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Effect of training on serum levels of skeletal muscle enzymes in athletes playing taekwondo

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ABSTRACT

Over the past 20 years, several reports focused attention on the study of serum enzyme activities in athletes and untrained individuals, suggesting their potential role as markers of skeletal muscle adaptation and physical performance.

The main goal of our study was to analyse the different effects of 5 weeks detraining and 6 weeks aerobic training on CK and LDH activity (total and isozymes) in a population of athletes playing taekwondo. Serum LDH activity was higher after detraining compared with that obtained after training, suggesting a possible effect of the training on LDH activity. Furthermore, studying the distribution of the specific isozymes in both tests, we found that detraining increased LDH4 and LDH5 values and decreased LDH1, LDH2 and LDH3 activities. A subsequent period of physical training was able to restore the normal values, except for LDH5 activity that remained higher. On the other hand, total serum LDH and specific isozyme activities changed according to the training status of the athlete even for short periods of training. These data probably reflect the physiological adaptation of the athlete following physical training. Long term physical training has only little influence on the total release of CK from tissue to blood of all isoenzymes.

KEY WORDS

LDH isozymes, detraining, aerobic training
INTRODUCTION
The serum level of skeletal muscle enzymes is a marker of the functional status of myocytes and varies widely in both pathological and physiological conditions. An increase in enzyme represents an index of cellular necrosis and tissue damage following acute (rhabdomyolysis) and chronic (dystrophinopathies) muscular injuries (1). Changes in the levels of muscular enzymes and isozymes has also been reported in normal subjects and athletes after strenuous exercise (2,3,4,5).
In athletes, several reports suggest that the amount of enzyme efflux from tissue to blood can be influenced by physical exercise. Muscle biopsy findings evidenced different activity of total lactate dehydrogenase (LDH) and LDH isozymes in endurance and strength athletes: the former had lower total LDH with prevalence of LDH1,2 isozymes activity compared with the latter, which showed higher values of total LDH and prevalence of LDH3 activity (6, 7, 8).
In addition, plasma LDH and creatine kinase (CK) activity showed different behaviour before and after physical exercise, depending on different protocols, intensity and level of training (9,10). An increase of plasma enzyme activity has also been observed after detraining (11).
However, because these studies have been performed mostly in sprint and distance runner athletes, little is known about enzyme activity in other sporting disciplines. The aim of this study is to evaluate the serum activity of skeletal muscle enzymes and isozymes at rest and after a short period of aerobic training in athletes playing taekwondo.

SUBJECTS
Seven athletes playing taekwondo (males, mean age 21±1.2), at the same level of physical training and athletic performance were consecutively enrolled and examined twice: after 5 weeks of detraining (D test); after 6 weeks of aerobic-anaerobic training (T test).
During D test, all the athletes underwent detailed personal history collection, physical examination, spirometry, and exercise test. The athletes were asked to fill a form to exclude smoke, alcohol, drug and/or ergogenic substances use during the five weeks before the test. During both tests, blood samples were collected in the morning after 12 hours of fasting and, only before T test, after 48 hours of detraining.

Analysis of plasma enzymes and isozymes activity
Serum LDH and its isozymes activities (LDH1, LDH2, LDH3, LDH4, LDH5) and CK and its isozymes activities (CK-MM, CK-MB, CK-BB) were analysed and within 12 hours after blood sample was taken. CK and LDH enzymes were determined according to standard protocols, (Pharmacia LKB-vitrospec) the normal values at 25°C of temperature were the following:
CK= 10-80 U/L; LDH= 113 - 189 U/L (151 ± 38)
Isozymatic evaluation was performed by agarose-gel electrophoresis and determined by Beckman Appraise Densitometer System method. Reference values are as follows:
• CK-MB= 0 – 4.8 %; CK-MM= 0 – 80 %; CK-BB= 0 %
• LDH1 = 25.5 ± 5.5%
• LDH2 = 33.7 ± 7.5%
• LDH3 = 20.8 ± 4.8%
• LDH4 = 10.7 ± 3.2%
• LDH5 = 9.4 ± 3.7%

Training protocol
Between D and T test, the athletes underwent to aerobic-anaerobic training three times per week (6 hours/week).
Every session training included:
• 10 minutes for warming up (slow run)
• 20 minutes of exercises for joint mobility
• 2 X 15 minutes of circuit training for muscular power
• 30 minutes of technical exercises
• 30 minutes of running at 75% maximal heart rate (5 minutes more every week)

Statistical analysis
Statistical analysis was performed by SPSS statistical package for Windows, release 10.0 (Chicago, IL, USA). Comparison between D- and T-test was performed by Student’s t test for correlated samples (paired t test). Differences were considered statistically significant when p<0.05.

RESULTS
CK activity
Total CK activity was always within the normal range and no significant differences were evidenced be-
between the D and the T test (52.83 ± 25.90 vs 47.25 ± 6.47, respectively; p = 0.59: Fig. 1). The analysis of isozymes showed exclusively the presence of CK-MM in both samples, while no CK-MB or CK-BB activity was measured.

**LDH activity**

Total LDH activity, although within the normal ranges, showed significant differences among the 2 tests (D test: 180.5 ± 12.48; T test: 161.5 ± 8.67; p=0.01; Fig. 2).

Serum LDH isozymes were evaluated either as in absolute value, either as in percentage. During D-test, in both absolute and percentage value, LDH$_4$ and LDH$_5$ activity was above the normal range, while LDH$_1$ and LDH$_3$ resulted lower. Also the percentage of LDH$_2$ activity was below the normal range. LDH isozymes activities were found normalized during T-test, except for LDH$_3$ activity which remained high.

**Statistical Analysis:** The results obtained during D- and T-test were then compared. LDH$_1$ and LDH$_2$ activities were higher in T-test compared with D-test, whilst LDH$_4$ and LDH$_5$ activities were higher in D-test both in absolute and percentage values (Tab I-II). LDH$_2$ activity resulted higher in T-test, reaching statistical significance only in percentage values (Tab. II). Finally, we evaluated the LDH$_1$/LDH$_2$ percentage activity ratio. Compared with T-test, in the D test LDH$_1$/LDH$_2$ ratio was significantly lower (0.41 vs 0.65; p = 0.00; Tab. III).

![Figure 1 - Total CK at rest](image1)

![Figure 2 - Total LDH at rest](image2)
DISCUSSION
Over the past 20 years, several reports focused attention on the study of serum enzyme activities in athletes and untrained individuals, suggesting their potential role as markers of skeletal muscle adaptation and physical performance (8,9,12). However, the main part of these studies analysed serum enzyme activities after physical effort and, particularly, in sprinter athletes (8,9,13).

The main goal of our study was to analyse the different effects of 5 weeks of detraining and 6 weeks of aerobic training on CK and LDH activity (total and isozymes) in a population of athletes playing taekwondo. No change in CK activity before and after training was found as far as no variation in isoform expression (only CK-MM was present). These data are in agreement with other reports (14), suggesting that physical training has probably little effect on CK activity. On the other hand, several studies reported higher release of CK after physical exercise in untrained subjects, as a marker of exercise-induced muscle injury (9). Therefore, the analysis of CK activity seems more suitable to study the effects of physical effort on muscles in pathological conditions, such as over-training and muscular injury, rather than to evaluate the physiologic status of muscles in athletes. The study of CK as a marker of muscular injury could be useful, particularly in athletes playing sports with high risk of muscular injuries, such as taekwondo.

Serum LDH activity was higher in D test compared with T test, suggesting a possible effect of the training on LDH activity. Klapcinska et al., studying the effects of sprint running on serum markers, showed that plasma LDH activity, measured immediately post-run, was higher in untrained individuals compared with competitive runners (9). Karlsson et al., comparing muscle biopsies from endurance athletes, strength athletes and untrained individuals, found that endurance athletes had lower LDH activity, while strength athletes had higher LDH activity (8). The different behaviour in serum LDH activity

| Table 1 – LDH isoenzymes in absolute value (U/l) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | D TEST          | T TEST          | f.d.           | p               |
| LDH1            | $18.00 \pm 4.28$ | $36.17 \pm 3.34$ | 6              | 0.00            |
| LDH2            | $44.75 \pm 3.20$ | $55.83 \pm 5.11$ | 6              | 0.00            |
| LDH3            | $23.75 \pm 3.28$ | $26.83 \pm 3.44$ | 6              | 0.20            |
| LDH4            | $28.75 \pm 4.91$ | $13.83 \pm 3.02$ | 6              | 0.00            |
| LDH5            | $65.25 \pm 9.53$ | $28.67 \pm 5.22$ | 6              | 0.00            |

D Test: test after detraining
T Test: test after training
observed in our athletes can be explained by the fact that despite they were strength-endurance athletes, the main part of the training protocol was based on aerobic training. In addition, studying the distribution of the specific isozymes in both tests, we found that detraining seems to have different effects on isozyme activities, increasing LDH4 and LDH5 values and decreasing LDH1, LDH2 and LDH3 activities. The subsequent period of physical training restored the normal values, except for LDH5 activity that remained high.

The increased activity of LDH1 and LDH2, evidenced in T test, is probably due to the wide involvement of aerobic metabolism: the aerobic training, although maintained for a short period (5 weeks), induced the physiological adaptation we expected. Conversely, the decrease of LDH4 and LDH5, involved in production of lactate from pyruvate, evidenced the lower involvement of anaerobic metabolism during physical training.

An increase in LDH3 activity is unusual and not previously reported in literature: however, since this isozyme has two “H” chain it is probably modified by aerobic training.

**LIMITS OF THE STUDY**

Our results, although interesting, are limited by the small number of individuals analysed, and need to be confirmed in a larger population study. Furthermore, because a muscle biopsy was not performed, the relationship between plasma activities and fibres type, as previously reported, cannot be assessed.

**CONCLUSIONS**

Long term physical training has only little influence on the release of total CK from tissue. On the other hand, serum total LDH and specific isozyme activities change according to the training status of the athlete, even for short periods of training. This behaviour, they probably represent part of the physiological adaptation of the athlete to the physical training.

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Mineromedicinal springs of Cuba and their potential for Public Health

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ABSTRACT
Cuban mineromedicinal water has a well known quality to be use in health resort medicine, tourism health medicine and rehabilitation. In this paper we show the mainly mineromedicinal spring waters of Cuba and their use in public health. With this we try to encourage a better understanding and use of this medicinal resource in prevention and rehabilitation of multiple health conditions.

KEY WORD
Health resort medicine, medical hidrology, Rehabilitation.
Natural Medicine in Cuba have been approved to the most higher of Health Ministry level no as an alternative or complementary procedure. Despite of that is a valid medical specialization that integrates procedures from Chinese Traditional Medicine, Homeopathy, Medical Hydrology, Physical Therapy Medicine and others. Even more a national health program on Natural and Traditional Medicine have been issued in order to integrate this modalities to the rest of conventional medical specialities. (1) In this paper we intend to give some picture about the state of art of medical hydrology changes in recent years. Cuba Island has more than 1000 of mineromedicinal springs waters, and many more springs still without a proper certification of quality. Also there is many muds springs all well know in their chemical and physical properties.

In early 80 years began starts the scientific age on muds research. The National Centre of Rehabilitation Julio Diaz Hospital started many biomedical research in which therapeutic effects of muds were determine in chronic diseases in functional rehab stages. But regarding mineromedicinal waters from ancient times like XV and XVI centuries were well known. In places were springs were located people empirically started to used seeking health benefits. During XIX century began a scientific activity in order to determine their properties, mineral composition and its therapeutical effects. In those year a few people could recived this benefits (2).

The constitution of the National Institute of Medical Hydrology and Climatology in 1945 headed by professor Victor Santamarina, allowed a better understandig and complete knowledge of mineromedicinal springs waters of Cuba. Academic activities were encouraged at that time and published their findings and international interactions in the Annals of the Medical Hydrology and Climatology Institute. Empirical stages keeps behind. After a few years of silence Cuban Medical Hydrology rises again in year 1996. After further activities of the National Group of Mineromedical Waters (formal National Group of Thermalism) under the direction of Jesus Montane Orpresa the National Centre of Thermalism Victor Santamarina were created until year 2003. This starts a new era of work (3).

Graph 1. Mineromedicinal springs waters of Cuba used in medical rehab and tourism.

Source: Tropical Geography Institute Tropical
Cuba has great mineromedicinal resources potential. In picture 1 we illustrate the wide variety of mineromedicinal springs waters in our country. Despite exists many classifications that depend according to the origin, the temperature, tonicity, global mineralization or quantitative mineralization, chemical composition, physiologic actions, therapeutic activity, flow, and even including types according to geologic standardises and tectonic characteristics of the place where it emerge (geologic classification) (3). From the point of view of therapeutic the classification actually used operatively is according to the osmotic pressure in connection with the corporeal fluids and the temperature for its practical value. In Cuba and other countries the diffused classification its based one in the water content of anions and predominant cations or balneologic classification. According to it chart 1 shows distribution of springs according to locations by counties and the different balneological groups present. We include the number of each spring studied. Recent national books and documents, pick up this type of classification (4) but the bigger operative difficulty of this type of classification for our doctors; rests in their integration according to the own characteristics of each sources.

Chart 2 show therapeutic uses according to these balneologic groups. The same one summarizes groups of pathologies that can be benefitted with the use of this particular type of water. Something very useful in Health Tourism.

Medical evidence has shown that cuban termal resources, such as mineral waters and muds are useful in keeping health (5,6) But still more research is needed.

<table>
<thead>
<tr>
<th>Yacimientos</th>
<th>Provincia</th>
<th>Grupo balneológico</th>
</tr>
</thead>
<tbody>
<tr>
<td>la Fé (13,17)</td>
<td>Youth Island</td>
<td>Iron and Sulfuric waters</td>
</tr>
<tr>
<td>Delita (12,13)</td>
<td>Youth Island</td>
<td>Arsenic an diron waters</td>
</tr>
<tr>
<td>El Rosario (17)</td>
<td>Youth Island</td>
<td>Sulfuric waters</td>
</tr>
<tr>
<td>Bermejales (14,17,18)</td>
<td>Pinar del Río</td>
<td>Floruride, sulfuric, Silicic waters</td>
</tr>
<tr>
<td>San Vicente (17,3,5)</td>
<td>Pinar del Río</td>
<td>Sulfuric, Sulfatic calcic waters.</td>
</tr>
<tr>
<td>Soroa(17)</td>
<td>Pinar del Río</td>
<td>sulfuric waters</td>
</tr>
<tr>
<td>Rancho Mar (1,13,14,17,18)</td>
<td>Pinar del Río</td>
<td>bicarbonate, iron, fluoric waters</td>
</tr>
<tr>
<td>Santa Maria del Rosario (17)</td>
<td>Havana City</td>
<td>Sulfuric waters.</td>
</tr>
<tr>
<td>El Sulfuroso (17,18)</td>
<td>Havana City</td>
<td>Sulfuric, silicic waters</td>
</tr>
<tr>
<td>Tarará(9,15,17)</td>
<td>Havana City</td>
<td>Bromuride, Stroncic, sulfuric waters</td>
</tr>
<tr>
<td>La Paila(17,18)</td>
<td>Havana</td>
<td>Sulfuric, Silicic waters</td>
</tr>
<tr>
<td>San Miguel de los Baños(17,18)</td>
<td>Matanzas</td>
<td>Sulfuric, Silicic waters</td>
</tr>
<tr>
<td>Menéndez(2,3,4,5,6,9,15,16,17)</td>
<td>Matanzas</td>
<td>Clorurate, sulfatic, sodic, calcic, magnesc, bromurade, stroncic, boric, sulfuric waters.</td>
</tr>
<tr>
<td>Elguea(2,3,4,5,6,8,9,17)</td>
<td>Villa Clara</td>
<td>Clorurate, sulfatic, sodic, calcic, magnesc, bromurade, stroncic, boric, sulfuric waters.</td>
</tr>
<tr>
<td>Amaro(7)</td>
<td>Villa Clara</td>
<td>Sulfuric waters</td>
</tr>
<tr>
<td>Ciego Montero(17,18)</td>
<td>Cienfuegos</td>
<td>Sulfuric, Silicic waters</td>
</tr>
<tr>
<td>Arima(o)</td>
<td>Cienfuegos</td>
<td>Without specific properties and composition waters</td>
</tr>
<tr>
<td>Yaguanao-San Juán(8)</td>
<td>Cienfuegos</td>
<td>Aguas Radónicas</td>
</tr>
<tr>
<td>El Guije(17)</td>
<td>Sancti Spiritus</td>
<td>Aguas Sulfuradas</td>
</tr>
<tr>
<td>San José del Lago(7)</td>
<td>Sancti Spiritus</td>
<td>Without specific properties and composition waters</td>
</tr>
<tr>
<td>El Azufr e(2,4,5,17)</td>
<td>Ciego de Avila</td>
<td>Clorurate, sodic, magnesc, sulfuric waters</td>
</tr>
<tr>
<td>Tamarindo(17,18)</td>
<td>Ciego de Avila</td>
<td>Sulfuric, silicic waters</td>
</tr>
<tr>
<td>Vera Cruz(2,4,5,6,17)</td>
<td>Ciego de Avila</td>
<td>Clorurate, sodic, calcic, magnesc, sulfuric waters</td>
</tr>
<tr>
<td>Camuñírio(2,4,5,8,17)</td>
<td>Camagüey</td>
<td>Clorurate, sodic, calcic, radon, sulfuric waters</td>
</tr>
<tr>
<td>La Morena(2,4,5,8,11,15,16,17)</td>
<td>Holguín</td>
<td>Sulfuric, calcic, bromurides, yodide, sulfuric waters</td>
</tr>
<tr>
<td>La Cuquita(2,4,5,8,9,10,15,17)</td>
<td>Santiago de Cuba</td>
<td>Clorurate, sodic, calcic, bromurides, yodide, sulfuric waters</td>
</tr>
<tr>
<td>El Cedrón(3,5,14,18)</td>
<td>Santiago de Cuba</td>
<td>Sulfatic, calcic, fluoride, silicic waters</td>
</tr>
<tr>
<td>Amores(7)</td>
<td>Guantánamo</td>
<td>Without specific properties and composition waters</td>
</tr>
</tbody>
</table>
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Seasonal variations and correlation coefficient in Atmospheric temperature, DO, BOD and COD at Harsool-Savangi dam, district Aurangabad, [M.S] India

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ABSTRACT

The present study deals with assessment of the physico-chemical parameters and correlation coefficient in atmospheric temperature DO, BOD and COD of Harsool-Savangi dam, Aurangabad [M.S] India. The physico-chemical characteristics and correlation coefficient were studied and analyzed during January 2009 - December 2009. Seasonal variations at four different sampling sites of the Harsool-Savangi dam, Aurangabad [M.S] India were observed. The results revealed that the condition of this dam in different seasons showed fluctuations in physico-chemical parameters. Correlation coefficient indicates negative correlation of atmospheric temperature with DO, BOD and COD. Correlation coefficient indicates negative correlation of atmospheric temperature with DO, BOD and COD. Correlation coefficient indicates show high significant positive and negative relationship (p < 0.01 level) and also show significant positive and negative relationship (p < 0.05 level).

KEY WARDS

Physico-chemical parameters, seasonal variations, correlation coefficient, Harsool-Savangi dam.
INTRODUCTION

Water dissolves numerous substances in large amounts, pure water rarely occurs in nature. Precipitation absorbs carbon dioxide and other gases as well as traces of organic and inorganic material from the atmosphere. Because water reacts with minerals in the soil, rocks, surface and groundwater may contain many different dissolved substances. Surface waters may also contain domestic sewage and industrial wastes. Groundwater from shallow wells may contain nitrogen compounds and chlorides, but water from deep wells generally contains only dissolved minerals.

Water quality deals with the physical, chemical and biological characteristics in relation to all other hydrological properties. Any characteristic of water that affects the survival, reproduction, growth and production of aquaculture species, influences management decisions, causes environmental impacts or reduces product quality and safety can be considered a water quality variable. Other factors being the same, aquaculture species will be better, production more, environmental impacts less and quality better in culture systems with “good” water quality than in those with “poor” water quality (1).

The physico-chemical parameters studied as abiotic components individually and collectively. Further, these parameters exhibit diurnal and seasonal variations apart from variations resulting from geographical and climatic conditions.

Due to open nature, continuous exchange of matter and energy goes between the aquatic ecosystems and its environment apart from stress resulting from man made activities. In general, pollution invariably alters water quality, in turn influencing biogeochemical cycles, diversity, biomass and overall trophodynamics. Any change in the physico-chemical environment has direct influence on biotic communities due to the fact that different species of flora and fauna exhibit great variations in their responses to the alter environment, (2).

In India some hydrobiological work on historic shallow water bodies like temple reservoir and village ponds have been done (3,4,5,6).

MATERIAL AND METHODS

The water samples for physico-chemical analysis were collected from Harsool-Savangi Dam, geographical coordination 19° 56′ 14.32″ N and 75° 21′ 30.56″ E Aurangabad, (M.S) India, at 4 different sites viz., Station 1 (South side), Station 2 (East side), station 3 (North side) and station 4 (West side) in the early morning between 8 am to 11 am in the first week of every month from January to December 2009. The samples were collected in acid washed five liter plastic container from a depth of 5-10 cms below the surface of water. Separate samples were collected for dissolve oxygen in 250 ml bottles and dissolved oxygen was fixed in the field by adding alkaline iodide-azide solution immediately after collection. The samples were analyzed immediately in the laboratory.

The physico-chemical characteristics of the dam water like Atmospheric temperature, DO, BOD and COD were determined in summer, monsoon and winter according to standard methods (7,8).

RESULT AND DISCUSSION

The seasonwise physico-chemical parameters data of Harsool-Savangi dam, Aurangabad [M.S] India have been presented seasonal mean values, seasonal standard deviation, seasonal coefficient variation and Correlation coefficient of different parameters data has been presented in table. No. 1 & 2 and fig. 1. A to D.

PHYSICO-CHEMICAL CHARACTERISTIC

Atmosphere Temperature

Temperature is very important parameter, because it influences the biota in a water body by affecting activities such as behaviour, respiration and metabolism. It is necessary to study temperature variations in water body, in animals ecophysiological and toxicological aspects because, water density and oxygen content are temperature related and hence temperature indirectly affects osmoregulation and respiration of the animal (9).

The maximum value was recorded 37.42±0.39 (°C) and coefficient variation was 1.04 % recorded during summer; minimum value was recorded 22.26±0.63 (°C) and coefficient variation was 2.83 % recorded during winter. The overall mean was 29.02±7.71 (°C) and coefficient variation was 26.56 % and correlation coefficient of atmospheric temperature with DO, BOD and COD respectively as follow - 0.94**, - 0.76**, and - 0.76** (Table No. 1 & 2 and Fig 1. A).

In the present investigation, the temperature values were maximum during summer and minimum during winter. Low temperature recorded in winter may be due to high water level, lesser solar radiation, low atmospheric temperature and high temperature in summer because of low water level, high solar radiation and clear atmosphere.
Similarly, results have been reported by (10,11,3) recorded minimum temperature, in winter season and maximum in summer.

**Dissolved oxygen (DO)**

Dissolved oxygen is one of the most important abiotic factors influencing life in an aquatic ecosystem. Its depletion perhaps is the most critical manifestation of pollution and effects of low level of dissolved oxygen.

The dissolved oxygen level in natural water depends on physical, chemical and biological activities of the water body. Concentration of dissolved oxygen decreases with increase in temperature. A healthy stream or Lakes should have adequate dissolved oxygen. The oxygen rich water, bacteria and protzoan and microorganisms multiply rapidly and then become food for advanced aquatic animals. The presence of dissolved oxygen is essential to maintain variety of forms of biological life in water. Non-polluted surface waters naturally saturated with dissolved oxygen (12).

The maximum value was recorded 5.54±0.69 (mg/l) and coefficient variation was 12.45 % recorded during winter; minimum value was recorded 4.13±0.44 (mg/l) and coefficient variation was 10.65 % recorded during summer. The overall mean was 4.78±0.71 (mg/l) and coefficient variation was 14.85 % and correlation coefficient of DO with BOD and COD respectively as follow 0.51 and 0.52 (Table No. 1 & 2 and Fig 1. B).

In the present investigation, the maximum Dissolved Oxygen recorded in the winter season and minimum during monsoon. High Dissolved Oxygen value during winter period could be due to increased rate of photosynthesis by increased density of Phytoplanktons in relatively stable environmental condition (13).

The higher values of Dissolved Oxygen during post-monsoon may be due to circulation of oxygen by cooling and draw down of Dissolved Oxygen in water (14,15) and the lower values during pre-monsoon probably due to decomposition of organic matter (16).

Similarly, results have been reported by (5,17,18) reported maximum Dissolved Oxygen during winter season, moderate during monsoon and minimum during summer. (19) observed the maximum Dissolved Oxygen concentration during winter and minimum during summer in religious Lake Budha Pushkar near Ajmer, Rajasthan. (20) reported maximum values of DO in winter or monsoon and minimum in summer in Girna Dam of Nashik (M.S.).

### Table 1 - Seasonal variations in physico-chemical parameters of Harsool-Savangi dam, (M.S) India. (During January 2009 - December 2009).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Summer</th>
<th>C.V</th>
<th>Monsoon</th>
<th>C.V</th>
<th>Winter</th>
<th>C.V</th>
<th>Average</th>
<th>C.V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric temperature (°C)</td>
<td>37.42±0.39</td>
<td>1.04</td>
<td>27.39±0.30</td>
<td>1.09</td>
<td>22.26±0.63</td>
<td>2.83</td>
<td>29.02±7.71</td>
<td>26.56</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>4.13±0.44</td>
<td>10.65</td>
<td>4.67±0.64</td>
<td>13.70</td>
<td>5.54±0.69</td>
<td>12.45</td>
<td>4.78±0.71</td>
<td>14.85</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>4.8±0.37</td>
<td>7.70</td>
<td>7.55±0.49</td>
<td>6.49</td>
<td>6.55±0.44</td>
<td>6.71</td>
<td>6.3±1.39</td>
<td>22.06</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>11.64±0.91</td>
<td>7.81</td>
<td>18.21±1.21</td>
<td>6.64</td>
<td>15.85±1.05</td>
<td>9.46</td>
<td>15.23±3.32</td>
<td>21.79</td>
</tr>
</tbody>
</table>

### Table 2 - Correlation matrix among the physico-chemical properties of Harsool-Savangi dam from January to December 2009.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Atmospheric temperature (°C)</th>
<th>DO (mg/l)</th>
<th>BOD (mg/l)</th>
<th>COD (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>-</td>
<td>-0.94**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>-0.76*</td>
<td>0.51</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>-0.76*</td>
<td></td>
<td>0.99**</td>
<td></td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>-0.76*</td>
<td></td>
<td></td>
<td>0.52</td>
</tr>
</tbody>
</table>

** = Correlation is high significant at p < 0.01 level, *' indicate negative correlation, ' = Correlation is significant at p < 0.05 level, DO= Dissolved Oxygen, BOD= Biochemical Oxygen Demand, COD= Chemical Oxygen.
**Biochemical Oxygen Demand: (BOD)**

BOD is an important parameter that indicates the magnitude of water pollution by oxidizable organic matter. The main sources of organic pollution include untreated domestic sewage, agricultural run-off, containing residual fertilizers and certain industrial effluents. The components of oxidizable matter include carbonaceous organic matter, nitrogenous compounds and chemically reducing compounds. In natural course the organic matters on oxidation enters into bio-geo-chemical cycles.
However, when an aquatic ecosystem receives excessive organic pollution load due to low availability of dissolved oxygen, net biological oxygen demand generates. BOD thus can be defined as the quantity of dissolved oxygen in mg/l required under test condition (aerobic bacteria) for the organic matter for test sample (21). The maximum value was recorded 7.55±0.49 (mg/l) and coefficient variation was 6.49 % recorded during monsoon; minimum value was recorded 4.8±0.37 (mg/l) and coefficient variation was 7.70 % recorded during summer. The overall mean was 6.3±1.39 (mg/l) and coefficient variation was 22.06 % and correlation coefficient of BOD with COD respectively as follow 0.99 (Table No. 1 & 2 and Fig 1.C).
In the present investigation, the BOD values were maximum during monsoon and minimum during summer. High values in monsoon as compared with winter and summer season. This might be because of presence of various types of pollutants mixed with rain water. Similarly, results have been reported by (22,23) observed high value of BOD in summer.

**Chemical Oxygen Demand (COD)**

COD is the measure of oxygen required in oxidizing the organic compounds present in water by means of chemical reactions involving oxidizing substances such as potassium chromate and potassium permanganate. The estimation of COD is of great importance for water having unfavorable conditions for the growth of microbes, such as in the presence of toxic chemicals. The chemical oxygen demand test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test, which is measured in terms of quantity of oxygen-required oxidation of organic matter to produce carbon dioxide and water. It is a fact that all organic compounds with few exception, can be oxidized for the action of strong oxidizing agents under acidic condition, COD test is useful in pinpointing toxic condition and presence of biologically resistant substances. High organic pollution indicates high value of COD.

The maximum value was recorded 18.21±1.21 (mg/l) and coefficient variation was 6.64 % recorded during monsoon; minimum value was recorded 11.64±0.91 (mg/l) and coefficient variation was 7.81 % recorded during summer. The overall mean was 15.23±3.32 (mg/l) and coefficient variation was 21.79 % (Table No. 1 & 2 and Fig 1. D). In the present investigation, the COD values were maximum during monsoon and minimum during summer. Maximum values of COD noted in monsoon and minimum in summer season. The maximum values in monsoon may be due to mixing run off rain water which carried mud, sand, high quantity of water, death and decay of aquatic flora and fauna and minimum COD in summer is due to settlement of organic matter and dilution effect. Similarly, results have been reported by (5) observed high value in summer.

**CONCLUSIONS**

The present study show physico-chemical characteristics and correlation coefficient of water in Harsool-Savangi dam, Aurangabad (M.S) India. The summer, monsoon and winter seasons shows different seasonal fluctuations in various physico-chemical parameters.

- Maxima value of DO in winter season and minima value in summer season.
- Maxima values of BOD and COD in monsoon season and minima values in summer season.
- The correlation coefficient indicates negatively highly significant correlation of atmospheric temperature with DO, BOD and COD for the collected water sample form Harsool-Savangi dam. With the increase in atmospheric temperature of water there is decrease in the amount of DO, BOD and COD.

**ACKNOWLEDGMENTS**

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Caratterizzazione del chimismo dell’acqua oligominerale “Prata”. Risultati di una indagine decennale

Chemical Characterization of Matese Mount waters: ten years analysis (1998/2008) of Acqua Prata

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RIASSUNTO

Nell’ambito di uno studio volto alla caratterizzazione chimico-fisica delle acque che nascono dall’Appennino Meridionale in Campania, sono esposti i risultati delle analisi effettuate sul chimismo dell’Acqua Prata nel decennio 1998-2008. Le analisi di numerosi campioni prelevati con scadenza quadrimestrale presso le sorgenti ricadenti nell’area di concessione mineraria della SGAM (Società Generale Acque Minerali) hanno riguardato la determinazione dei 23 parametri chimico-fisici caratterizzanti previsti dal D.M. 542/92 allo scopo di valutare la qualità delle acque e considerare eventuali variazioni del chimismo nel periodo considerato. E’ stata rivolta inoltre attenzione alle analisi delle sostanze indesiderabili o contaminanti di natura inorganica ed organica in linea con i decreti ministeriali succedutisi e che hanno stabilito di volta in volta nuovi parametri e nuove metod per effettuare le valutazioni. L’acqua minerale Prata ha presentato caratteristiche chimico-fisiche peculiari per un’acqua oligominerale, con elevati valori di calcio e di bicarbonati ed un ampio margine di sicurezza d’uso con valori di contaminazione sempre al di sotto dei limiti di rilevabilità dei metodi, evidente segno della purezza e dell’integrità sia delle aree di ricarica della falda che delle aree prossimali all’utilizzazione delle risorse acquifere.

SUMMARY

Water is essential for life and contains minerals which play an important role in human nutrition. The market of mineral water has been growing steadily over the last few years. Italy is the country with the highest production and consumption in the world. Società Generale delle Acque Minerali produces two of Italy’s best known brands of mineral water (Acqua Lete and Acqua Prata). This study presents the concentrations of about 29 metals and ions in 30 different samples of Acqua Prata mineral water analysed for ten years from 1998 to 2008. The analysis shows that Acqua Prata is rich in natural elements that unequivocally characterise its taste and quality. Acqua Prata showed calcium (Ca) concentrations (143.9-156.1 mg/L) and bicarbonate (510.0-540.4) implying very interesting calcium and bicarbonate oligomineral water. Such waters may make a substantial contribution to the daily intake of Ca high water consumers. Chemical analysis of inorganic and organic contaminants reported in Italian drinking water regulation (D.M. 29/12/2003), was performed on all Acqua Prata samples collected from 1998 to 2008. The analysis was performed according to APAT IRSA-CNR Methods. All water samples were found to be completely free of organic and inorganic contaminants.

PAROLE CHIAVE


KEYWORDS

INTRODUZIONE
Il contenuto di sali nelle acque naturali dipende essenzialmente, sia sotto l’aspetto quantitativo che qualitativo, dalla composizione chimica e dalle proprietà chimico-fisiche delle formazioni rocciose con le quali l’acqua viene a contatto, nonché dalla durata del contatto stesso. La sorgente dell’acqua minerale “Prata” è localizzata al piede dell’estremo versante Nord-Occidentale del massiccio del Ma-
tese, nel Comune di Pratella, provincia di Caserta; nella medesima regione si realizza tutto il ciclo idrogeologico della falda di acqua minerale, dall’area di ricarica ai processi di mineralizzazione ed al deflus-so sotterraneo verso i recapiti sorgivi nella bassa val-
le del Fiume Lete.
I riferimenti topografici sono IGM 25000 Foglio 161 quadrante III-NE, cartografia 1:25000 della Provin-
cia di Caserta Tav. 2 Capriati al Voltumo quadrante 161-III. L’acquifero, che si estende su tutta l’area dell’attuale concessione, si identifica sotto l’aspetto geologico-stratigrafico, ad una formazione descritta come “dolomie e calcari dolomitici allo stato cata-
clastico”.
Nel caso delle acque coltivate nella concessione Le-
te, nelle aree di ricarica della falda le litologie con cui il flusso idrico viene in contatto e da cui l’acqua 
acquista la mineralizzazione ionica sono in massima 
parte formate da rocce carbonatiche (calcari, calca-
rì dolomitici e dolomie) e in minima parte e solo in 
superficie da suoli residuali di processi carsici (terre 
rosse) misti a ceneri vulcaniche (vulcanismo di Roc-
camponfina). Nel percorso ipogeo le acque pertanto 
interagiscono praticamente solo con rocce calcarea 
e subordinatamente calcareo-dolomitiche. I calcari 
dolomitici hanno come costituente caratteristico la 
dolomite, un vero e proprio sale doppio di calcio e 
magnesio [MgCa(CO3)2].
Nell’ambito di uno studio teso alla valorizzazione del 
patrimonio idrico e termale della Regione Campania 
ed in linea con lavori precedentemente pubblicati 
(1, 2), si riportano i dati di uno studio decennale 
presentato ai Grandi Sorgenti di Marotta e Sica (8, 9).
Parametri caratterizzanti
Per quanto attiene gli elementi caratterizzanti di 
un’acqua minerale, l’articolo 5 del D.M. 542/92 
(6, 7) indica i parametri che devono risultare dalle 
analisi chimiche e fisico-chimiche, oltre alla tempe-
ratura dell’aria al momento del prelievo. Nella Ta-
bella 1 si riportano i dati di uno studio decennale 
(1998/2008) sulla qualità dell’Acqua Prata, valutata 
dalla Commissione per la definizione dei principali parametri chimico-fisici (temperatura pH, conducibilità elettrica) e quella di una gran serie di anioni e cationi (Tabella 1). Nella maggior parte dei casi, i metodi di analisi utilizzati derivano da metodi di riferimento (ISTISAN, IRSA-CNR, UNI e altri). Nel decennio considerato è stata rilevata una variazione dei parametri che non ha superato il 5%, risultato che dunque evidenza l’acqua Prata (Tabella 1) è risultata essere un’acqua oligominerale bicarbonato-calcica secondo la classifi-
cazione di Marotta e Sica (8, 9). L’acqua Prata (Tabella 1) pur presentando valori di risalto di 121/1992, n. 542 (3) e 
successive modifiche, che stabilisce nell’articolo 5 e 
nell’articolo 6 che vengano effettuati analisi riguar-
danti tutti i parametri chimico, chimico-fisici, biolo-
gici e microbiologici su campioni di acqua minerale 
alla fine di stabilirne purezza e potabilità nonché per 
valutare eventuali variazioni dei suddetti. Si è fatto 
inoltre riferimento agli articoli 1 e 2 e all’allegato II 
del Decreto del Ministero della Salute datato 29 di-
cembre 2003, pubblicato in Gazzetta ufficiale n. 302 
del 31 dicembre 2003 (4), che fissa i valori massimi ammissibili per i parametri chimici delle acque mi-
nerali naturali, la natura ed i limiti massimi ammessi 
per i contaminanti inorganici ed organici e supera in 
tal senso i regolamenti 542/1992 e 31/05/2001 (5).
sostanzialmente acaloriche. La biodisponibilità del calcio nelle acque minerali è eccellente, essendo simile a quello del calcio del latte (10). Le acque oligominerali con caratteristiche bicarbonato-calcaree come l’Acqua Prata possono essere utili nel divezzamento di neonati intolleranti alle proteine del latte vaccino. L’utilizzo di un’acqua bicarbonato-calcaica o alcalino terrosa per la ricostituzione dei lattini formulati, dopo i dodici mesi di vita, sembra rispondere a criteri di ottima tolleranza e favorire la funzione assimilativa; assicura inoltre un buon introito di calcio e altri elettroliti, fondamentale in età di rapido accrescimento staturo-ponderale. Nel bambino l’acqua rappresenta il 70-80% del peso corporeo. Quindi un adeguato apporto idrominerale è indispensabile per coprire i fabbisogni e soddisfare le esigenze di crescita. Un bambino in fase di crescita ha bisogno inoltre di molti sali minerali che sono contenuti in diversi alimenti, tra cui l’acqua: a questo scopo sono consigliabili acque con residuo fisso compreso tra 250 e 500 mg/L, oppure acque con residuo fisso più elevato con le caratteristiche di un’acqua bicarbonato-calcaica e con una equilibrata presenza di mineralizzazione. Anche la prevenzione primaria dell’osteoporosi durante l’infanzia e l’adolescenza richiede un adeguato introito di Ca^{2+} (11). Dati derivanti da studi eseguiti prevalentemente in ragazze sane tra i 9 ed i 18 anni suggeriscono che la massima ritenzione netta di calcio è raggiunta con introiti di tra i 1200 e i 1500 mg/die. Per le acque bicarbonate oligominerali è riportata un’azione diuretica da ascrivere all’ipotonia oltre che alla presenza di numerosi mineralizzatori (9). La bevuta di acque bicarbonate a digiuno eleva il pH gastrico ed inibisce la secrezione per stimolazione riflessa duodenale. Assunte durante i pasti l’effetto è prosecretorio. L’anione HCO_{3}^- sembra possedere un’attività protettiva specifica sulla mucosa gastrica nei confronti dell’eccesso di secrezione acida, calcio e magnesio sembrano implicati nella liberazione di gastrina e di altri enterormoni (12). La presenza di discrete quantità di magnesio (11.99-13.27 mg/L) rende Acqua Prata utile nella prevenzione dell’urolitiasi per l’attività inibitrice della cristallizzazione di questo ione (13).

Contaminanti

I parametri di analisi per la valutazione della composizione e dei requisiti di qualità delle acque minerali...

In generale è bene affermare che tutte le leggi e decreti relativi ai controlli, indicano metodi di riferimento che possono essere sostituiti da altri quando sia dimostrata la loro affidabilità.

Il successivo Decreto 29/12/2003 ha ulteriormente modificato i Decreti precedenti ponendo dei limiti ben precisi sia per quanto riguarda i metalli che per i contaminanti organici a condizioni che si raggiungono determinati limiti di rilevabilità utilizzando metodi riconosciuti a livello nazionale o internazionale, in questo modo recependo la recente Direttiva 2003/40/CE del 16 maggio 2003, dove non si stabiliscono metodi ufficiali di analisi per i vari parametri nelle acque minerali, ma viene espressamente dichiarata la possibilità di usare differenti metodi, purché vengano garantite prestazioni analitiche sufficienti e conformi a quanto riportato negli allegati del D.M. Il testo specifica semplicemente che i metodi “…devono essere quelli che si avvalgono delle più moderne tecniche analitiche e che sono indicati da organismi internazionali o comunitari o nazionali…” Inoltre si aggiunge che “…i livelli minimi di rendimento riportati saranno riesaminati alla luce di nuove metodologie analitiche e di regola ogni tre anni…” Sostanzialmente ogni laboratorio cui sia demandato il controllo sanitario delle acque minerali può scegliere il metodo analitico più idoneo, fatto salvo che abbia i requisiti minimi in termini di sensibilità, accuratezza e precisione.

Nella Tabella 2 si riportano i risultati delle analisi dei contaminanti inorganici in acqua Prata nel decennio 1998/2008. Le analisi hanno riguardato la determinazione di metalli (Sb, As, Ba, B, Cd, Cr, Pb, Mn, Hg, Ni, Se) e anioni inorganici (NO$_3^-$, NO$_2^-$, PO$_4^{3-}$, F-, CN-), nella maggior parte dei casi, i metodi di analisi utilizzati derivano da metodi di riferimento (ISTISAN, IRSA-CNR, UNI e altri). Tra i metalli che possono essere presenti nelle acque sono di rilevanza tossicologica quelli comunemente noti come metalli pesanti (Cd, Cr, Pb, Hg, Ni) per i quali la contaminazione naturale è piuttosto rara. La loro origine è infatti quasi sempre antropica: scarichi industriali.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimonio</td>
<td>mg/l</td>
<td>&lt;0.001</td>
<td>3060 APAT IRSA-CNR</td>
<td>0.001 mg/L</td>
<td>0.0050 mg/L</td>
</tr>
<tr>
<td>Arsenico</td>
<td>mg/l</td>
<td>&lt;0.0001</td>
<td>3080 APAT IRSA-CNR</td>
<td>0.00001 mg/L</td>
<td>0.010 mg/L calcolato come As totale</td>
</tr>
<tr>
<td>Bario</td>
<td>mg/l</td>
<td>&lt;0.1</td>
<td>3090 APAT IRSA-CNR</td>
<td>0.1 mg/L</td>
<td>1.0 mg/L</td>
</tr>
<tr>
<td>Boro</td>
<td>mg/L</td>
<td>&lt;0.08</td>
<td>3110 APAT IRSA-CNR</td>
<td>0.080 mg/L</td>
<td>5.0 mg/L</td>
</tr>
<tr>
<td>Cadmio</td>
<td>mg/l</td>
<td>&lt;0.002</td>
<td>3120 APAT IRSA-CNR</td>
<td>0.002 mg/L</td>
<td>0.003 mg/L</td>
</tr>
<tr>
<td>Cromo totale</td>
<td>mg/l</td>
<td>&lt;0.002</td>
<td>3150 APAT IRSA-CNR</td>
<td>0.002 mg/L</td>
<td>0.050 mg/L</td>
</tr>
<tr>
<td>Rame</td>
<td>mg/l</td>
<td>&lt;0.01</td>
<td>3250 APAT IRSA-CNR</td>
<td>0.01 mg/L</td>
<td>1.0 mg/L</td>
</tr>
<tr>
<td>Cianuro</td>
<td>mg/l</td>
<td>&lt;0.001</td>
<td>4070 APAT IRSA-CNR</td>
<td>0.001 mg/L</td>
<td>0.010 mg/L</td>
</tr>
<tr>
<td>Fluoruri</td>
<td>mg/l</td>
<td>&lt; 0.07</td>
<td>4020 APAT IRSA-CNR</td>
<td>0.070 mg/L</td>
<td>5.0 mg/L (1.5 mg/L per acque destinate all’infanzia)</td>
</tr>
<tr>
<td>Piombo</td>
<td>mg/l</td>
<td>&lt;0.0002</td>
<td>3230 APAT IRSA-CNR</td>
<td>0.0002 mg/L</td>
<td>0.010 mg/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/l</td>
<td>&lt; 0.01</td>
<td>3190 APAT IRSA-CNR</td>
<td>0.01 mg/L</td>
<td>0.50 mg/L</td>
</tr>
<tr>
<td>Mercurio</td>
<td>mg/l</td>
<td>&lt;0.0001</td>
<td>3200 APAT IRSA-CNR</td>
<td>0.0001 mg/L</td>
<td>0.0010 mg/L</td>
</tr>
<tr>
<td>Nichel</td>
<td>mg/l</td>
<td>&lt;0.0004</td>
<td>3220 APAT IRSA-CNR</td>
<td>0.0004 mg/L</td>
<td>0.020 mg/L</td>
</tr>
<tr>
<td>Selenio</td>
<td>mg/l</td>
<td>&lt;0.0002</td>
<td>3260 APAT IRSA-CNR</td>
<td>0.0002 mg/L</td>
<td>0.010 mg/L</td>
</tr>
</tbody>
</table>

1Media di due analisi annuali. 2Le caratteristiche di prestazione della metodica analitica sono quelle riportate nell’Allegato I del D.M. del Ministero della Salute del 29-12-2003.
attività agricole, ecc. I metalli pesanti, data la loro tossicità, hanno una soglia di concentrazione ammessa molto bassa, dell’ordine dei µg/L. Gli effetti tossici dei metalli pesanti sono molteplici e notevoli, a causa della loro persistenza nell’ambiente: gli ioni positivi Cd\(^{2+}\), Hg\(^{2+}\) e Pb\(^{2+}\), ad esempio, riescono a sostituire ioni essenziali in reazioni fisiologicamente importanti come il trasporto dell’ossigeno o reazioni enzimatiche. Gli anioni inorganici nitriti (NO\(_2^-\)) e nitrati (NO\(_3^-\)) possono essere prodotti in natura dallo ione ammonio oppure da fenomeni conseguenti all’impiego dei fertilizzanti azotati in agricoltura. Lo ione nitrato è infatti presente come componente di sali molto solubili impiegati come fertilizzanti e può passare velocemente nelle acque sotterranee per dilavamento del suolo agricolo. Questi anioni sono precursori di sostanze cancerogene. Altri anioni comunemente presenti in acque contaminate sono i fosfati (PO\(_4^{3-}\)) che hanno un’origine quasi sempre antropica, essendo contenuti nei detersivi o nei fertilizzanti.


**CONCLUSIONI**


<table>
<thead>
<tr>
<th>Parametro</th>
<th>Unità di misura</th>
<th>1998-2003(^2)</th>
<th>Valori limiti DM 542</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenoli</td>
<td>µg/l</td>
<td>&lt; 0.5</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
<tr>
<td>Agenti tensioattivi (MBAS anionici)</td>
<td>µg/l</td>
<td>&lt; 0.025</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
<tr>
<td>Oli minerali - disciolti o emulsionati</td>
<td>µg/l</td>
<td>&lt; 0.5</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
<tr>
<td>Idrocarburi policiclici aromatici</td>
<td>µg/l</td>
<td>&lt;0.0001</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
<tr>
<td>Pesticidi e bifenili policlorurati</td>
<td>µg/l</td>
<td>&lt;0.001</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
<tr>
<td>Composti organo allogenati</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>Assenti al limite di rilevabilità del metodo</td>
</tr>
</tbody>
</table>

\(^1\) Media di due analisi annuali. \(^2\) I risultati sono riportati in unica colonna essendo i dati sempre al di sotto dei limiti di rilevabilità dei metodi.

<table>
<thead>
<tr>
<th>N.</th>
<th>Parametro</th>
<th>Unità di misura</th>
<th>Risultati 2003-2008</th>
<th>Metodo</th>
<th>limite di rilevabilità</th>
<th>LMRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Agenti tensioattivi</td>
<td>µg/l</td>
<td>&lt; 5</td>
<td>5170 APAT IRSA-CNR Tensoattivi anionici 5180 APAT IRSA-CNR Tensoattivi non anionici</td>
<td>5</td>
<td>50 (come LAS)</td>
</tr>
<tr>
<td>2</td>
<td>Oli minerali-idrocarburi disciolti o emulsionati</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>ISO 9377-2 (2000)</td>
<td>0.05</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Benzene</td>
<td>µg/l</td>
<td>&lt; 0.1</td>
<td>5140 APAT IRSA-CNR</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Idrocarburi policiclici aromatici</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzo (a) pirene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Benzo (b) fluorantene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td>Benzo (k) fluorantene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Benzo (ghi) perilene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Dibenzo (a, h) antracene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Indeno (1, 2, 3 – cd) pirene</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Altri</td>
<td>µg/l</td>
<td>&lt; 0.002</td>
<td>5080 APAT IRSA-CNR</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>5</td>
<td>Antiparassitari*</td>
<td>µg/l</td>
<td>&lt; 0.005</td>
<td>5060 APAT IRSA-CNR</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>(singolo composto)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(insetticidi, erbicidi, fungicidi, nematocidi, acaricidi, alghicidi, rodenticidi, prodotti connessi e i pertinenti metaboliti, prodotti di degradazione e di reazione)</td>
<td>µg/l</td>
<td>&lt; 0.001</td>
<td>5090 APAT IRSA-CNR</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>Policlorobifenili</td>
<td>µg/l</td>
<td>&lt; 0.001</td>
<td>5110 APAT IRSA-CNR</td>
<td>0.001</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>Composti organoalogenati che non rientrano nelle voci 5 e 6 (singolo composto): cloroformio clorodibromometano dichlorobromometano bromoformio</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>5150 APAT IRSA-CNR</td>
<td>0.05</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Tricloroetilene</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>5150 APAT IRSA-CNR</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Tetrachloroetilene</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>5150 APAT IRSA-CNR</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-2 dichloroetano</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>5150 APAT IRSA-CNR</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Altri</td>
<td>µg/l</td>
<td>&lt; 0.05</td>
<td>5150 APAT IRSA-CNR</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

1 Media di due analisi annuali. 2 I risultati sono riportati in unica colonna essendo i dati sempre al di sotto dei limiti di rilevabilità dei metodi. 3 Le caratteristiche di prestazione della metodica analitica sono quelle riportate nell’Allegato I del D.M. del Ministero della Salute del 29-12-2003. 4 Limiti minimi di rendimento richiesti ai metodi analitici.
della purezza e dell’integrità sia delle aree di ricarica della falda che delle aree prossimali all’utilizzazione delle risorse acuifere ricadenti nell’Appennino Meridionale.

**BIBLIOGRAFIA**

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Study of biochemical and mechanical response to moderate exercise

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³Laboratorio di ricerche diagnostiche “E.Roecker” - Marano di Napoli

Abstract
Aim of the study is the evaluation of metabolic response to lactic exercise. Have been tested 8 males athletes. All the subjects underwent blood chemistry, clinical and instrumental examination after a Wingate test. Muscular ultrasound of quadriceps showed an higher muscle volume, with 30.64 ± 2.47 mm before exercise and 31.89 ± 2.27 mm after exercise (Figure 3). The study demonstrate that moderate levels of physical exercise trigger anaerobic lactic pathway as well, and these produce detectable biochemical and mechanical reaction. We can say that ultrasound is a valid method to observe the changing in muscle also after moderate exercise.

Key words
Muscle Ultrasound, Wingate test, lactic acid
BACKGROUND
There are marked changes in intramuscular architecture of the quadriceps following a bout of cycloergometry to exhaustion, with significant increase of quadriceps thickness. The increased muscle volume after exercise is probably consequence of muscle oedema produced even by light workloads, and also a result of a slowing of muscle relaxation due to intracellular accumulation of Ca++ and H+. The increased muscle thickness may be attributed to increased vascular perfusion for oxygen glucose delivery and metabolic waste removal, and to the inflammatory response promoted by an increase in intracellular calcium which activates phospholipase A2.

AIM
Aim of the study is the evaluation of metabolic response to lactic exercise.

MATERIALS
Have been tested 8 males athletes with the following features

<table>
<thead>
<tr>
<th>Feature</th>
<th>Mean</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age (years)</td>
<td>25</td>
<td>6.3</td>
</tr>
<tr>
<td>Weight (Kg)</td>
<td>73.58</td>
<td>6.68</td>
</tr>
<tr>
<td>Height (cm)</td>
<td>177.63</td>
<td>5.04</td>
</tr>
</tbody>
</table>

None of the subjects suffered for cardiovascular or metabolic disease and nobody usually took drinks or drugs for improving performance.

METHODS
All the subjects underwent the following study protocol:

CLINICAL EXAMINATION:
physiological and pathological hystory, to have information about sport and status of training (kind of sport, years of training, number of workout/week)

Instrumental examination:
Measurement of environmental temperature and wetness
Measurement of body temperature by tympanic thermometer
Examination of body composition by Bodygram AKERN, Firenze Italia, evaluating: total body water (TBW), extracellular water (ECW), intracellular water (ICW), cellular mass (BCM), free fat mass (FFM), fat mass (FM), body muscle cells (BCM), basal metabolic rate.
Measurement of lactic acid by Lactate Pro ARKRAY, Kyoto, Japan
Measurement of serum glucose by digital venipuncture with “one touch ultra 2” Johnson & Johnson.
Muscular ultrasonography of quadriceps femoris measuring the thickness of the anterior side of thigh-making by rictus femoris and vastus intermedius.

CHEMISTRY:
Urinalysis by URIPADS URSA-10 URSH-10 with evaluation of: ph, specific weight, glucose, bilirubin, ketones, erythrocytes, proteins, urobilinogen, nitrates, leukocytes.
Venous sample to evaluate:
- Muscular enzyme Creatina Kinase by spectrophotometric method at 25°C (EOS 880 CGA Scientific Instruments, Firenze, Italy)
- Serum electrolytes (sodium, potassium) by flame photometer (FP 20 SEAC, Firenze, Italy)
- Serum electrolytes (calcium and magnesium) by photometer BT 2000 plus Biotecnica Instruments s.p.a. Roma, Italy and calcium-arsenate method for calcium and magnesium-calmagite for magnesium
- Hematocrit by automate contaglobuli HeCo 5 plus with laser measurements Multi-Element-Forward-Scattering (MEFS).

We exercised the subject with an electrically braked ergometer (SECA Hamburg, Germany) and a repeated Wingate protocol: all the subjects performed three sessions of 30” with a mean speed of 80 RPM and one minute of recovery between the sessions. The workload was 85% of their maximal workload calculated in a preliminar session a week before the test timing of examination was:

Rest: before the exercise (T0)
Anamnesis, measure of body temperature, measure of peripheral venous lactic acid and glucose, muscular ultrasound, test for body composition, urinalysis, venous blood for creatine kinase, electrolytes and hematocrit evaluation.

During exercise: after first session (T1), after second session (T2) and after third session (T3)
Heart rate (HR), systolic and dyastolic blood pres-
Study of biochemical and mechanical response to moderate exercise

5 minute after exercise (T4)

measure of body temperature, test for body composition, muscular ultrasound, measure of peripheral venous lactic acid and glucose, venous blood for electrolytes evaluation.

20 minutes after exercise (T5)

measure of peripheral venous lactic acid, urinalysis, venous blood for creatine kinase, electrolytes and hematocrit evaluation.

STATISTICAL ANALYSIS

We studied mechanical and metabolic response after lactic exercise. Statistical analysis was performed by SPSS statistical package for Windows, release 17.0 (Chicago, IL, USA). Statistical significance was evaluated by Student’s T Test for paired samples: descriptive statistics were calculated, and values reported are mean ± standard deviation. Relationships between the measures collected were calculated with a bivariate correlation measuring the Pearson’s correlation coefficient. Differences were considered statistically significant when $p < 0.05$.

RESULTS

Body temperature at rest was of 36.51 ± 0.33 °C, and it increased significantly after exercise with 36.76 ± 0.27 °C ($p=0.00$). The athletes performed an exercise studied to trigger lactic anaerobic pathway. In fact peripheral blood lactate was higher in each session of workload, besides heart rate and blood pressure had only a slight increase. Lactic acid at rest was of 2.4 ± 1.3 U and showed a significant increase at time T2 (4.6 ± 1; $p=0.17$), T3 (5.2 ± 0.8; $p=0.00$), T4 (4.6 ± 1.8; $p=0.04$), returning at rest level at time T5 (3.31 ± 0.9; $p=NS$). In table 1 were reported mean values and the standard deviation of examined parameters:

Statistical analysis showed a significant increase of HR in the first 30 seconds of workload (HR at T0 vs HR at T1: $p=0.00$) with a steady state till the end of exercise, when it was only slightly higher than resting levels (HR at T0 vs HR at T4: $p=0.02$). The same trend had SBP and HR, with significant differences at the same time (SBP at T0 vs SBP at T1: $p=0.00$; SBP at T0 vs SBP at T4: $p=0.05$). We did not find significant variation of DBP, which was settled during the exercise (Figures 1). The analysis of body composition performed before and after the exercise, did not show any significant data (table II). In table III have been reported the levels of electrolytes, glucose, creatine kinase and urinalysis which did not show significant differences due to effort. Besides we found a significant variation of hematocrit (Hct), which was of 42.31 ± 2.33 at rest and of 41.71± 1.86 ($p=NS$) and 40.94 ± 1.73 ($p=0.02$), respectively 5 and 30 minutes after exercise (Figure 2). Muscular ultrasound of quadriceps showed an higher muscle volume, with 30.64 ± 2.47 mm before exercise and 31.89 ± 2.27 mm after exercise (Figure 3). We evaluate the relation between biochemical and instrumental results with a bivariate correlation and we found a significant relation between quadriceps volume and serum levels of lactic acid and creatine kinase measured after exercise. The levels of lactic acid measured after exercise (fig. 4 and 5) are related to serum levels of enzyme CK due to exercise (lactic acid at T4 and CK at T4: $R=0.716; p<0.05$; lactic acid at T4 and CK at T5: $R=0.763; p<0.05$). Besides serum levels of lactic acid correlate to serum calcium levels with a significant Pearson’s correlation at rest and after exercise.

DISCUSSION

Wingate test has often used to study the lactic metabolism (1, 2, 3, 4). We used an amended Wingate test cause the ergometer we had was electrically braked, with a speed of 80 RPM, to avoid that inertial force will reduce the load. Each test was made of three sessions, each one of 30 seconds followed by 1 min of recovery and as workload as 25 watt minus than the maximal workload.

All the subjects performed the exercise as well as

Table 1

<table>
<thead>
<tr>
<th></th>
<th>T0</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC</td>
<td>71.63±11.87</td>
<td>121.38±17.82</td>
<td>127.88±16.81</td>
<td>131.13±16.41</td>
<td>84.25±17.70</td>
</tr>
<tr>
<td>PAS</td>
<td>116.25±13.83</td>
<td>144.38±15.91</td>
<td>149.38±12.66</td>
<td>159.38±13.21</td>
<td>126.25±10.68</td>
</tr>
<tr>
<td>PAD</td>
<td>69.38±7.76</td>
<td>70.00±13.09</td>
<td>61.25±10.26</td>
<td>57.50±13.89</td>
<td>61.25±9.91</td>
</tr>
</tbody>
</table>

HR: heart rate - SBP: sistolic blood pressure - DBP: diastolic blood pressure
expected with a poor perception of effort. In fig 1 are reported the hemodinamic parameters, demonstrating that HR and BP have such trend of a submaximal exercise: HR had a significant but slight increase respect the resting values (HR at T0: 71.63 ± 11.87 rpm vs HR at T1: 121.38 ± 17.82 rpm; p=0.00) reaching levels lower than 70% of resting HR an therefore appropriate for an aerobic metabolism. HR behaviour, without significant peaks through the exercise, shows a metabolic and hemodinamic steady-state, where energy production depends mostly on oxidation of energy substrate (5). Farther blood pressure behaviour, which had only a poor increase of SBP at the beginning of exertion (T0: 116.25 ± 13.83 mm/Hg vs T1: 144.38 ± 15.91 mm/Hg; p=0.00), testify a submaximal exercise. Moreover we did not find changes in DBP (T0: 69.38 ± 7.76 mm/Hg vs T1: 70.00 ± 13.09 mm/Hg; p=NS), as usually are during maximal exertion (T0: 116.25 ± 13.83 mm/Hg vs T1: 144.38 ± 15.91 mm/Hg; p=0.00), reaching levels lower than 70% of resting levels. DBP behaviour shows three steps of exertion and are reported the hemodinamic parameters, demonstrating that HR and BP have such trend of a submaximal exercise of short duration (7). Besides we found a relation between lactic levels and the levels of serum electrolytes, agree with most of the literature (8): conversely other works show a decreasing of electrolytes through lactic exercise (9, 10), but probably the type and duration of effort are important to understand the result. Moreover we found a negative correlation among serum calcium and lactic acid both at rest and after exercise. To support this finding there is in literature evidence of a relation among intracellular calcium and the decreasing of blood pH, because the acidosis cause a decrease sensitivity of contractile proteins to calcium (11) and a decreasing of its re-uptake in endoplasmic reticulum (12). Stronger is the relation between lactic levels and serum CK after exercise. CK is the enzyme which catalyze the followed reaction: 

$$PCr + ADP → ATP + Creatine$$

This reaction represents the faster pathway of energy production without oxigen and lactic acid (anaerobic pathway).

Serum release of enzymes may be the consequence of the alteration in skeletal muscle after strenuous exercise (13, 14). Morphological changes consist of degeneration of striated muscle cell, with thickening, disjunction and total disorganization of Z-line: this alteration appears one hours after exertion, reaching the peak three days after. Stronger changes are localized in type II fiber, though type-I fiber may have degeneration as well. A biochemical point of view provides two explanations: a metabolic and a mechanic ones. In fact the leakage of enzymes from muscles may be due to the depletion of energetic source at exaustion and consequent reduction of high energy phosphate reserve at a critical point, whereby cell membrane lost its characteristics becoming more permeable to ions and small molecules, as cytoplasmic enzymes. Another explanation sustain the mechanical stimulus: sarcomere contraction exert an high tension on stromal scaffold and therefore damage the integrity with pain and lost of enzymes.

Anyway the blood draw performed only 30 minutes after exercise do not allow us to appreciate significant changes in enzymatic values after exercise. Both serum lactic and CK resulted strictly related to the quadriceps thickness measured by ultrasound, showing that for exertion of high intensity there is a relation between biochemical and morphological parameters (table II). As referred in literature, ultrasound is a useful method to study morphologic and anthropometric changes of muscles (15, 16) and to evaluate muscular response to exercise (17). In our study, agree with literature (18-21), we found a significant increase of muscular thickness in rectus anteriors and vastus intermedius, after exercise (before exercise 30.64 ± 2.47 mm vs after exercise 31.89 ± 2.27 mm; p= 0.00) (fig. 3) and this finding related to effort, is followed by a decrease of strenght through exercise (22).

No change has been found screening the other parameters. (tables I e II): the exercise did not induce changes detectable by analysis of body composition (23, 24.), and urinalysis as well (25). Serum glucose had only a slight increase after exertion (table II), probably due to the exaustion of glicogen store in muscle, as Moussa et coll. Say in a work of 2003 (3).

An interesting data is the hematocrit (fig. 2), which show a progressive and significant decrease after exercise (42.31 ± 2.33 vs 40.94 ± 1.73; p=0.02). There is a lot of literature which confirm the increase of hematocrit after exertion as a result of dehydra- tion under prolonged exercise (26, 27), whereas there are no evidence for a decreasing during exercise of short duration: In exercise of endurance instead, there is an effusion of extracellular water with an increase of plasmatic volume finalized to an increase of cardiac output (28). Therefore our data need a confirmation on a wide population.

Finally our work enabled to detect slight but significant increase of body temperature after moderate exercise (36.51 ± 0.33 °C vs 36.76 ± 0.27


C: p=0.00). The thermal response to exercise is linked to environment rather than athlete’s physical features (29) and differ for measurements site (30): however it increase through strenuous exertion (31, 32), becoming an important factor of perceived stress induced by exercise (33).

**CONCLUSIONS**

This study demonstrate that moderate levels of physical exercise trigger anaerobic lactic pathway as well, and these produce detectable biochemical and mechanical reaction. Data related to hematocrit decrease and body temperature increase need a confirmation on a wide population, whereas we can say that ultrasound is a valid method to observe the changing in muscle also after moderate exercise.

**BIBLIOGRAFIA**

28. Fellmann N, Ritz P, Ribeyre J, Beaufreere B, Delaitre


Evalution of ground water quality due to impact of local industries in and around Chidambaram town, Tamilnadu, India

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ABSTRACT
In this work ground water pollution by minor, major and non essential elements in and around Chidambaram area is studied using ICP – AES spectrometric method. The pH is found constant in all the areas ranging between 7.05 and 7.82. Among the major elements calcium and potassium concentrations is well within the limit but the other two elements slightly above the permissible value in few sampling stations which got diluted during rainy seasons and becomes non-toxic to human life. However excess magnesium give rise to high salinity nature of water samples. The minor elements iron, chromium and nickel are well within the permissible limit. The two non essential elements are highly toxic for human life even if it present in a very low concentration. However the cadmium concentration is within the permissible value but the concentration of lead alone slightly exceeds the permissible limit in all the areas. Metal ratio and anthropogenic input calculated shows that the lead value is high in all the sampling stations. Statistical approach like ANNOVA test, Pearson's correlation and factor analysis were used to support the results.

KEY WORDS
water pollution; toxicity; ICP – AES; Lead; anthropogenic
INTRODUCTION

Heavy metals are the major sources of contamination in the environment, especially in aquatic medium. Metal compounds enter the aquatic environment through various factors like industrial effluent, domestic sewage disposal, dumping, surface run-off, atmospheric fallout, etc. Among these industrial effluent is the major source for contamination of ground water. It has been a huge task for the industries to increase the productivity and profit without contaminating the environment [1, 2].

Domestic sewage due to human activities is the second major factor for contamination. In addition to the contamination by industries and human activities, natural mineral deposits containing particularly large quantities of heavy metals are present in many regions of the globe. For instance, the toxic metal arsenic is commonly found in sediments (or) rock and this can be present in ground water at concentrations that exceed the permissible levels for drinking water [3, 4, 5]. Major elements like Na, Ca, K, etc., are essential nutrients in ground water unless they exceed permissible level, if it exceeds they become toxic for bio-organisms.

For instance, fluorine is an essential element for protection against dental caries and weakening of the bones, but higher levels can have an adverse effect on health. Excess fluorides can cause yellowing of the teeth and damage to the spinal cord and other crippling diseases.

The heavy metals are considered as minor (or) trace elements which is essential for growth at low concentration [6]. The most common heavy metal contaminants are: Chromium (Cr), Cadmium (Cd), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn) [7, 8, 9]. Chromium is considered as essential trace elements for the maintenance of an effective glucose, lipid and protein metabolism in mammals. High doses of chromium cause liver and kidney damage and chromate dust is carcinogenic [10]. Nickel and iron is also essential for biological activities but high concentration of these metals can cause skin allergies, rhinitis, dermatitis, leukemia, etc. The lung is the target organ for nickel toxicity in humans. The lead and cadmium are highly toxic even at low concentrations when compared to other metals, which are totally nonessential elements for biological activities. Cadmium toxicity produces symptoms such as nausea, vomiting, respiratory difficulties and loss of consciousness at high doses [11, 12]. Continuous exposure to lead metal can affect adversely to nervous system and kidneys [13, 14].

Toxic metal contamination of aqueous water steams and ground water posses a major environmental and health problem which needs an effective and affordable technological solutions. Moreover, the Chidambaram is famous place for imitation gold and its leads to development of many industries which leads to deteriorations of ground water. Hence keeping in view of the serious threat to the ground water the present study aims at studying ground water quality of major and minor elements at selected places in and around Chidambaram town.

MATERIALS AND METHODS

Study site

The study site Chidambaram located in Cuddalore district, Tamilnadu. Eight different places were selected where human activities suspected to contaminate ground water they are East car Street, West car Street, South car Street, North car Street, Vanidgate, Annamalai Nagar, Min Nagar and Ammapatai (refer Fig. 1). Chidambaram is famous for temple and imitation gold which glitter like gold. The making of imitation gold required many metal solutions which is the major source for heavy metal contamination of ground water in these regions. This study helps to access the water quality in and around Chidambaram area.

Sample Preparation

Water samples were collected during the period summer (April – May 2008), winter (December 2008 – January 2009) and Rainy season (October – November 2008). A total of 8 samples in duplicate, as in Table II, were collected from various sources randomly for determination of chemical parameters, such as hydrogen ion concentrations (pH), calcium (Ca++), magnesium (Mg++), sodium (Na+), potassium (K+), total copper (Cu), total iron (Fe), total lead (Pb), total cadmium (Cd), total manganese (Mn). The sample collection, preservation and analysis of the parameters were carried out by the standard methods prescribed by the American Public Health Association (APHA, 1998). While sampling, greater emphasis was given on the areas where pollution was suspected and local people complained of the taste of water.

Chemical Analysis

The pH was measured immediately on collection of the samples in the field using portable digital pH meters, while all other parameters were determined.
in laboratory. In the laboratory, Na+, Ca+ and k+ were analyzed by flame photometric method. Cu, Fe, Zn, Pb and Mn were determined as total metals after the digestion of samples by ICP – AES spectroscopic method.

For the analysis of heavy metals all glassware were filled with 2N HNO₃ overnight and rinsed several times with double distilled water. The samples were digested by adding concentrated nitric acid and perchloric acid in 3:1 ratio. Digestion was performed on a hot plate at 40 – 60° C for approximately 30 minutes or until the solution clears. The sample was allowed to cool before being filtered through a Whatman No.42 filter paper using a vacuum pump [15]. The estimation of heavy metal concentrations was made using an Inductively Coupled Plasma Atomic Emission Spectrometer (ISA JOBIN YVON 24 MODEL) available at Annamalai University, Chidambaram.

Statistical analysis
Statistical analysis was performed using SPSS 16.0 software. Pearson correlation matrix was performed to evaluate the relation between various metals. The differences were tested by a one way ANOVA (Duncan Test) at P<0.05. Principle component analysis was carried out to find the factors which influence the ground water pollution [16,17]. The metal ratio was calculated to find the contamination indices.

RESULTS AND DISCUSSION
Detection of pH and major elements
The concentration of major elements and pH in selected areas for three different seasons was tabulated in Table 3.1. It shows the value of pH was maintained in neutral ranging from 7.03–7.49. The major elements calcium, magnesium, sodium and potassium concentration ranges from 43–94 mg/l, 93–315 mg/l, 93–345 mg/l and 52–201 mg/l respectively. The concentration of calcium (200 mg/l) and potassium (200 mg/l) is well within the permissible value and the concentration of the sodium (200 mg/l) and magnesium (150 mg/l) are found high in few sampling stations. The maximum concentration was found during summer season and there is considerable reduction in concentration (around 30%) during rainy season. This variation in concentration occurs during winter and rainy season due to dilution factor of elements [18].

Assessment of irrigation water quality
The quality of irrigation water was assessed through Magnesium Hazard Ratio (MHR), Soluble Sodium Percent (SSP), Kelly’s Ratio (KR) and Sodium Adsorption Ratio (SAR) etc. Sodium hazard in ground water can be determined by calculating the sodium absorption ratio (SAR) and soluble sodium percentage (SSP). Although sodium contributes directly to the total salinity the main problem with a high sodium concentration is its effect on the physical properties of soil. Irrigation with Na-enriched water results in ion exchange reactions: uptake of Na⁺ and release of Ca²⁺ and Mg²⁺. This causes soil aggregates to disperse, reducing its permeability [19]. The role of sodium in the classification of groundwater for irrigation was emphasized because of the fact that sodium reacts with soil and as a result clogging of particles takes place, thereby reducing the permeability [20].
**Table 1** Minor elements concentration in ground water of Chidambaram town at selected sampling stations.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Summer Season Concentration mg/l</th>
<th>Winter Season Concentration mg/l</th>
<th>Rainy Season Concentration mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td>East car Street</td>
<td>7.30 ±0.20</td>
<td>64.00 ±1.04</td>
<td>184.00 ±2.35</td>
</tr>
<tr>
<td>West car Street</td>
<td>7.20 ±0.10</td>
<td>51.00 ±1.10</td>
<td>93.00 ±1.50</td>
</tr>
<tr>
<td>South car Street</td>
<td>7.35 ±0.10</td>
<td>93.00 ±2.30</td>
<td>315.00 ±5.20</td>
</tr>
<tr>
<td>North car Street</td>
<td>7.05 ±0.15</td>
<td>53.00 ±1.25</td>
<td>156.00 ±5.25</td>
</tr>
<tr>
<td>Vanidgate</td>
<td>7.28 ±0.10</td>
<td>61.00 ±1.40</td>
<td>189.00 ±3.12</td>
</tr>
<tr>
<td>Annamalai Nagar</td>
<td>7.49 ±0.14</td>
<td>73.00 ±1.50</td>
<td>203.00 ±4.50</td>
</tr>
<tr>
<td>Min Nagar</td>
<td>7.82 ±0.12</td>
<td>83.00 ±1.06</td>
<td>49.00 ±0.90</td>
</tr>
<tr>
<td>Ammapatai</td>
<td>7.04 ±0.15</td>
<td>51.00 ±1.20</td>
<td>167.00 ±6.26</td>
</tr>
</tbody>
</table>

± Standard deviation (No. of Samples n=3)
### Table 2: Heavy metals concentration in ground water of Chidambaram town at selected sampling stations.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Summer Season</th>
<th>Winter Season</th>
<th>Rainy Season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration mg/l</td>
<td>Concentration mg/l</td>
<td>Concentration mg/l</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>Maximum permissible limit</td>
<td>1.000</td>
<td>0.050</td>
<td>0.070</td>
</tr>
<tr>
<td>East car Street</td>
<td>0.004±0.001</td>
<td>0.040±0.003</td>
<td>0.040±0.001</td>
</tr>
<tr>
<td>West car Street</td>
<td>0.035±0.002</td>
<td>0.020±0.004</td>
<td>0.020±0.001</td>
</tr>
<tr>
<td>South car Street</td>
<td>0.006±0.002</td>
<td>0.010±0.003</td>
<td>0.010±0.002</td>
</tr>
<tr>
<td>North car Street</td>
<td>0.002±0.001</td>
<td>0.010±0.001</td>
<td>0.130±0.001</td>
</tr>
<tr>
<td>Vanidgate</td>
<td>0.005±0.002</td>
<td>0.070±0.002</td>
<td>0.050±0.003</td>
</tr>
<tr>
<td>Annamalai Nagar</td>
<td>0.008±0.001</td>
<td>0.030±0.001</td>
<td>0.080±0.004</td>
</tr>
<tr>
<td>Min Nagar</td>
<td>0.004±0.001</td>
<td>0.090±0.005</td>
<td>0.040±0.002</td>
</tr>
<tr>
<td>Ammapatai</td>
<td>0.002±0.001</td>
<td>0.080±0.004</td>
<td>0.060±0.003</td>
</tr>
</tbody>
</table>

± Standard deviation (No. of Samples n=3)
The magnesium hazard ratio is well above the permissible value in all the sampling stations for all the seasons ranging from 54.81 to 79.70. Symptoms from increased magnesium intake are not common in humans because the body eliminates excess amounts. But excess magnesium will increase the salinity in water which in turn affects the growth of crops. High Mg ratio is due to surface water and subsurface water more reacted and passage through the limestone, kankar and granitic rock formation in the study area.

Detection of minor elements

The concentration of minor elements are nickel ranging from 0.01 to 0.08 mg/l, chromium 0.01–0.09 mg/l and iron 0.001–0.035 mg/l were observed for samples collected from selected areas for three different seasons. The major source for heavy metal contamination is industrial effluent which strongly affects the soil and water qualities. Nickel, chromium and iron are some essential elements for human life when its concentration is within permissible value [21]. The nickel is used in electroplating industry, electronic industry and can be coated as corrosion preventing metal in utensils. The periodic usage of the nickel metal by this way can account

Table 3 - Standard specifications for the irrigation parameters

<table>
<thead>
<tr>
<th>Irrigation Parameters</th>
<th>Formula Used (all Values in EPM)</th>
<th>Standard Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Hazards Ratio (MHR)</td>
<td>( \frac{Mg \times 100}{Ca + Mg} )</td>
<td>( &lt;50% = \text{suitable} ) ( &gt;50% = \text{unsuitable} )</td>
</tr>
<tr>
<td>Soluble Sodium Percent (SSP)</td>
<td>( \frac{Na \times 100}{Ca + Mg + Na} )</td>
<td>( &lt;20% = \text{excellent} ) ( 20 – 40 = \text{good} ) ( 40 – 60 = \text{permissible} ) ( 60 – 80 = \text{doubtful} ) ( &gt; 80 = \text{unsuitable} )</td>
</tr>
<tr>
<td>Kelly’s Ratio (KR)</td>
<td>( \frac{Na}{Ca + Mg} )</td>
<td>( &lt;1 = \text{suitable} ) ( 1 – 2 = \text{marginal} ) ( &gt; 2 = \text{unsuitable} )</td>
</tr>
<tr>
<td>Sodium Adsorption Ratio (SAR)</td>
<td>( \frac{Mg \times 100}{Ca + Mg} )</td>
<td>( 0 – 10 = \text{excellent} ) ( 10 – 18 = \text{fair} ) ( &gt; 20 = \text{poor} )</td>
</tr>
</tbody>
</table>

The table 4 shows the calculated values of all the irrigation parameters for samples collected in three different seasons. The sodium concentration found high in three sampling stations for all the seasons which were observed from the calculated SAR, SSP and KR values. In all the other sampling stations it was well within the permissible limit. So there is very less contribution of sodium for the saline nature of water samples.

The magnesium hazard ratio is well above the permissible value in all the sampling stations for all the seasons ranging from 54.81 to 79.70. Symptoms from increased magnesium intake are not common in humans because the body eliminates excess amounts. But excess magnesium will increase the salinity in water which in turn affects the growth of crops. High Mg ratio is due to surface water and subsurface water more reacted and passage through the limestone, kankar and granitic rock formation in the study area.

Table 4 - The irrigation parameters calculated for all the three seasons and in all areas under study

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Summer MHR</th>
<th>Summer SAR</th>
<th>Summer SSP</th>
<th>Summer KR</th>
<th>Winter MHR</th>
<th>Winter SAR</th>
<th>Winter SSP</th>
<th>Winter KR</th>
<th>Rainy MHR</th>
<th>Rainy SAR</th>
<th>Rainy SSP</th>
<th>Rainy KR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastcar Street</td>
<td>74.19</td>
<td>12.57</td>
<td>46.90</td>
<td>0.56</td>
<td>74.63</td>
<td>14.52</td>
<td>51.65</td>
<td>0.72</td>
<td>74.86</td>
<td>17.65</td>
<td>55.03</td>
<td>0.93</td>
</tr>
<tr>
<td>Westcar Street</td>
<td>64.58</td>
<td>27.81</td>
<td>69.56</td>
<td>1.64</td>
<td>75.94</td>
<td>35.68</td>
<td>68.83</td>
<td>1.84</td>
<td>70.83</td>
<td>12.02</td>
<td>52.32</td>
<td>0.71</td>
</tr>
<tr>
<td>Southcar Street</td>
<td>77.21</td>
<td>8.75</td>
<td>37.61</td>
<td>0.31</td>
<td>74.24</td>
<td>21.33</td>
<td>52.65</td>
<td>0.83</td>
<td>79.70</td>
<td>16.77</td>
<td>45.44</td>
<td>0.65</td>
</tr>
<tr>
<td>Northcar Street</td>
<td>74.64</td>
<td>18.00</td>
<td>56.18</td>
<td>0.88</td>
<td>71.70</td>
<td>17.27</td>
<td>57.60</td>
<td>0.97</td>
<td>72.00</td>
<td>14.66</td>
<td>56.01</td>
<td>0.85</td>
</tr>
<tr>
<td>Vanidgate</td>
<td>75.60</td>
<td>28.71</td>
<td>67.28</td>
<td>1.28</td>
<td>74.74</td>
<td>29.14</td>
<td>67.74</td>
<td>1.49</td>
<td>72.45</td>
<td>28.69</td>
<td>67.06</td>
<td>1.45</td>
</tr>
<tr>
<td>Annamalai Nagar</td>
<td>73.55</td>
<td>13.28</td>
<td>56.40</td>
<td>0.57</td>
<td>71.69</td>
<td>8.89</td>
<td>53.21</td>
<td>0.42</td>
<td>55.63</td>
<td>14.36</td>
<td>66.98</td>
<td>0.85</td>
</tr>
<tr>
<td>Min Nagar</td>
<td>64.22</td>
<td>27.02</td>
<td>67.28</td>
<td>1.25</td>
<td>57.54</td>
<td>33.09</td>
<td>70.46</td>
<td>1.75</td>
<td>60.64</td>
<td>12.27</td>
<td>59.04</td>
<td>0.63</td>
</tr>
<tr>
<td>Ammapatai</td>
<td>76.61</td>
<td>16.76</td>
<td>54.20</td>
<td>0.80</td>
<td>62.24</td>
<td>49.79</td>
<td>77.55</td>
<td>2.94</td>
<td>54.81</td>
<td>19.23</td>
<td>63.11</td>
<td>1.17</td>
</tr>
</tbody>
</table>
for increase in concentration of this metal. Next to nickel, the chromium plays an essential role in day to day life. Naturally occurring chromium is mostly present in the trivalent oxide chromite which has a very stable spinel crystal structure. Hexavalent chromium is more toxic than trivalent state and its presence in environment totally derived from human activities. Chromium salts and chromate are used in painting, lithography, textile printing, tanning, dyeing, photography, wall paper, electric storage battery cells, matches and rubber goods [22]. These are some major factors which influence the increase in concentration of toxicity in soil and ground water. Iron is also an essential element for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders. The usage of iron is more in the form of utensils, rods, pipes, etc. Rusting of iron can result in increasing iron concentration in ground water. However these three trace elements or minor elements Ni, Cr, and Fe were within the permissible limit.

**Detection of non-essential elements**

The non-essential elements are even more toxic when they exceed the permissible limit and can cause serious threat to human life. The concentration of cadmium ranges 0.001–0.006 mg/l and lead ranges 0.20–0.44 mg/l for the three seasons. Cadmium is not involved in any known biological processes (non essential metal) and may be quite toxic as it is accumulated by organisms [23]. It is known to disturb enzyme activities, to inhibit the DNA – mediated transformation in microorganisms, to interfere in the symbiosis between microbes and plants, as well as to increase plant predisposition to fungal invasion. Cadmium is one of the most widespread and toxic metals in soils. It is mainly produced by industrial activities, mining and zinc refining. This metal has been reported to be the one with the highest rate of global emission to soil [24]. The cadmium concentration is found within the permissible limit in all the sampling stations during all the three seasons. Lead is probably the most frequently occurring heavy metal in contaminated environment. Sources of Pb contamination include various human activities. Lead is also a non essential element for biological activities. Pb is proven animal carcinogen on the basis of sufficient animal data. It is currently considered by the International Agency for Research on Cancer (IARC) to be a possible human carcinogen (group2B) on inadequate evidence [25]. In Chidambaram area imitation gold is so famous and prepared in greater extent than other area. The lead metal plays an important role in Chidambaram area due to activities on preparation and usage of imitation gold. For washing the imitation gold and for preparation lead is used as accessories and hence it can be dumped in soil which can affect the ground water quality.

**Table 5** - The metal ratio for all the three seasons and in all areas under study

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Summer</th>
<th>Winter</th>
<th>Rainy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>East car Street</td>
<td>0.004</td>
<td>0.800</td>
<td>0.571</td>
</tr>
<tr>
<td>West car Street</td>
<td>0.035</td>
<td>0.400</td>
<td>0.286</td>
</tr>
<tr>
<td>South car Street</td>
<td>0.006</td>
<td>0.200</td>
<td>0.143</td>
</tr>
<tr>
<td>North car Street</td>
<td>0.002</td>
<td>0.200</td>
<td>1.857</td>
</tr>
<tr>
<td>Vanidgate</td>
<td>0.005</td>
<td>1.400</td>
<td>0.714</td>
</tr>
<tr>
<td>Annamalai Nagar</td>
<td>0.008</td>
<td>0.600</td>
<td>1.143</td>
</tr>
<tr>
<td>Min Nagar</td>
<td>0.004</td>
<td>1.800</td>
<td>0.571</td>
</tr>
<tr>
<td>Ammapatai</td>
<td>0.002</td>
<td>1.600</td>
<td>0.857</td>
</tr>
</tbody>
</table>
Contamination index

In calculating the contamination indices of the metals in water samples, the control samples were taken to represent the background concentration. The calculation was done using the formula:

\[ \text{Metal ratio} = \frac{\text{Concentration of metal in sample}}{\text{Background concentration of metal}} \]

The results in Table 6 and Fig. 2 indicate that metal ratio ranges 15 - 40 for Lead metal which is well above the permissible limit. The usage of lead metal in processing imitation gold is the prime reason for high metal ratio. The metal ratio found to decrease during rainy and winter season but still it is well above the permissible value. Since it does not involved in any biological the water quality affected to a greater extent.

Quantification of Anthropogenic metal

Considering the metal content of the control sample or permissible value as representing the lithogenic metal, the proportion of anthropogenic metal was determined for each metal means of the following formula,

\[ \text{Anthropogenic metal} = \frac{\bar{X} - \bar{X}_C}{\bar{X}_C} \times 100 \]

Where \( \bar{X} \) = average concentration of the metal in the groundwater

\( \bar{X}_C \) = average concentration of the metal in control sample or permissible limit

Lead is the only element which has high anthropogenic input. The remaining elements are very little or having no anthropogenic input in all then sampling stations which can be observed from the Fig. 3. The anthropogenic input of lead metal is mainly due to the making of imitation gold in these areas.

Pearson correlation coefficient

This coefficient measures the strength of a linear relationship between any two variables on a scale of -1(perfect sympathetic relation). In this study, the metal concentration data was used in calculating the correlation coefficient using the SPSS computer software package [26]. The matrix of linear correlation coefficient is show in Table [3]. The correlation coefficient values varies from -0.436 between Pb and Na, to 0.572 between Ca and Mg. The following results obtained from correlation matrix.

i. Calcium shows a better positive correlation with magnesium and potassium.

ii. Sodium shows a better positive correlation with chromium and negative correlation with lead. The negative correlation suggests that lead concentration decreases with increase in sodium. The unusual trend was absorbed between sodium and lead and does support with the pearson's correlation matrix and this may be due to the more influence of lead for making imitation gold ornaments by the local industries. The lead concentration decreases during rainy and winter season due to dilution factor but the corresponding increase in sodium is due to the rise in sodium absorption ratio (SAR). So the lead concentration does not influenced by sodium.

Table 6 Pearson Correlation coefficient matrix for minor and major elements

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>.572**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>.025</td>
<td>-.051</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>.544**</td>
<td>.139</td>
<td>.038</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>.015</td>
<td>-.057</td>
<td>.052</td>
<td>0.107</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>.182</td>
<td>-.057</td>
<td>.435*</td>
<td>0.400</td>
<td>-.085</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>-.283</td>
<td>-.101</td>
<td>-.133</td>
<td>0.058</td>
<td>-.155</td>
<td>.043</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>-.082</td>
<td>.247</td>
<td>-.436*</td>
<td>0.158</td>
<td>0.180</td>
<td>-.115</td>
<td>.308</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>-.194</td>
<td>.017</td>
<td>-.250</td>
<td>-.205</td>
<td>0.100</td>
<td>-.153</td>
<td>.316</td>
<td>.273</td>
<td>1</td>
</tr>
</tbody>
</table>
All other metal combinations have weak correlation between them which shows that there is very less influence of each metal over the other.

**One way ANNOVA for seasonal & sampling station variation**

One way ANNOVA Duncan’s test was carried out for seasonal variance of macro & micro element concentration. The results show that the concentration of all the metals except lead does not vary with summer, winter and rainy seasons. Lead alone shows a considerable variation in concentration for all the three seasons (P<0.05). The mean concentration of lead is more during summer season, it decreases during rainy season and the minimum concentration was found during winter season which was observed from table 5.

The Duncan’s test for variation of metal concentration with sampling station shows a wide range of variation in most of the metals. The following results obtained from Duncan’s test,

- Ca, Mg, K, Cr, Ni & Cd have variation in metal concentration with sampling station.
- Na, Fe & Pb does not vary with sampling station.

The sodium and lead concentration is high in all the water samples collected in the study area which is attributed to the non variance in concentration with sampling station. Iron is the most common metal...
found in all the area due to its high usage as metal pipes and lead is due the usage of the local industries for making imitation gold ornaments.

R – Mode Factor analysis for

Using rotated factor loading and commonalities varimax rotation analysis, informations about the main factors in the studied samples was obtained. The successive factors account for decreasing amounts of residual variance using four factors (varimax rotation) for the elements Ca, Mg, Na, K, Fe, Cr, Ni, Pb & Cd in the ground water. The main factor (>0.6) for Lead, Nickel, Cadmium & Sodium is noted as factor 1. Factor 2 contributes Calcium & Magnesium while factor 3 contributes Chromium & Potassium. Factor 4 contributes only Fe. Factor analysis or named principle component analysis is a useful tool in the examination of multivariate data. The cumulative percentage of explained variance in ground water is 72.65%. Factor 1 account for 21.21% of the total data variance. Lead and cadmium are the elements with higher concentration. The anthropogenic input of these metals is mainly due to the processing of imitation gold. Factor 2 accounts for 20.66%, while factor 3 accounts for 18.08%. Factor 4 which has iron alone accounts for 12.70% of the total data variance.

CONCLUSIONS

The pH, major and minor element concentration of ground water in Chidambaram area was found to be within the permissible limit except a slight increase in sodium and magnesium metals. The sodium metal shows a slight increase in few sampling stations and which also diluted during winter and rainy seasons so there are no toxic effects due to sodium metal. On the other hand the magnesium is high as it is supported from MHR ratio in all the sampling stations and may cause toxic effects for growing plants. Among the non essential elements cadmium is well within the permissible limit but the
lead metal is high in all the sampling stations. Since these are not involved in any biological activities even a slight increase in concentration is hazardous to organisms. The level of increase in Lead and Cadmium metals are attributed to the usage of these metals in preparing imitation gold ornaments. The ground water pollution by these metals has to control or it will lead to a hazardous situation in future.

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