 27 Variation of Cl<sup>-</sup> concentration in column experiment with the Josso clay.

exchange reaction with the cations in the clay, whereas the other part moves with anions continually.

Chloride ions may be concluded characteristically to be retained in solution through most of the processes that tend to separate out other ions. Because the chloride ion is physically large compared with many of the other major ions in water, it could be expected to be held back in interstitial or pore water in clay while water itself was transmitted.

The differential permeability of clay may be a major factor in the behavior and composition of groundwater associated with fine grained sediment. For example, chloride held back while water molecules passed through a clay layer might accumulate until high concentration was reached. The selective behavior of such a layer also influences the residual concentration of cations. The more strongly retained ions in such a solution would be the ones most strongly attached to cation exchange sites. Calcium is commonly the ion preferentially held. Thus, a mechanism is suggested for the origin of calcium chloride observed in the study area.

In Table 1, the hydraulic conductivity of Joso Clay Bed is very large comparing with that of clay in Narita Formation. Mineral compositions of Joso Clay Bed is different from that of clay in Narita Formation. Therefore, Joso Clay Bed give more paths for the groundwater flows than the clay in Narita Formation can do, which make possible for the chloride moving through Joso Clay Bed freely. From the

field observations and the experiment results, it has been found that chloride can not be used as a tracer where the clay exists.

As described above, movement of chloride in soil can be influenced by both charge on the soil surface and the hydraulic conductivity of the soil. Therefore, considering the synthetic effects of the charge on the soil surface and the hydraulic conductivity, the behavior of chloride in the soil can be estimated.

### 5.3 Field tracer experiment with NaCl solution

From the results of other researchers and the present experimental results described above, it can be concluded that both Kanto loam Formation and Joso Clay Bed have no influence on the chloride ion moving through them. In these soils, it can be considered that chloride ion moves with water, and can be used as a tracer for studying the movement of chemicals in soil.

As described in Chapter 2, about three fourth part of the study area were the fields producing chestnut, wheat and corn. In order to make clear how these fields influence the groundwater quality, it was necessary to know the movement of major elements in the unsaturated zone.

At the plot P3, the salt (NaCl) was put into the soil surface in the August, 1985. In order to trace the movement of chloride ion, the soil water samples were collected by



vacuum technique with soil water samplers twice a month.

Figure 28 shows the profile variation of chloride ion concentration during the experiment. In April, 1986, the peak concentration of chloride was found at 40 cm in depth, and reached at 80 cm in depth in March, 1987. It was found that in spite of irrigation period and precipitation, the peak concentration of chloride moved slowly, with the rate less than 40cm/year. Therefore, exclusive of recharge area, the soil water contributes little to seasonal changes in groundwater quality.

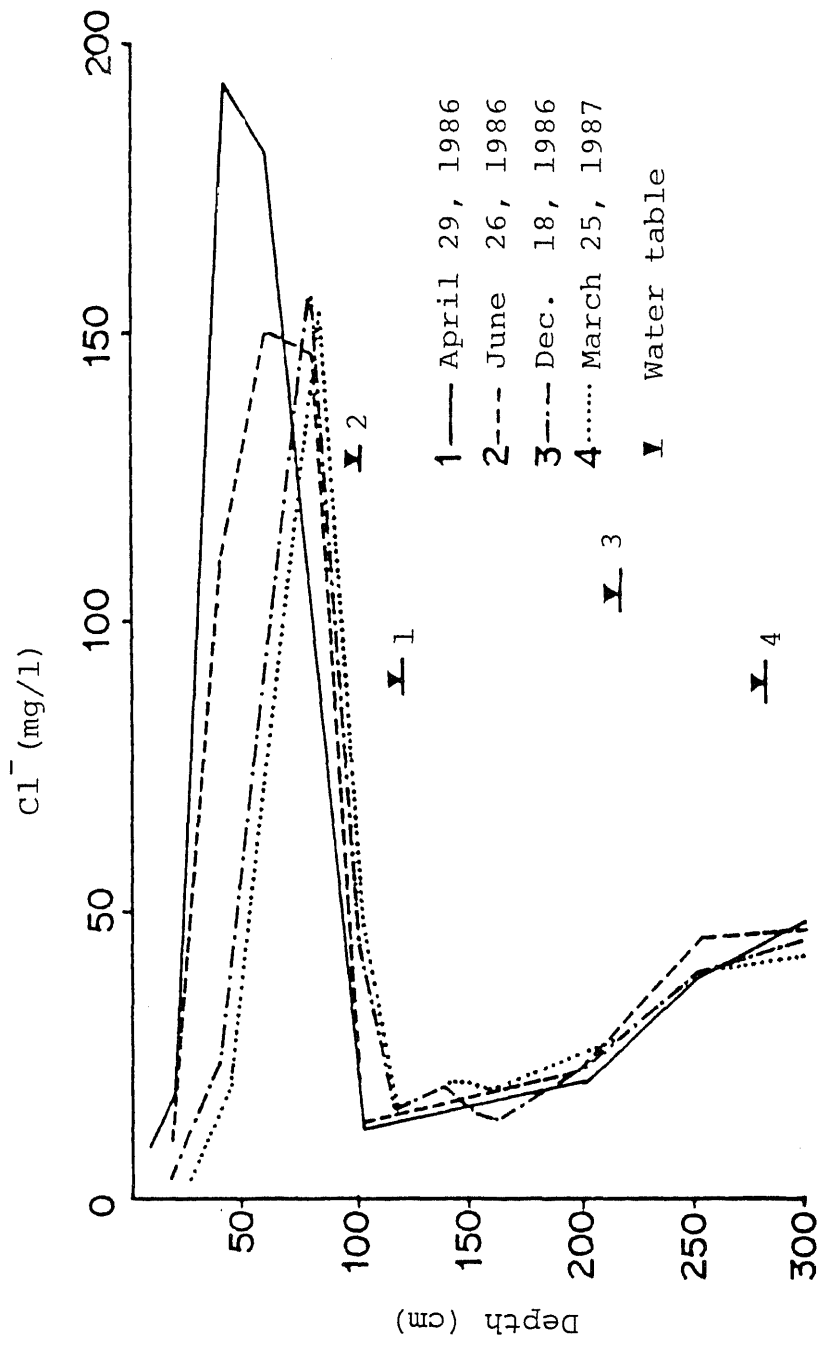


Figure 28 Variation of Cl<sup>-</sup> concentration profile in tracer experiment (P3).

## VI DISCUSSION

The characteristics of groundwater flow system and groundwater quality in the study area have been analyzed by the collected data in chapter 3 and chapter 4, respectively. In addition, chapter 5 reported the results of laboratory and field experiments. Here, some results will be discussed further.

The geochemical properties of various groundwater bodies are determined by the chemistry of water in recharge areas as well as by different geochemical processes taking place in the subsurface. The evolution of water quality along the course of its underground movement is thus dependent upon the chemical and physical properties of surrounding rocks, the quantitative and qualitative properties of flowing water bodies, and the products of human activity. According to Mercado (1977), a "hydrogeochemical system" is a complex natural framework including liquid, gaseous and (several) mineral phases. The input of solutions and the physical and chemical reactions occurring in the hydrochemical system of an aquifer define the chemical properties of its groundwaters.

Therefore, evolution of water quality can be explained simply as following:

input water + reactant phases

--> output water + product phases

A few studies about water quality has been done in this way. This study has been done to try to bridge the gap

between the groundwater flow system and groundwater quality evolution in a small area.

The results of this study have revealed the complexity and variability of groundwater in chemical quality at the microscale level. When many variables of quantity, quality and periodicity of the input waters, as well as the multidimensional flow, are considered, variations in water quality at a single sampling site are to be expected. The findings reported herein are unique in : (1) the range of variations of chemical quality is within microscale (0.5-500 meters) parcels of water, and (2) the sharpness of boundaries between these parcels exists.

Piezometers were used to monitor the hydraulic head variations in aquifers, then groundwater flow system could be estimated. Some groundwater supplied by irrigation water and precipitation flow in the upper aquifer, forming a local groundwater flow system, and the other flows across the clay of Narita Formation, entering a larger groundwater flow system in the Dejima upland.

The understanding of transport phenomena of pollutants in the water of an aquifer requires detailed real-time distribution of chemical species with a high spatial resolution. Such data have been unavailable until soil water sampler and piezometer were used in the study. These techniques are effective in the investigation of polluted aquifers that underlies cultivated fields.

The ten measured elements of hydrochemical constituents in water samples have been used to characterize the

groundwater quality in groups. It is found that the groundwater quality are distributed in stratification in space, which is believed to be controlled by geological setting. Stability diagrams have been used to explain the evolution of groundwater quality. From the results of this study, stability diagrams is a very powerful tool to estimate the evolution of groundwater quality.

The results obtained from the field and laboratory experiments show that groundwater quality changes greatly when clay exists. It has been known that some clays have low permeability; subsurface environments which are composed of these media and lacking well developed secondary permeability form the groundwater system with many distinctive characteristics. Moreover, groundwater flow in these environments appears to influence the evolution of certain hydrologic, geologic, and geochemical systems. On the other hand, the composition and nature of clay control not only groundwater flow, but also the chemical reaction which occurs in the groundwater. Since chemical equilibrium between groundwater and the media can reach in a short time, it is believed that microscale heterogeneity will be found in most polluted aquifers.

As a whole, the evolution of groundwater quality in the study area can be considered as follows.

The input of solutes may come from several sources:

(1) Solutes originating in irrigation water recharging the aquifers.

(2) Solutes originating in rain water recharging the

aquifers.

(3) Dissolution of salts occurring in the aquifer materials by flowing groundwaters.

(4) Diagenetic processes, such as hydration, hydrolysis, oxidation-reduction and ion-exchange reactions.

(5) Agricultural activities, such as fertilizer, agricultural chemicals, and livestock activities.

Groundwater moves down across the different layer or along the same aquifer. Therefore, the chemical composition of groundwater in each layer depends upon the chemical composition of water leaking vertically from the above layer or recharging laterally from upstream and the properties of soil the water flowing through. Especially, it varies greatly between the clay layer and overlaid aquifer.

The relationships between hydrology, clay mineralogy of weathered plagioclase products and aqueous geochemistry are analyzed and summarized systematically in Figure 29.

The Kanto loam Formation is located at upper part in the study area, where the water in this soil is influenced greatly by the human activities. All major ions can be found here, and the standard deviations show that variations of all major ions are the largest in the study area.

The groundwater flows down from Kanto loam Formation into Joso Clay Bed, which is the first clay layer that groundwater meets when it flows from the recharge area. Little of potassium was detected in Joso Clay Bed; it is considered that potassium is absorbed by soil in Kanto loam Formation when it moves through with groundwater. Calcium in

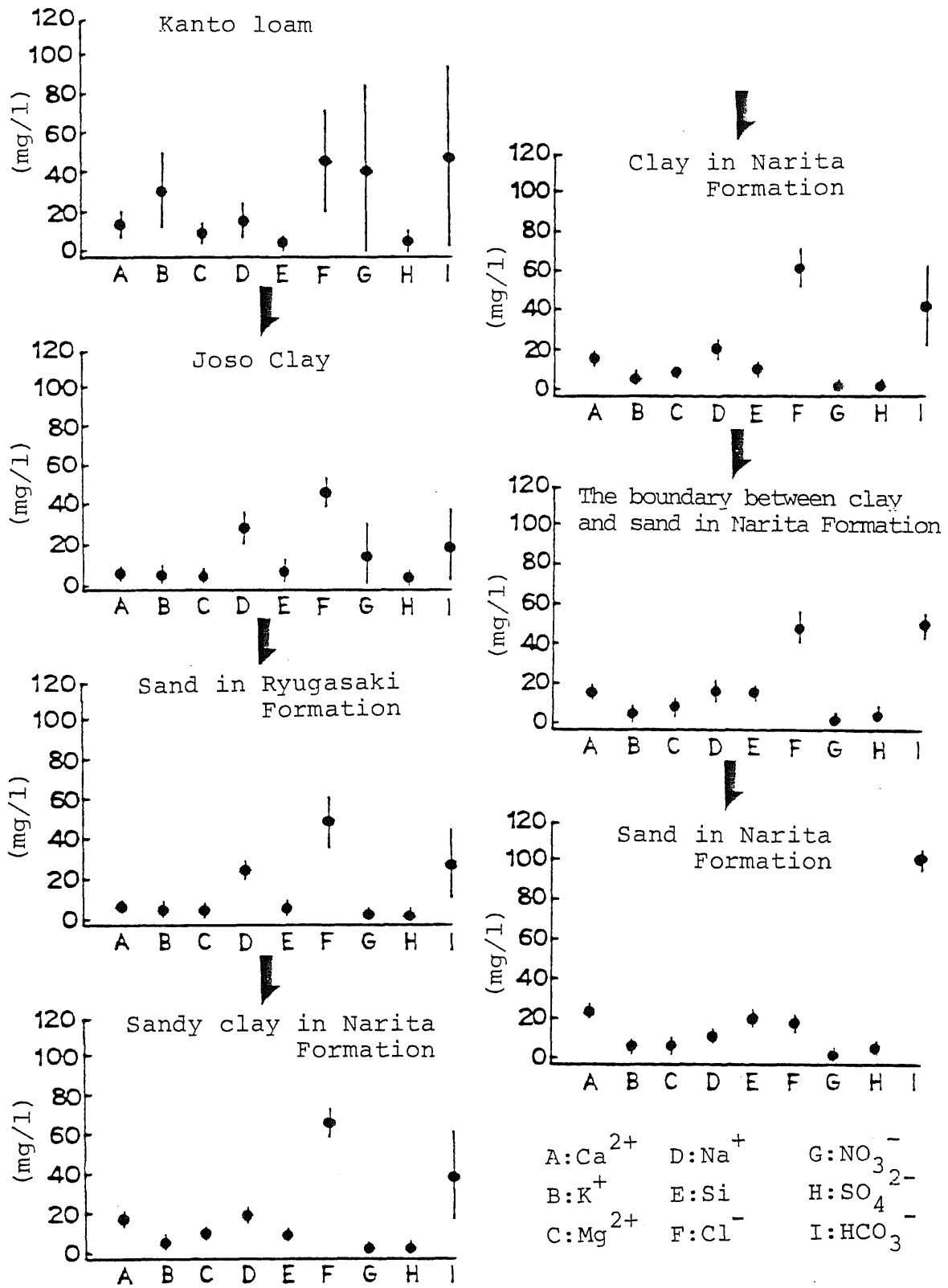


Figure 29 Schematic diagram of groundwater quality evolution in the study area.

groundwater is exchanged by sodium in this clay layer and causes the increasing of concentration of sodium in the groundwater up to 30 mg/l. At the same time, the concentration of nitrate decreases to about 10 mg/l. This decrease might be caused by biochemical reactions in the soil.

The groundwater quality in sand of Ryugasaki Formation has the same characteristics as that in Joso Clay Bed. Considering the groundwater flow system, the groundwater in the sand of Ryugasaki Formation is recharged by the groundwater in Joso Clay Bed. Because velocity of groundwater in the sand layer is high, there is not enough time for chemical reactions to take place when the groundwater flows through this layer. On the other hand, it can be said that the sand had no influence onto the groundwater quality because of its composition and feature in mineral phase.

The dramatic variations take place when the groundwater flows through the clay layer in Narita Formation. The concentration of silica increases to 20 mg/l, because the silica dissolves from the clay. Opposite to Joso Clay Bed, sodium in the groundwater is exchanged by calcium, and caused the concentration of calcium in the groundwater increases to 20 mg/l. The most interesting phenomena is the increase of chloride concentration in this layer. As described in the Section 2 of Chapter 5, the synthetic operations of physics and chemistry of clay in Narita Formation may resist the chloride ions moving through it,



and let only groundwater flowing freely. According to this fact, it can be concluded that the velocity of groundwater is different from that of chemicals , even chloride ion, when clays exist in the groundwater flow system.

After the groundwater flowed through the clay layer in Narita Formation, the groundwater quality evolution is controlled only by the mineralogy. Sodium in the groundwater is continually exchanged by the calcium. Concentration of chloride is less than 20 mg/l. On the other hand, the concentration of  $\text{HCO}_3^-$  increases up to 100 mg/l, because of the dissolution of the minerals in the Narita Formation.

## VII CONCLUSIONS

Groundwater quality evolution in groundwater flow system has been studied on microscale in a small valley head basin, located on an upland with multilayered geological Formations. The study area has been chosen in Dejima upland area, Ibaraki Prefecture, Japan. Studies were undertaken through field observations and laboratory experiments.

The results are summarized as follows:

(1) Annual irrigation water is three times larger than precipitation in the study area. Comparing with the precipitation in which each of major elements is less than 2 mg/l, the irrigation water quality is  $\text{Cl}^-$ - $\text{SO}_4^{2-}$ - $\text{Na}^+$  type. Therefore, groundwater is mainly recharged by irrigation water in quantity and quality.

(2) It was observed that the study area is divided into local and intermediate groundwater flow system by clay of Narita Formation. The groundwater quality evolution processes occur both in local and intermediate groundwater flow system.

(3) Each aquifer has its own groundwater quality characteristics, but groundwater quality is different from aquifer to aquifer. Especially, the groundwater quality varies greatly where clay exists. Therefore, distribution of groundwater quality is stratified in the study area.

(4) On the other hand, structure and mineral compositions of clay control not only the cations and silica concentrations in the groundwater, but also movement of

chloride ion. From the field observations and laboratory experiments, it was found that chloride ion is concentrated where the clay of Narita Formation exists. This phenomenon does not occur in the Joso Clay Bed.

(5) Clay layer in the groundwater flow system is one of the most important factors to control the variation of groundwater quality in the study area, and in turn the movement of chemicals in the groundwater system.

(6) The ion exchange reactions that occurred in groundwater and clay layer through which groundwater flows influence the concentration variations of both 1 value cations and 2 value cations in groundwater.

(7) The  $\text{Ca}^{2+}/\text{Na}^{+}$  ratio variation in spring water is controlled by the mixing ratio between the groundwater in the upper aquifer and in lower aquifer in irrigation period.

Although the conclusions are local and confined to the aquifers in the upland, the proposed methods may have applicability in other locations.

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