TIME AND SPACE DEPENDENCE OF IONIC COMPOSITION OF THE KEBENA RIVER IN ADDIS ABABA

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DEREJE TSEGAYE
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Dedicated to the memory of

Jimma Leku Addisie

(Wolde Selassie)

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ABSTRACT

The Kebena River traverses Addis Ababa from north to south. The river starts upstream from a scarcely populated area and goes to the south through the densely populated areas. The difference in ionic compositions as one goes from upstream to down stream is then an indication of human impact on the quality of water. The geogenic ions, which are introduced from the natural environment through which the water passes, and the anthropogenic ions, which mainly enter into the water by the action of man, have been determined. The pH, conductivity, alkalinity, the chemical oxygen demand (COD), ammonium, nitrite, nitrate, phosphate, sulfate, chloride, fluoride, sodium, potassium, magnesium, calcium ions and silica have been determined from three different sampling sites, which represent upstream, midstream and downstream using standard methods of analysis.

Time and space dependence of ionic composition has been studied starting from the end of the rain season (September, 2000) to the beginning of the small rain (April, 2001). The diy season dominates in between. The increase in concentration of the anthropogenic ions as nitrate, nitrite, ammonium, phosphate, COD, and chloride, as one goes from upstream to downstream through the highly populated areas and the increase in these ions as the rain ceased and the surface runoff decreased were very good indications of the deterioration of water quality by human activities; by direct disposal of liquid and solid wastes to the river.

The Addis Ababa city solid waste disposal site is the landfill at Kore (Jimma Road). Two samples were taken to determine the ionic composition of the runoff from this landfill. Emphasis was given for trace elements, especially cadmium, lead, copper, and zinc, differential pulse stripping voltammetry (DPSV) was used for their determination. The trace elements (Cu, Pb, Cd and Zn) were not detected using DPSV, which has a detection limit of 10^{-7}-10^{-8} M.

1. INTRODUCTION

Water and air are the fundamental media in which life exists [1]. Water is the most widely occurring substance in the world. Over 72% of the earth's surface is covered by water. This means that, if the body of the water were evenly distributed, it would cover the globe to an average depth of over four kilometers [2]. Therefore, total abundance of water on earth is not a problem; the problem is its availability where and when it is needed in the appropriate form (Table 1) [3].

Table 1. The world's water supply

Location	Surface area (km^2)	Water volume (x 1000 m^3)	% Total water
Oceans	361,000,000	1,230,000,000	97.2
Atmosphere	510,000,000	12,700	0.001
Rivers & Streams	-	1,200	0.0001
Ground water: Shallow to depth of 0.8 km.	130,000,000	4,000,000	0.31
Lakes (fresh water)	855,000	123,000	0.009
Ice caps and glaciers	28,200,000	28,600,000	2.15

Throughout history, the quality and quantity of water available to humans have been vital factors in determining their well being [4]. All life on earth depends on water. Water is the most important substance for human existence. The form in which the chemical compound

Table 2. Some important properties of water, effects and significance

Property	Magnitude	Effects & significance
Heat of Fusion (kJ/g)	0.334	Strong cushion against both rising and falling of temperature.
Heat of Vaporization (kJ/g)	2.3	Determines transfer of heat and water molecules between the atmosphere and bodies of water.
Specific Heat (J/g) at 0UC	4	Keeps the temperature constant, Stabilization of temperatures of organisms and geographical regions.
Dielectric Constant (at 25^{0}C)	78	Makes water a powerful solvent for both polar and ionic compounds.
Dipole Moment (D)	1.834	
Surface Tension (N/m)	7.2 x 10-6	Gives ability to water droplet formation and wetting a surface.
UV cut-off (rnn)	180-195	Allows solar radiation to reach the earth and restricts rapid heat loss, allows light required for photosynthesis to reach considerable depths in bodies of water.
Density	1 (max. at 4^{0}C)	Ice floats, makes life possible even at colder conditions.

Chemical compounds constantly enter the water by leaching from sediments, runoff from land, dissolution from atmosphere, and other sources. Equally constantly, they depart through volatilization, sequestration, adsorption on to sediments, and so on. These factors should cause the concentration of any dissolved environmental chemical to reach a steady different solubility equilibria of the constituents of the geological formation the water is seeping through. Ions entering the water from these sources are refereed to as *geogenic*. On the other hand ions introduced from different human activities are termed as *anthropogenic*. A society's ever expanding utilization of materials, energy, and space is accompanied by an increasing flux of anthropogenic impurities to the environment [13-15].

Regardless of the purpose for which water is required, other substances dissolved or suspended in it can affect its suitability for that purpose. Substances that appear in the natural environment as a result of weathering phenomena and human activity play a critical role in determining water borne pollutants [16]. Natural waters are afflicted with a wide variety of inorganic, organic, and biological pollutants, a significant fraction of which come from the improper disposal of wastes [17]. Man's physiological, domestic, and industrial use of water degrades its quality [18]. Industries, municipalities, and storm water runoff contribute to the pollution of natural water systems. Most industrial and municipal wastes end up in rivers, lakes and the sea [19-20].

The root cause of pollution of waters is man's tendency to dilute and disperse wastes than to remove them at the source. Pollution occurs when too much of unwanted substances enter a body of water. There are two main ways to contaminate water:

a) A steady flow, e.g., from sewage plants

b) A sudden discharge of several dangerous chemicals [21-22].

Pollution of water doesn't appear to have been a serious problem until relatively recently. With high-density settlement in towns and cities came the question of sewage disposal, which had not troubled more dispersed communities. Excrement had undoubtedly entered rivers and streams. With the growth of industry rivers and oceans provide a means of dispersing waste products from industrial processes [23].

It has been shown that rivers undergo self-purification by dilution effects and by the action of different microorganisms, which depend on organic pollutants and nutrients [12,24]. At present, the problem of biological self-cleaning of polluted waters is of great importance because the anthropogenic pollution of waters often exceeds permissible limits [25]. Chemically pure water would not support life, but its ability to dissolve more substances than any other liquid in nature ensures that natural waters usually contain those substances needed by living organisms [26]. When one adds organic pollutants, such as sewage, it increases the amount of allochthonous organic matter, which enhances the amount of animal production that thrives on dissolved organic matter [27]. It has been shown that organic pollution is responsible for the increment of nitrate and phosphate contents of a stream and river, which are plant nutrients [28-29].

Nutrients are those environmental substances necessary for the growth and development of the nutrition of green plants, which in turn provide the organic nutrients for non- green plants and animals. The characteristic pathways in which these substances circulate from the environment to the organisms and back again are known as biochemical cycles. Oxygen, carbon, and nitrogen are the principal elements involved, while more than forty minerals, such as phosphorus and potassium, come from the crust of the earth. The synthesis of protoplasm by living organisms from their decomposition after death forms the energy basis for these cycles and provides for a classification of organisms into producers, consumers, and reducers [1,30]

The producers take energy from the sun and nutrients such as nitrogen and phosphorus from the water and soil and through the process of photosynthesis produce high-energy chemicals. The energy from the sun is thus stored in the chemical structure of their organic molecules. These organisms are often referred to as autotrophs (e.g. algae). A second group of organisms are the consumers who use some of this energy by ingesting the high -energy molecule. The third group of consumers, the decomposers (reducers), use the energy in animal wastes and dead plants and animals (e.g. bacteria), and in so doing convert the organic molecules to stable inorganic compounds. The residual inorganics then become the building blocks for new life, using the sun as the source of energy. Such organisms have great impact on the quality of water. Many aquatic chemical processes are influenced by the action of algae and bacteria [19,31].

The other point of interest, which endangers river water quality, is contamination from the disposal of solid wastes. Deposition of solid waste on dumping ground (landfill) is a widely used and inexpensive method, but it has a number of disadvantages, the most important one is the possibilities for contaminating water bodies [32-34].

In countries like Ethiopia many people depend on river waters for their day-to-day activities. They use river waters for bathing, for cleaning purposes and even for drinking beyond the usual use for irrigation. It is also obvious that many municipal water supply wells are located adjacent to rivers to ensure adequate flows and they can serve as important ground water pollution mechanisms [35]. It is thus a crucial task to follow and assess the quality of river waters, which has high potential to cause direct health problems to the society.

At present time environmental pollution is one of the most investigated subjects of research. Studies on water pollution are the most important one. Water bodies are means for the disposal of wastes. Hence, a continuous water quality survey is the most crucial aspect.

Even if a number of works have been reported on the quality of waters, there is not much work done on the quality of Kebena and Tinishu Akaki (Kolfe) rivers. Lemma [36] on his study of the Little Akaki appreciated the nature of spatio-temporal variations in stream water quality and tried to see a significant areal, monthly and seasonal quality variation in municipal stream water. His work was also designed to discover whether there was a significant relationship between the loading of physical and chemical parameters and population density of the Little Akaki.

Pitwell [37-38] has done a more elaborate work on water quality determinations. On his subsequent and related works he showed oxygen depletion of Kebena river due to local pollution and Little Akaki river due to high industrial and local pollution.

The Environmental Protection Authority of Ethiopia [39] has done a preliminary survey of pollutant load on Great Akaki, Little Akaki, and Kebena rivers by industries, residential houses and commercial institutions. The Addis Ababa Water and Sewage Authority (AAWSA) [40] conducted a number of surface and ground water analysis of Addis Ababa waters and revealed different levels of pollution at different sample sites.

Tesfaye [41] has conducted a study of biological and chemical characteristics of Abo-Kebena river. This study was carried out over a one-year period and observations were made at 20 stations starting from upstream to downstream which covered a total of 13.6 km. In this study water quality deterioration caused by organic pollutants was indicated chemically by increased concentrations of nutrients (nitrates and phosphates) and BOD_5 values. The biological determination of water quality was made using macro invertebrates as indicators.

Abraha [42] surveyed Addis Ababa drinking and surface waters. He determined the anionic and cationic composition of Kebena river at three different sampling points. He showed the correlation in increase in pH, alkalinity, and COD values with the population density and the waste dumped in to the river.

The main objective of this study is to assess the effects of human activities on the quality of Kebena river. Kebena river is chosen because it is far from industries and the effluents directed to it are of domestic and municipal type. Therefore, studies on this river could clearly indicate the role of human activities in polluting rivers.

The concentration of anthropogenic ions (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}) and the COD values are good indicators how much a water body is polluted. The Kebena River, which traverses Addis Ababa north to south passes through the densely populated areas. The river starts up from scarcely populated area, at Entoto, passes through the highly populated areas and enters to Abasamuel. The anthropogenic ions concentration variation from upstream to downstream and concentration differences from wet season to dry seasons clearly shows the human impact as the human activity is intense downstream and as the surface runoff decreases and the waste water influx remains constant when the rain ceases. Hence, determination of the concentration of these indicator ions and following their time and space variation are the specific aims of this study. To study the influence of the runoff from the landfill at Jimma road (Kore) on the surrounding water bodies (Jemmo stream and the squeezed pond), Determination of the concentration of trace elements (Cd, Pb, Zn, & Cu) is an additional task of this study.

2. EXPERIMENTAL

2.1. Sampling and sample preparation

Sampling of Kebena river, Jemmo stream and the squeezed pond around the landfill was done cautiously to minimize sample contamination, using the standard methods [43-44].

Sampling of Kebena river was done every month, starting from the end of September 2000 to the beginning of April 2001, at the three sampling points representing upstream, midstream and downstream. Every month samples were collected from the same sample point. For the last three months a fourth sampling site was introduced (Table 3). Furthermore, the last sampling (at the beginning of April) included Abo river and Kebena river before they merge.

Each month samples were collected in the mornings (7.00-12.00 a.m.) and for some samples parameters like pH, conductivity, dissolved oxygen, and temperature were determined at the sampling sites. Samples were collected using one litter polyethylene bottles that were repeatedly washed with detergents and rinsed with distilled water before sampling and pre-rinsed with the water to be sampled immediately before sampling. Most of the analytical determinations were done promptly as the samples reach the laboratory. Samples were filtered using a 0.45 μm pore size filter paper and stored in the refrigerator at about 4^0C for the remaining analysis. The four sampling points; upstream at Kidane Mihret church (A), midstream at German Embassy (B), lower midstream at German school (C) and downstream at Urael church (D), are convenient sampling points to represent the river.

The river is shallow and it is believed that it does not show chemical stratification. Furthermore, these points are relative points of turbulence (Fig.3). The water samples from the area of the landfill were collected with a similar procedure as the kebena. The Jemmo stream and the pond are near the landfill. All the samples were collected using grab method.

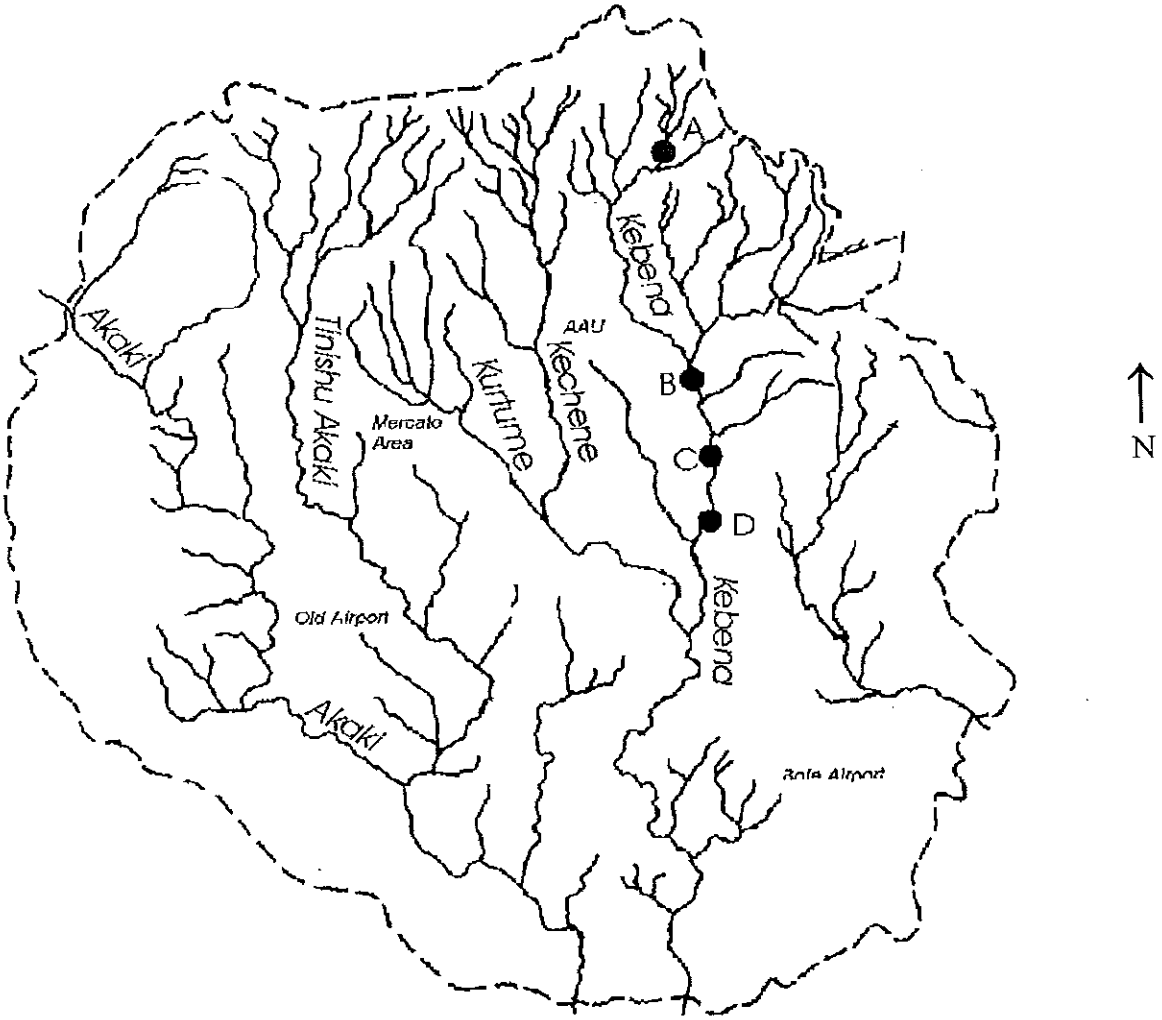
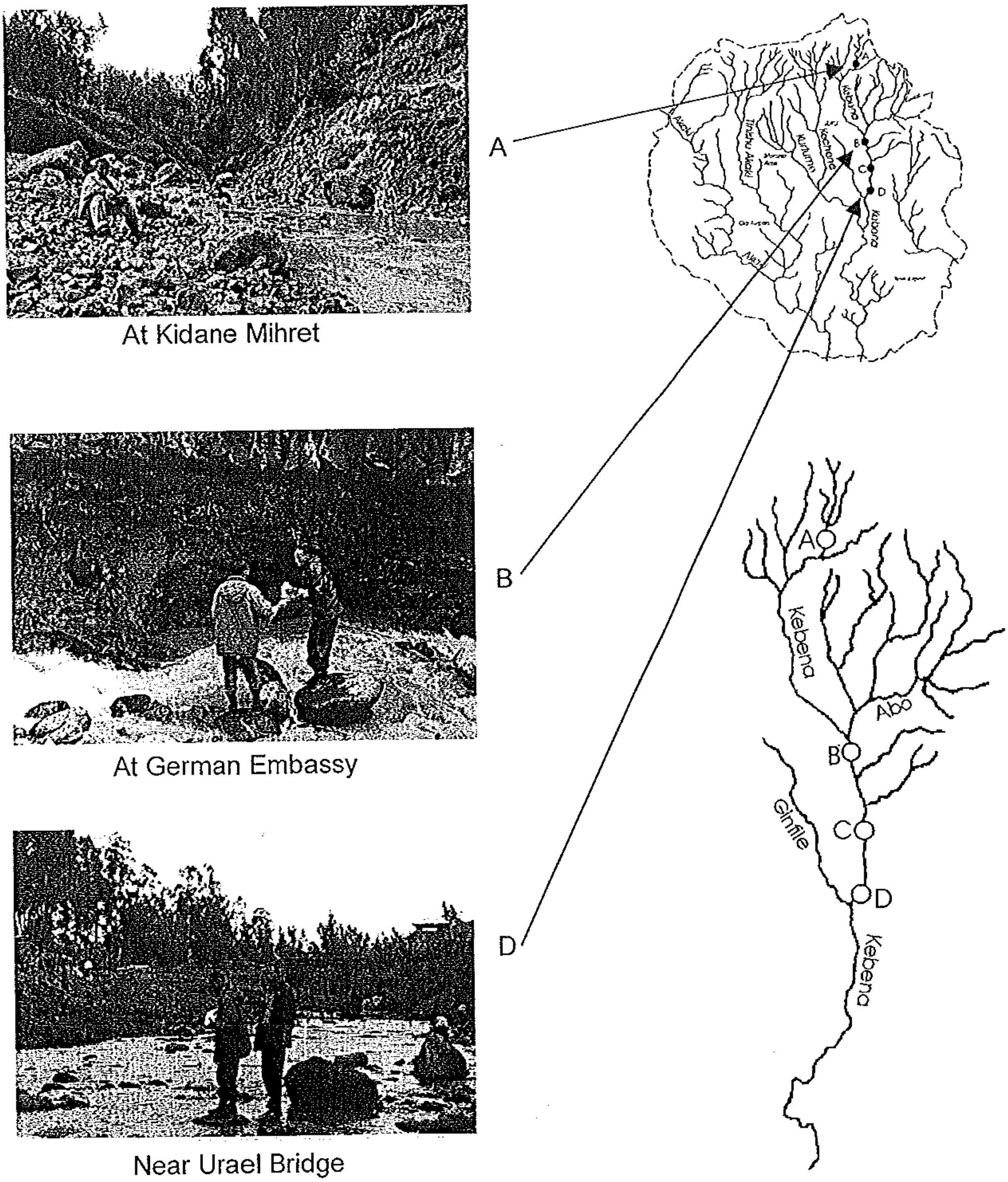


Fig 2. The rivers of Addis Ababa showing the sample points of Kebena river (A,B,C &D).


At Kidane Mihret

At German Embassy

Near Urael Bridge

Fig 3. The sample points at Kebena River

The sample sites at the Kebena are shown in the map above. The distance between sample point A and sample point D is about 7.5 km.

(10 ml) was added and the hot solution was back titrated with 0.1 N potassium permanganate solution until a just visible pink color appeared and remained for at least 30 seconds. The chemical oxygen demand is expressed in terms of oxygen in mg l^{-1}.

$$O_2\ (\text{mg } l^{-1}) = \text{Volume of } KMnO_4 \times 0.8 \times 1000/\text{Volume of sample}$$

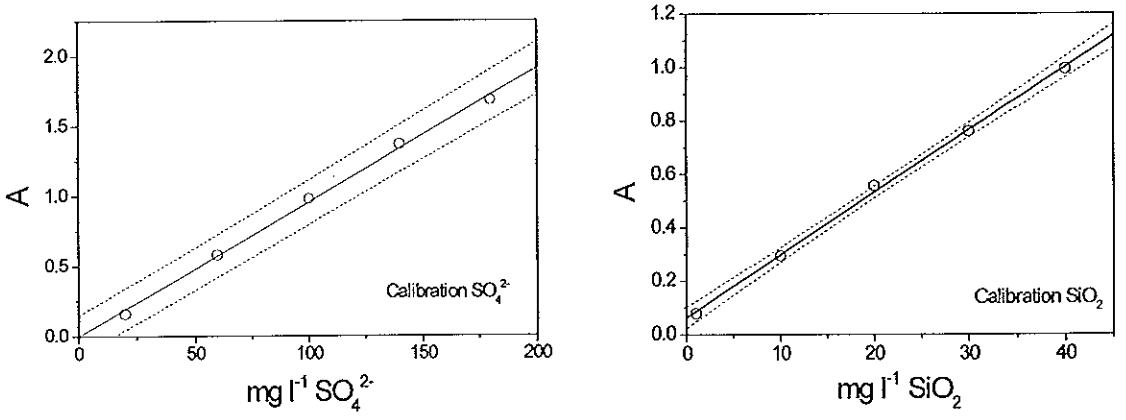
Alkalinity Determination

A 50 ml of unfiltered sample was transferred into a 250 ml Erlenmeyer flask and phenolphthalein indicator was added (pink color development resulted in titration by 0.1 N hydrochloric acid), if no color change occurred, methyl orange indicator was added and the solution was titrated using 0.1 N HCl until the color changed from yellow to orange.

Nitrate Determination

The absorbance of the filtered sample at 220 nm and 275 nm was measured. Twice the absorbance at 275 nm was subtracted from the absorbance measured at 220 nm in order to correct for the absorbance due to the presence of humic and fulvic acids. The calibration curve is shown in Fig. 4.1 (a). The Standard deviation of the method is reported to be $\sigma = 0.054$. The curve is linear within the range 0 - 10 mg l^{-1} with a correlation coefficient of 0.9985.

of the method is reported to be σ = 0.00725. The curve is linear within the range of 0 – 200 mg l^{-1} with a correlation coefficient of 0.9986.



(a) (b)

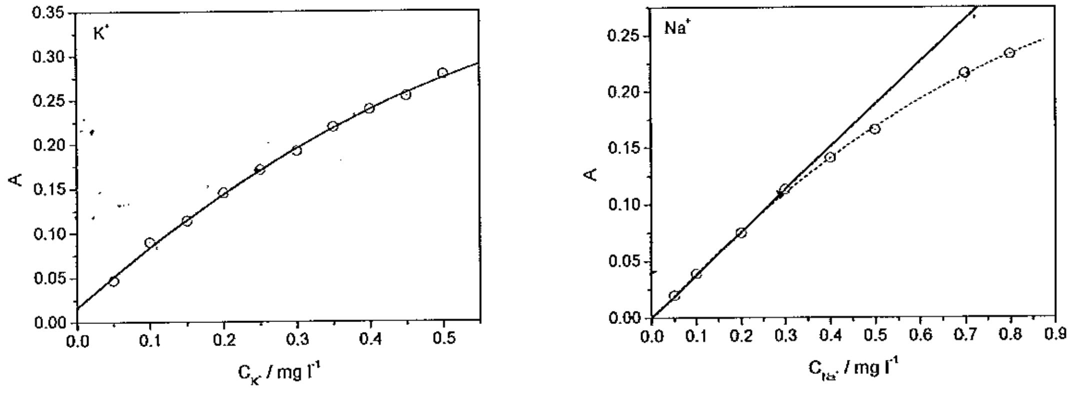
Fig. 4.3. Calibration curves for (a) SO_4^{2-} and (b) SiO_2

Determination of Silica

1 ml 1+1 hydrochloric acid (distilled water and conc. HCl) and 2 ml ammonium molybdate reagent (10 g to 100 ml) were added, in rapid succession, to 50 ml filtered sample. After 5-10 minutes 1.5 ml oxalic acid solution (10g dissolved to 100 ml) was added and the absorbance at 410 nm was measured after two minutes. The calibration curve is shown in Fig. 4.3 (b). The curve is linear within the range of 0 - 40 mg l^{-1} with a correlation coefficient of 0.9993.

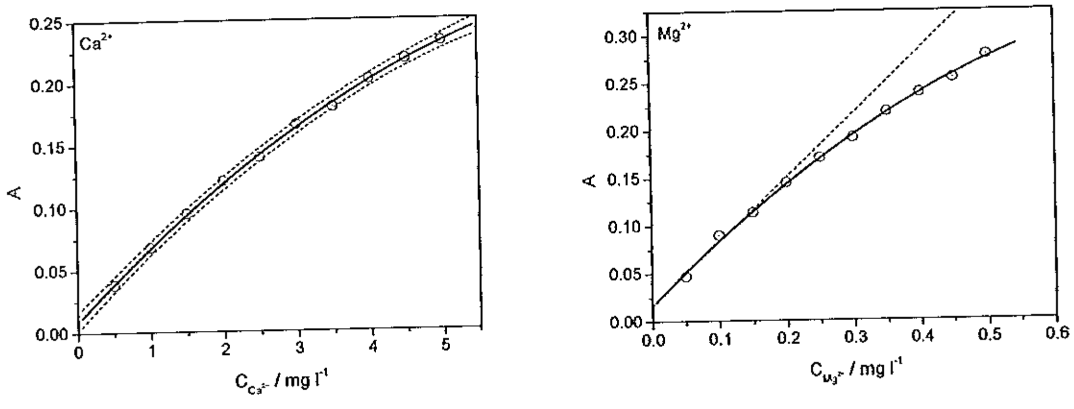
Determination of Major Cations (using Atomic Absorption Spectroscopy, AAS)

Determinations of Sodium, Potassium, Calcium, and Magnesium were accomplished using an air-acetylene flame atomizer and Na/K hollow cathode lamp at 589 nm for sodium and 766.5 nm for potassium. Ca/Mg hollow cathode lamp at 422.7 nm for calcium and 285.2 nm for magnesium were used as excitation source. The filtered samples were diluted to the desired level (within the linear range of the AAS) and aspirated to the flame atomizer and the absorbance recorded. The calibration curves are shown in Fig. 4.4.



(a) (b)

Fig. 4.4. Calibration curves for (a) K^+ and (b) Na^+



(c)

(d)

Fig. 4.4. Calibration curves for (c) Ca^{2+} and (d) Mg^{2+}

Chloride Determination

To 10 ml of filtered water sample 0.1 ml saturated potassium nitrate was added and the potential was measured (while stirring) using chloride selective electrode.

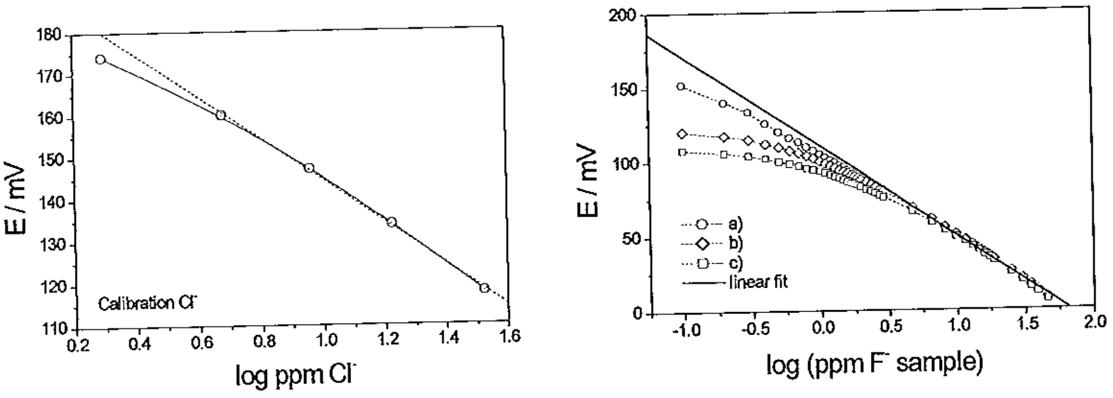


Fig. 4.5. Calibration curve for Cl^- and F^-: a) TISAB without ligand
b) TISAB with ligand (Original ORION)
c) TISAB with ligand (lab. Prepared)

Fluoride Determination

To 10 ml of filtered sample 1 ml TISAB (prepared by dissolving 4 gm cyclohexylene diamine tetra acetic acid (CDTA) in 500 ml distilled water and 57 ml glacial acetic. The pH was adjusted with 5 M NaOH to the range 5 - 5.5 and the solution was made to a liter) was added and the potential was measured (while stirring) using fluoride selective electrode.

Determination of trace elements

The determination was conducted using a mercury film electrode (mercury film was formed on glassy carbon electrode by adding 0.1 ml of 5 mmol mercuric nitrate solution to 10.0 ml sample and sweeping the potential from 0 to –2 V) with a Ag / AgCl reference electrode. The deposition of the metals on the mercury film was accomplished simultaneously with the film formation as the voltage changes from 0 to –2V. The dissolution (stripping) took place by sweeping the voltage to the positive direction (from –2 to 0 V).

3. RESULTS AND DISCUSSION

Water sample contamination is always a problem, and it increases in importance as the analyte concentration level decreases. The shore of the Kebena river is a place for different human activities (washing cloths, taking baths) and animal activities (for drinking) which rise the concentration of the anthropogenic ions and result in exaggerated ionic composition values. In order to avoid such misleading results, the Kebena river was sampled at the middle of the river using grab method.

Determinations like the COD and alkalinity should be conducted without filtering the sample since the species that contribute to these parameters might also be found in suspended form. The other parameters were determined after filtration in order to avoid interference from the suspended particles.

The analytical results of Kebena river at different dates and sample points are compiled in Tables 5 & 6.

The samples taken on the 29th of September 2000 were collected after a night of heavy rain, thus the water contains a considerable amount of surface runoff. Therefore the obtained results cannot be compared with those obtained from samples collected during the dry season and therefore they will be discussed separately. It is interesting to notice the pronounced increase in the concentration of chloride, bicarbonate, total nitrogen (nitrate, nitrite and ammonia) and phosphate (Fig. 5). With the justified assumption that at sample point *A* geogenic ions dominate, the increase in the concentration of these ions clearly shows their anthropogenic origin. When the concentrations obtained from a sample taken at sample point *D* are compared with those obtained from a sample collected at *A* chloride increases by a factor of about 10, bicarbonate by 6, phosphate by 5, sulfate by 1.3, silicate by 1.5 and fluoride remains unchanged. None of the nitrogen containing ions (nitrate, nitrite, ammonium) could be detected in the sample taken at *A*. The increase in the concentration of the cations follows a similar pattern. The increase factor for cations was found to be 15 for Na^+, 22 for Ca^{++}, 7 for K^+, and 14 for Mg^{++}.

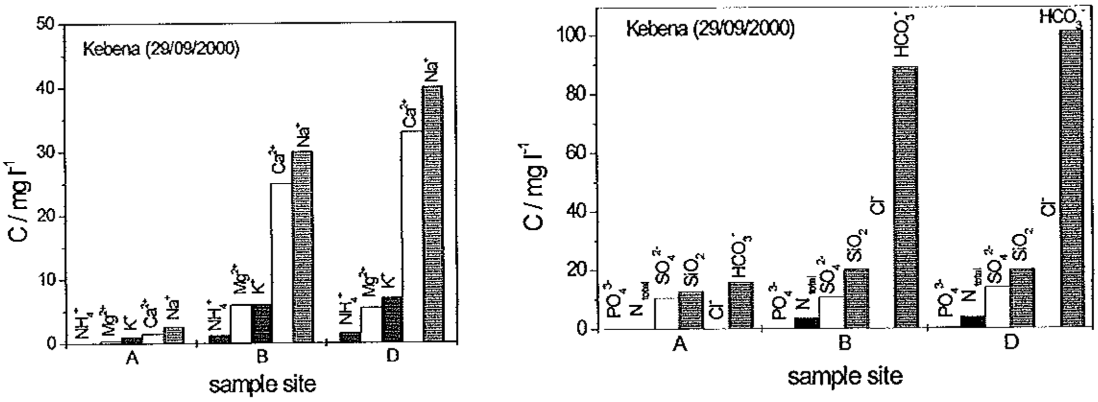


Fig. 5. Cation and anion composition of Kebena river at the three sample points (29/09/2000)

Table 5. Analytical Results of Kebeña River

Date	29/09/00			27/10/00			27/11/00			03/01/01		
Sample Point	A	B	D	A	B	D	A	B	D	A	B	D
Temperature/°C	17	15.8	15.9	17.7	18.7	16.2	17.5	15.9	15.3	8	11.7	12.9
COD/mg O l^{-1}	6.8	8.8	12	2	10	12	2.4	7.6	8.8	4	12	24
pH	6.9	7.4	7.6	7.9	8.0	8.0	8.1	7.9	7.8	7.4	7.6	7.9
Conductivity/mS	0.029	0.269	0.314	0.053	0.329	0.398	0.069	0.493	0.492	0.179	0.582	0.526
Nitrate/ppm N	N.D.	2.2	2.0	0.4	4.7	4.7	0.4	4.1	4.8	0.07	1.6	3
Nitrite/ppm N	N.D.	0.2	0.3	N.D.	0.52	0.63	N.D.	0.7	0.75	N.D.	0.37	0.17
Bicarbonate/ppm HCO_3^-	15.9	89.1	101.3	30.06	120.42	144.5	30.6	180.6	180.6	33.1	117.2	105.2
Sulfate/ppm SO_4^{2-}	10.5	10.7	13.9	4.95	7.96	8.17	7.5	9.9	11.9	24.3	11.1	12.9
Chloride/ppm Cl^-	3.3	33.0	37.4	3.3	43	47	3.5	59.3	61.6	3.4	64.8	59.5
Phosphate/ppm PO_4^{3-}	0.06	0.2	0.3	0.03	0.42	0.48	0.05	0.54	0.51	N.D.	0.81	0.69
Fluoride/ppm F^-	0.6	0.6	0.6	0.5	0.6	0.6	0.39	0.38	0.4	0.3	0.3	0.3
Silicate/ppm SiO_2	12.2	20	19.9	19.4	26	25.4	18.5	26.5	26.2	19	18	14
Sodium/ ppm Na^+	2.6	30	40	6	20	20	5	30	33	8	35	25
Potassium/ ppm K^+	1	6	7	3.6	5.6	7.4	2.2	9.1	10	4.3	10.5	9.5
Calcium/ ppm Ca^{2+}	1.5	25	33	0.8	34	33	1.2	46	32	3	36	32
Magnesium/ ppm Mg^{2+}	0.4	6	5.5	1.1	9	8.5	1.9	13.5	3.5	4	3.5	2.9
Ammonia/ ppm N	N.D.	1.2	1.5	N.D.	2	1.4	N.D.	4	0.9	N.D.	4	0.2

Table 5. Analytical Results of Kebena River (Continued)

Date	01/02/01				02/03/01				03/04/01			
Sample Point	A	B	D	C	A	B	D	C	A	B	D	C
Temperature/ °C	18.5	17.3	19	17	18	18	18	18	17	18	18	19
COD/mg O l^{-1}	2	8.8	10.4	10.8	3.2	13.2	7.6	12	4	11.2	10.8	9.2
pH	8.2	8.05	8.2	8.3	8.3	7.8	8	8	6.9	7.7	7.9	7.9
Conductivity/mS	0.195	0.598	0.588	0.631	0.306	0.745	0.633	0.708	0.064	0.575	0.569	0.557
Nitrate/ppm N	0.1	0.4	1.2	0.7	0.2	0.3	0.6	1.0	N.D.	0.9	0.8	0.7
Nitrite/ppm N	N.D.	0.07	0.31	0.22	0.003	0.013	0.21	0.1	N.D.	0.77	0.77	0.71
Bicarbonate/ppm HCO_3^-	72.1	270.5	240.5	276.6	90.18	330.6	270.5	314.6	30.6	228.5	228.5	234.5
Sulfate/ppm SO_4^{2-}	28.6	12.3	20.1	15.6	31.8	8.8	9.3	8.9	14.8	14.3	19.4	17.1
Chloride/ppm Cl^-	2.6	75.1	61.4	68.7	4.4	90	76.7	77	1.8	64.1	66.6	64.6
Phosphate/ppm PO_4^{3-}	0.06	0.97	0.86		0.04	1.87	0.68	1.36	0.09	0.89	0.76	0.85
Fluoride/ppm F^-	0.4	0.4	0.3	0.5	0.5	0.4	0.4	0.4	0.35	0.35	0.35	0.39
Silicate/ppm SiO_2	19.1	17.7	15.8	19.2	19.8	25.5	20.8	24.6	17.8	21.6	20	18.7
O_2 / mg l^{-1}					7.85	1.83	6.14	4.88				
Sodium/ ppm Na^+	9	33	40		9	45	50	40	3	44	34	34
Potassium/ ppm K^+	5	13	18		5	15	28	15	3	15	17	17
Calcium/ ppm Ca^{2+}	5	48	43		9	45	45	42	4	28	28	28
Magnesium/ ppm Mg^{2+}	5	18	13		8	22	17	21	2	24	24	24
Ammonia/ ppm N	0.0	7.6	4.5	9.0	0.1	13.7	3.1	12.5	0.0	5.6	6.5	5.5

3.1 Nitrogen containing ions

The nitrogen containing ions nitrate, nitrite and ammonium are mainly anthropogenic in origin and therefore good indicators for the human impact on the water quality. The source of inorganic nitrogen can be either the application of nitrogen fertilizers by farmers or the decay of organic matter. The term organic matter is rather wide and includes dead plant material as well as animal and human excretions. The first step in this decomposition process is the formation of ammonium ion from amino acids, proteins and urea by the action of a great variety of heterotrophic microorganisms. This step is referred to as ammonification and is followed by the nitirfication steps. The oxidation of NH_3 to nitrite is catalyzed by *Nitrosomonas* while the further oxidation to nitrate is mediated by *Nitrobacter*. *Nitrosomonas* and *Nitrobacter* are autotrophs and are believed to be the main genera of bacteria involved in the oxidation of ammonia and nitrite, respectively. Nitrification occurs under aerobic conditions at a higher reaction rate as ammonification. Thus the main product will be nitrate. At low oxygen concentrations the nitrification becomes slow and ammonia will accumulate. In the absence of oxygen nitrate can even been reduced by microbial mediation to the lower oxidation states. There are two other possible ways in the nitrogen cycle which have to be taken into consideration and are usually referred to as denitrification. On the one hand nitrogen gas can be formed from nitrite and nitrate, which will return to the atmosphere. The second possibility is the loss of chemically fixed nitrogen to the atmosphere by the formation of NO and N_2O catalyzed by bacteria. Finally it should be kept in mind that nitrate is utilized by algae as nutrient. The changes in the total nitrogen concentration are shown in Fig. 6.

followed by a rise at March after the time of the small "Belg" rain. The seasonal variation in nitrate content may primarily relate to the constant sewage influx while the surface runoff decreases. The variation in nitrate amount at the different sample points might be related with the nitrification process. As dissolved oxygen gets lower as one goes down stream the nitrification process slows down and the nitrate concentration decreases (sample point B). The lower part of the river is proved to regain oxygen due to the turbulent flow and reaeration that makes the nitrification process faster and the concentration of the nitrate ion to rise (sample point C).

A more or less similar trend is observed for nitrite ion. When we consider the ammonium ion, it shows almost a reverse pattern with the nitrate, at the first two months the ammonium ion concentration remains constant, then for the next two months the ammonium ion exhibits a constant increase (especially at B). As the dry season dominates and the organic matter increases (not subjected to dilution) the microorganisms consume the DO and the reduced form, ammonia, gets higher in amount. The other point, which might be in accordance with the amount of nitrate and ammonium ions, is the growth of algae. It has been observed that the growth of algae was significant starting from December until they were washed away during the small rainy season in March. Nitrate is more preferred than ammonium as nutrient for plants and algae that results in a decrease in its amount.

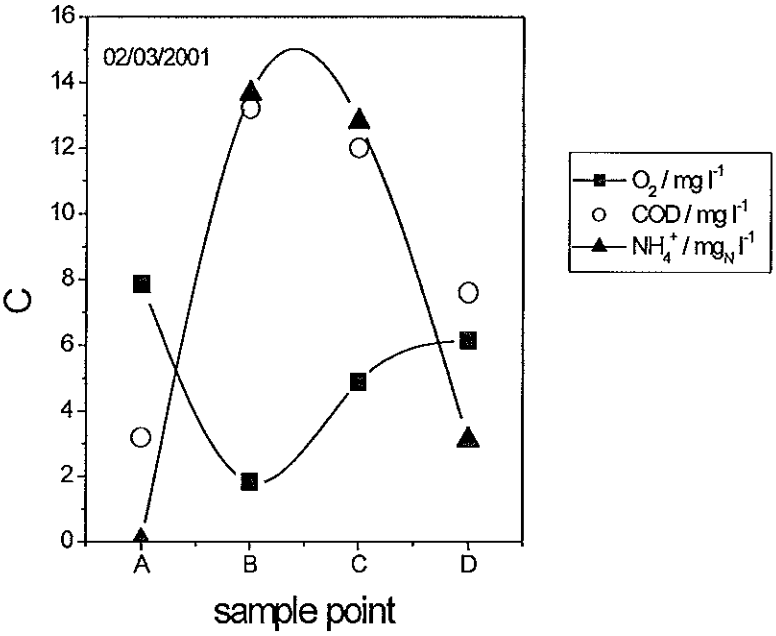


Fig. 8. The correlation between the DO, ammonium ion and COD values (02/03/2001) at the four sample points

As it can be seen from Fig. 8 the ammonium ion and DO values are inversely related. Upstream, where there is less organic load, the amount of DO is high and the environment gets oxidizing in which the reduced form (NH_4^+) is negligible in amount. As one goes down to sample point B where high organic load is introduced and depletion of DO is significant then the environment goes to reducing and ammonium ion concentration becomes maximum, as the DO is recovered the amount of the reduced form (NH_4^+) gets lower. The COD is also similarly related with the DO. The COD, which is an indicator for organic load and as a result indicator for the microorganisms that consume the DO for their metabolic process, has inverse relation with the DO as shown in the diagram.

The ternary diagram below (Fig. 9) compares the relative amounts of nitrate, nitrite and ammonium in samples taken one month after the rainy season (27/10/ 2000) and four month later (02/03/2001).

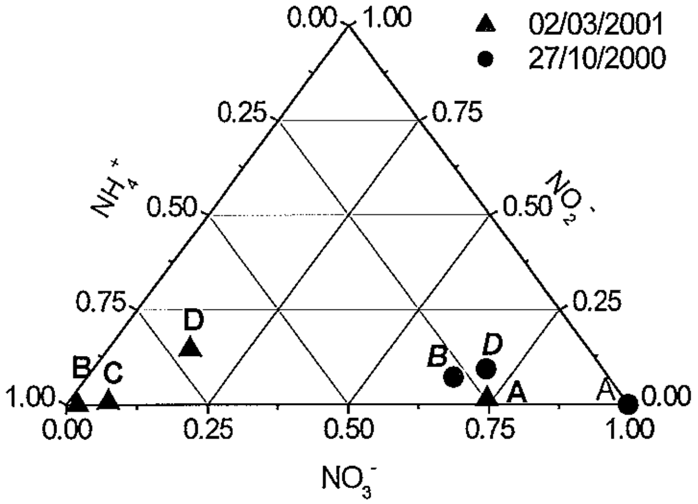


Fig. 9. Correlation of nitrate, nitrite and ammonium ions

During this period without any significant precipitation the flow rate of the Kebena river has drastically decreased. As a consequence the intake of oxygen from the air by turbulent flow of the shallow stream decreases while the influx of sewage remains unchanged and at the same time the consumption of dissolved oxygen by microorganisms reduces the DO content. It is clearly shown that the fraction of nitrate content drops from about 0.75 at sample point A where there is little organic matter introduction to almost zero at sample point B where high organic wastes and bacterial activity dominates, as the DO gets replenished the fraction of nitrate increases (C). The condition is not worse on the 27th of October since the dilution effect is not completely gone and no algal growth observed.

3.2 The phosphate ion

Naturally phosphorus is found in some rock forming minerals. Phosphorus is also one of the elements found in organic compounds and it is usually found in washing powders. It has been long since polymeric phosphorus oxoanions have been used as detergent builders. Hence, decomposition or degradation of organic matter gives phosphate ions. Phosphate ions are the limiting nutrients of most green plants and algae. The pH Range of Kebena River signifies that the dominating species found are $H_2PO_4^-$ and HPO_4^{2-} (Fig. 10).

As it is shown from Fig. 11 the amount of phosphate is increasing as the rain ceases and as one goes downstream, which clearly shows introduction of phosphate ion from anthropogenic source (organic waste and detergents).

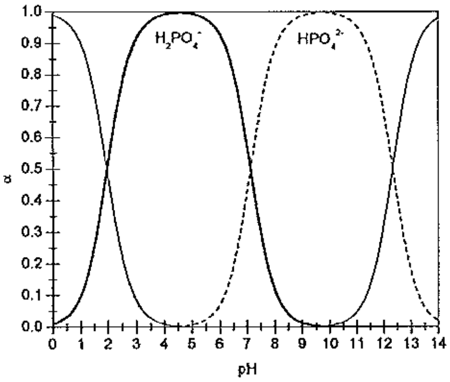


Fig. 10. Fraction of phosphate species with pH

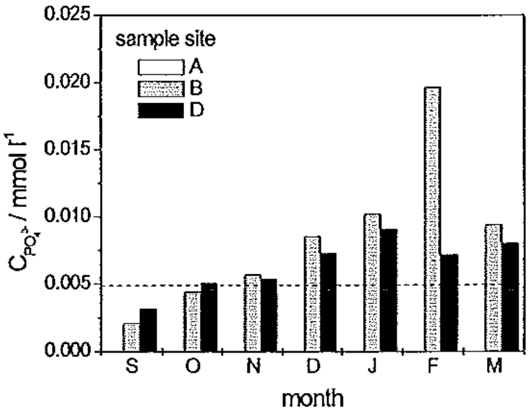


Fig. 11. Time and space dependence of phosphate ion concentration at the three sample points. (broken line shows the critical level of pollution.)

3.3 The sulfate ion

Sulfate ion is contained in some rock forming minerals and it is a widely distributed ion in nature. Its origin is therefore geogenic. The change of the concentration of sulfate with time and sample site is shown in the figure below (Fig.12).

The human impact on the sulfate ion concentration seems not so significant to draw conclusions about human activities from the concentration pattern shown in Fig. 11. The considerable increase of sulfate at sample point *A* in December, January and February is most probably caused by the utilization of two remaining water ponds (about 200 m upstream from the sample point) for laundering by nearby residents. Due to the very low flow rate of the river, sulfate can accumulate in the ponds. The contribution of less polluted water from the Abo river short before sample point *B* and the influx of waste water with a rather low sulfate concentration might be responsible for the decrease in the sulfate ion concentration observed at sample point *B* and *D*. The assumption that the reducing environment lowers the sulfate ion concentration cannot be proofed since no sulfide could be detected in the samples.

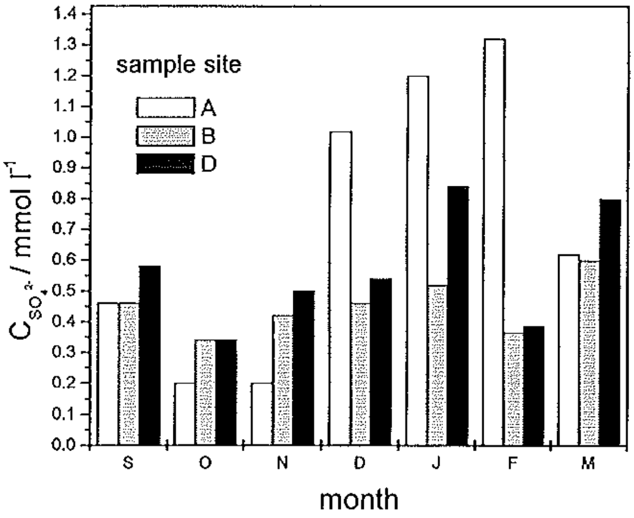


Fig. 12. Time and space dependence of the sulfate ion concentration at the three sample points *A, B* and *D*

3.4. The silicate ion

Silica is next to oxygen in abundance in the earth's crust. It is appearing as the oxide in many rocks and combined with metals in the form of silicate minerals. Degradation of these silica-containing rocks results in the presence of silica in natural waters. The pH range signifies the existence of silicic acid other than its ionic forms (Fig. 13).

As it is shown in Fig.14, the variation in silicate amount is not significant. These minor changes in amount of silicate tell us that it is more of geogenic origin than anthropogenic. The silicate values are also in accordance with the solubility of quartz and it is within the range SiO_2 is found in natural waters. The slight increase in the amount of the silicate (at B) may be due to some cleaning soaps that contain sodium meta silicate as binder.

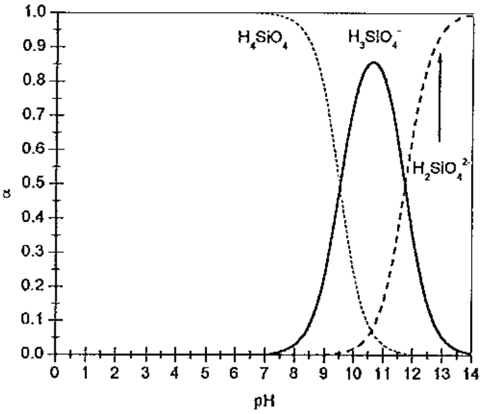


Fig.13.Fraction of silicate ions with pH.

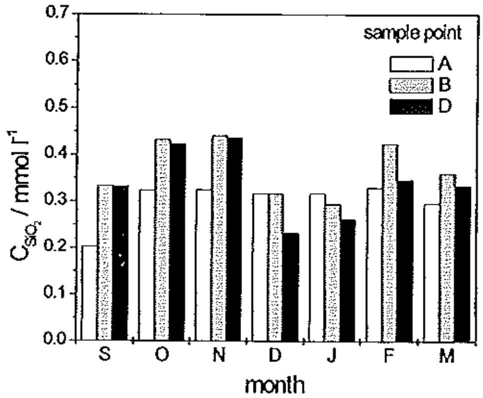


Fig.14. Time and space dependence of the amount of silicate at the three sample points.

3.5 The COD and the carbonate ion

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in a water sample. The main source of the bicarbonate ion is organic matter. The decomposition products of organic matter are CO_2 and H_2O but the pH range observed indicates that the bicarbonate ion is the dominant species found (Fig. 15).

Figure 16 indicates that the amount of COD and bicarbonate ion increase significantly from sample point A to B and then slightly decreases to C. This variation might be the result of high organic waste disposal at sample point B. It has been proved that at this point sewage lines are directly drained to the river.

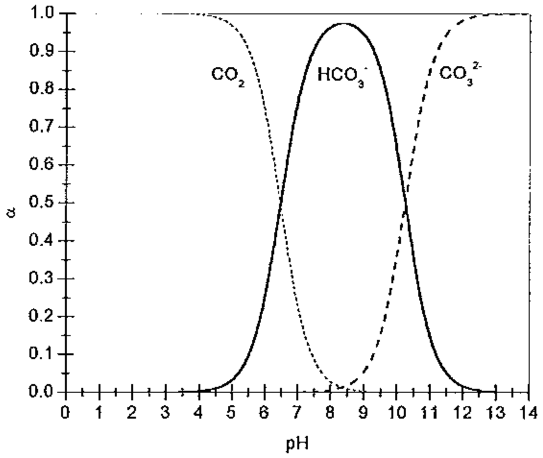


Fig. 15. Fractions of CO_2, HCO_3^- and CO_3^{2-} with pH

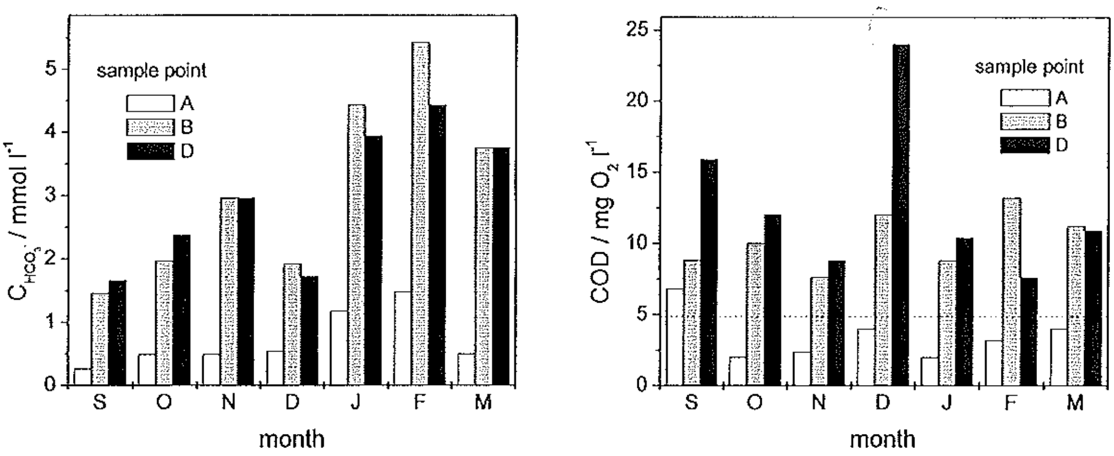


Fig. 15. Time and space dependence of bicarbonate ion and COD at the three different sample points (broken line shows the critical level of pollution).

The other point of interest at the fourth sampling date (Fig 15. D) is the high COD value and low bicarbonate content. The time of sampling was early as compared to the others. The temperature was low at all sample sites that was not convenient for bacterial action, as a result the action of microorganisms on the organic materials may be much less and the decomposition product, the bicarbonate ion, is small in amount. At the same time since the activity of microorganisms is low the biodegradation process is going to be slow and the COD value rises.

3.6 The chloride and sodium ions

The main source of sodium and chloride is the common salt, which is consumed by humans and most of it given out with out change during the excretion process [45].

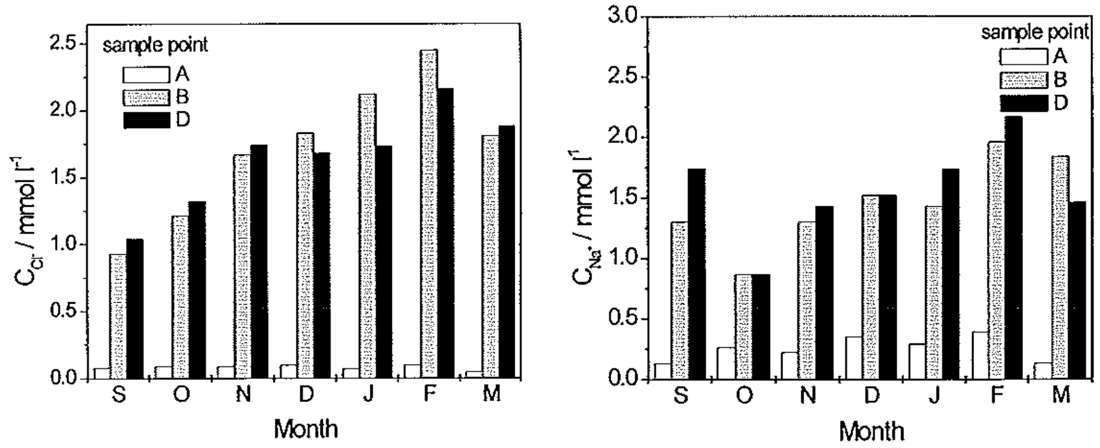


Fig. 17. The time and space dependence of composition of Cl^- and Na^+ ions at different sample points

Fig. 17 clearly shows that the amount of chloride ion increases continuously with the dry season and the population. Somewhat similar condition is also observed for the sodium ion. The sewage and municipal wastes usually contribute much for the introduction of these ions to the Kebena river as it is shown in Fig.17.

The correlation of these two ions is shown in Fig. 18. The graph is drawn to show the correlation of the amount of sodium ions with chloride ions to indicate their origin might be the same. The curve obtained is with a slope of one, y intercept –0.295, and with a correlation coefficient of 0.8576. The 95% confidence limit is also shown using the broken lines. The results signify that the two ions might be originated from the same source.

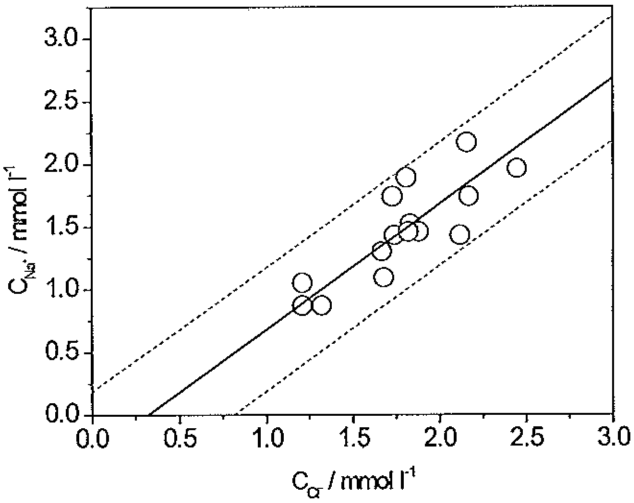


Fig. 18. Correlation of Na^+ with Cl^-

3.7 The fluoride, calcium, magnesium, potassium ions and trace elements

The fluoride ion shows no variation with time and space. This clearly indicates its geogenic origin. There are changes in concentration of the other cations (Ca^{2+}, K^{+}, Mg^{2+}) with time and space. These changes may be related with the different geologic environments through which the river is passing. There may also be some contribution from the human excretion [45]. Significant increase in concentration of the calcium ion may be related to the increase in the amount of CO_2 that increases in solubility of some calcium minerals. The increase in these cations needs much more investigation to arrive at a satisfactory conclusion.

The main aim of the analysis done to the water bodies around the landfill (Jemmo River and the squeezed pond) was to determine trace elements. The DPSV technique, which has a detection limit of 10^{-7} – 10^{-8} M for the trace elements, could not detect any of the trace elements of interest (Cu, Pb, Cd, Zn).

3.8 Abo and Kebena rivers

In order to follow the difference in contaminations due to the population density, samples were taken from the Kebena river and the Abo river short before they merge to compare the analytical data with those obtained at sample point B. The population density is much less at Abo than at Kebena. The results for the anthropogenic nitrogen containing ions are shown in Fig. 19.

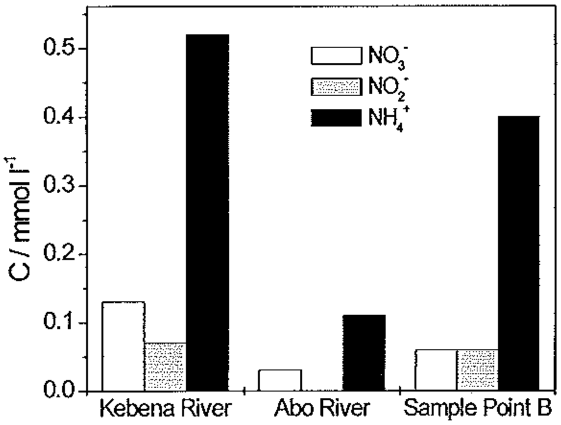


Fig.19. Comparison of nitrate, nitrite and ammonium ion concentration of Kebena, Abo and after merging at sample point B

The high population density around Kebena is clearly reflected in the significant difference in the concentration of these ions (Table 6). A similar picture is obtained if we compare concentrations of the other ions except fluoride, calcium and magnesium, which are nearly occurring at the same concentration in both rivers. This is illustrated in Fig. 20. Figure 20 shows the ratio of the concentration of ions in Kebena river (C_K) to the concentration of ions in Abo river (C_A).

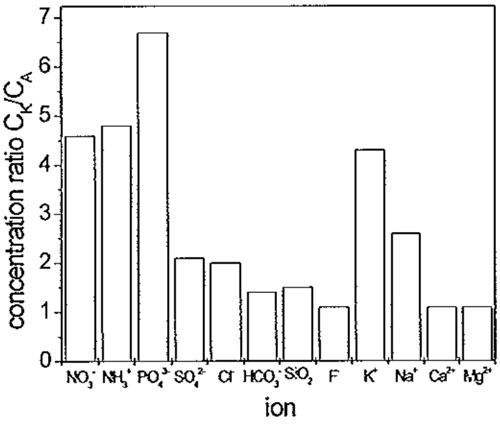


Fig. 20. Concentration ratio of Abo and Kebena rivers for different cations and anion

4. CONCLUSIONS

It has been seen from this work that nitrogen-containing ions contribute much for the deterioration of the Kebena river. The sources of nitrogen, which are believed to be organic matter from domestic waste and urea and ammonia from sewages, have very high contributions and they are good indicators of how human activities introduce much of the impurities into the river.

The corresponding values of phosphate, chloride and sodium ions, which increase with population, are proved to be more of anthropogenic than geogenic. Therefore, introduction of these species to the river results in pollution of the water body.

The COD is the main means for the increment of microorganism populations. As the value of the COD increases the microorganisms, which depend on the organic matter increase. Most of these microorganisms are responsible for causing health risks.

It has been seen from the results obtained that the amount of all the anthropogenic ions are above the level of the critical pollution point. This may not be a problem for ground waters since nature may undergoes limited self-purification processes and by filtration and adsorption the seeping water gets purified. The problem arises when people use surface waters. As it is seen the banks of Kebena are busy with people who use the water for bathing, washing clothes, and for irrigation purposes. These activities are exposing people to the microorganisms that cause health problems.

To curb such problems it is advisable to build seepage type septic tanks in the unsaturated zone, to avoid connection of septic tanks with storm drains, and to avoid direct discharge of solid and liquid wastes directly into the river.

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