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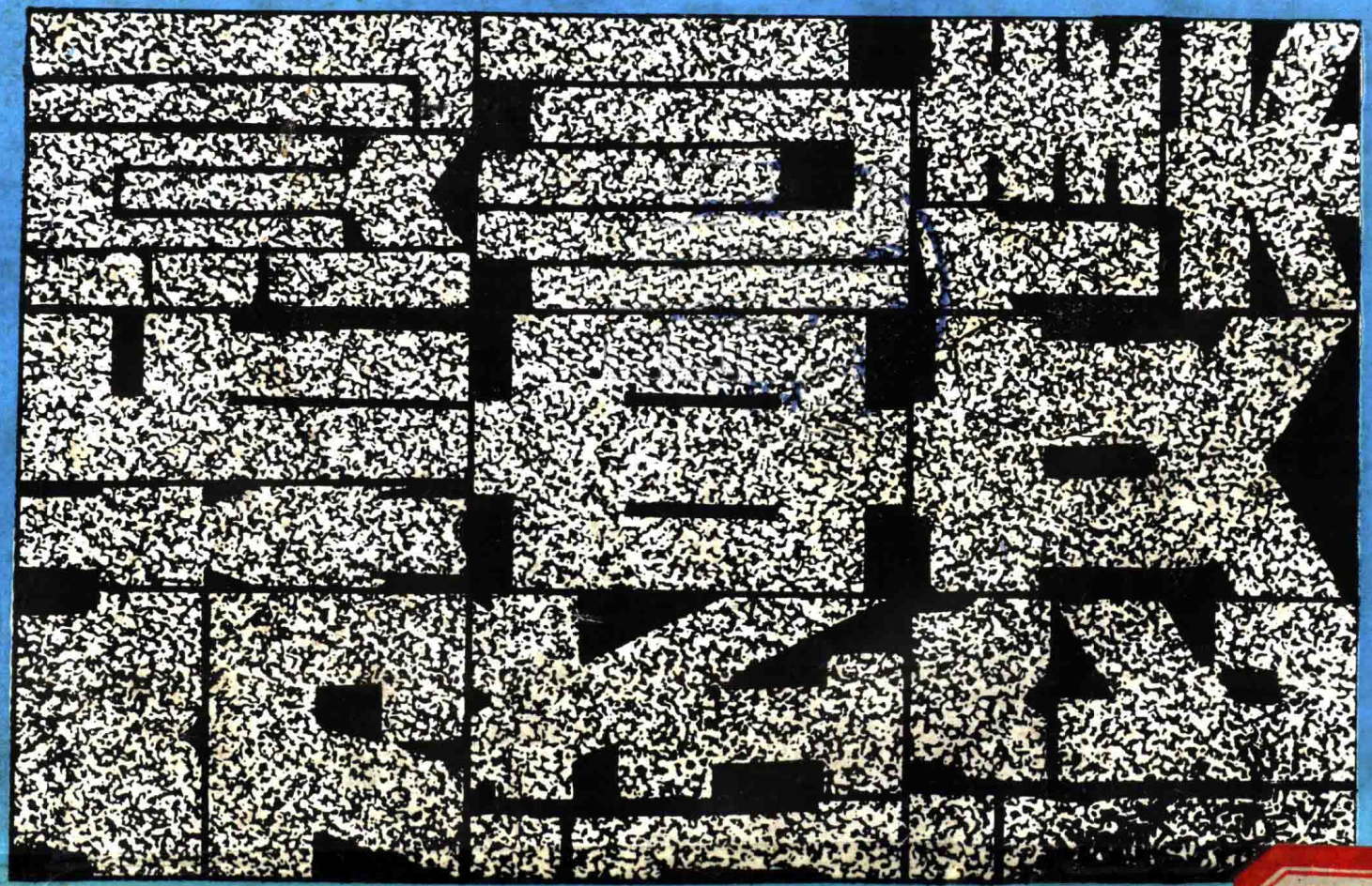
湖南大学测试分析中心



前　言

随着电子技术、生物技术、新材料技术和新能源技术的迅速发展，它们对分析化学的要求越来越高，要求分析科学从宏观到微观，从表面到内层，从结构到价键，从静态到动态。既要担任常规成分分析，又要准确分析物质的表面组分，元素空间分布、氧化及络合状态、晶体形态以及中间不稳定体及其活化状态等等，以此推动其它学科的向前发展，另一方面，其它学科，特别是电子学、物理学、数学的发展，也大大促进了分析化学的飞跃，从而使得分析化学远远超出了原来传统的范围，也因此而构成了当今分析化学的主要发展趋势：①仪器化、自动化、微量化、②高效、高精度、高灵敏度。③各种分析方法的相互渗透，各种分析仪器的联用（GC/MS、LC/MS、GS/FTIR，LC/FTIR，GC/AAS，HPLC/AAS，GC/NMR等）④多学科渗透交叉，横向结合。

无疑，以先进的大型精密仪器为主要实验手段的分析测试技术是现代科学技术的重要组成部分，特别是在“生物学世纪”的21世纪，它有着无可争议的重要地位和作用。

在校处领导及有关部门的关怀和帮助下，校分析测试中心于去年正式成立。在许多教授专家和兄弟单位的支持下，在这段的时间内，我们开发了现有的所有设备，为我校科研教学作了一些工作，我们选择了使用我室仪器完成的教学科研中部分论文，以及我室现有仪器简介等汇编成册，其目的是为了使全校教师和研究生等对该方面的工作有进一步的了解，以便更好地开发和发挥各种仪器在我校科研，教学中的作用，并以此祝贺我校第四届科研工作会议的召开。同时也作为一个科技交流资料，敬望国内外同行指正。

我们还想提出的是：在我们开展工作过程中，先后得到美国贝克曼公司(Beckman)瓦特斯公司（Waters），瑞典LKB公司，日本岛津公司（Shimiadzu），日立公司（Hitachi）等国外公司的有关部门免费修理了已过期的有关仪器，并无偿的赠送了有关电路板及元件。我们的全部工作，得到了学校科研处领导的大力支持，在此，一并致谢。

鉴于编者水平及条件的限制，错误和不妥之处在所难免，敬请诸位专家，读者批评指正。

湖南医科大学分析测试中心

1990年3月

封面设计　朱力

目　　录

第一部分：分别测试中心论文

第二部份：本校教师、研究生代表性论文

分析测试中心论文

Trace Elements in Medicine, Vol.5, No.3 - 1988(pp.93-96)

TRACE ELEMENT CONTENT IN DRINKING WATER OF NASOPHARYNEAI CARCINOMA PATIENTS (I)

中文摘要

随着对癌症的深入研究，许多作者注意到钴、铬、镍、碲、铍、镉、铁、铅、锌、砷等元素化合物的致癌与促癌作用［1—4］

关于鼻咽癌的发病与环境致癌因素的关系 Clifford提出与苯并芘有关［5］，潘世成、何鸿超提出与亚硝胺化合物有关［6］，近年来宝祥等提出与饮用水中镍含量有关［7—8］马来西亚及香港的学者提出与食用熏鱼有关〔14〕。

本文就我省曾对鼻咽癌高发区进行了综合考察。我们根据鼻咽癌综合考察组的调查设计，曾对高发区病人、健康人及低发区健康人的饮用水中铜、镉、铅、锌、镍、铬、锰等元素作了对照分析测定，经统计处理得到，鼻咽癌高发区与低发区饮用水中镍、锌、铅、镉的含量有显著性差异，与鼻咽癌死亡率呈正变关系。鉴于体系中PH值对存在于体系中的任何元素，不论在价态、化合形态、离解状态，化合能力以及人体对微量元素的吸收程度和由此引起人体生理功能的变异均有着重要的作用。为此，对高低发区饮用水中微量元素含量与饮用水PH的比值作了统计处理，结果表明：所测微量元素，仅Ni／PH与鼻咽癌死亡率呈正变关系，我们认为：鼻咽癌死亡率与饮用水中微量元素的关系，不能单纯根据饮用水中微量元素浓度的大小来衡量，而与环境因素PH有关，与M/PH有关（M为饮用水中金属离子浓度，PH为饮用水的酸度）。

本文就上述实验作了报道，并就所提出看法进行了讨论，同时对研制的离子交换—原子吸收法作了介绍。

该文已有美国等25个国家来函要求索取原文及资料。

Trace element content in drinking water of nasopharyngeal carcinoma patients* (I)

XIA LING-WEI, LIANG SHAO-XIAN, JIANG JI-WEN, ZHOU XIAO-JUAN AND LI JIAN

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Abstract. Residents of the Xiangxi region of Hunan province in China show a high incidence of nasopharyngeal carcincma (NPC) . To analyze the relation between NPC and trace elements, the concentrations of 7 trace elements in drinking water from high and low-incidence areas were studied (75 samples) . The results showed that the concentrations of Ni, Zn and Cd in drinking water from the high-incidence area were significantly higher than those in the low-incidence area. Especially, the Ni level in drinking water had a significant positive correlation with NPC morbidity. These observations are consistent with earlier studies. We also found a highly positive correlation between Ni/pH value in drinking water and NPC morbidity. This suggested that considering the ion concentration alone was not sufficient; we should also pay attention to the pH of the drinking water when we study the reationship between NPC and trace elements. Because pH in the medium can strongly affect trace element chemical characteristics and its metabolic state in living systems, the M/PH (M = metal concetration) ratio may be a considerably important factor, worthy of further research.

Key words: trace elements-nasopharyngeal carcinoma M/pH-nasopharyngal carcinoma morbidity-carcinogen

Introduction

previous research on nasopharyngeal carcinoma(NPC)found several environmental factors related to NPC. Ho [1971, 1972] suggested that salted fish, a traditional food of the sonthern Chinese, might be a risk factor for NPC. Researches in Malasia and Hong Kong [Yu et al. 1985] showed a highly significant association between salted fish intake and NPC. Clifford [1983] suggested that NPC may relate to benzpyrene. Pan et al. (unpublished) related NPC to nitritoamine chemical compounds. Korenberg and Freedlander [1976] and Qu Bao-ziang et al. (unpublished) found the Ni content in drinking water was related to NPC. A study in Chung shan also showed Ni level in drinking water [Tannenbaum ct al, 1985] . Numerous environmental factors have been found [Fedder and Gonzalez 1985, Ho 1972] ; conclusive results, however, are not available.

Hunan province is one of the high-risk provinces for NPC in southern China [National Caacer Control Office 1980 a and b] . Compared with other environmental carcinogenic factors, trace elements in drinking water may be a more important risk factor for NPC. A correlation to

NPC has shown trace element differences in NPC patients.

The purpose of this study was to meaasure the concentrations of 7 trace elements in drinking water of high-and low-incidence areas, and the pH value of the samples. The second objective was to analyze the relation between NPC and trace elements, and the relation between NPC and M/pH.

Materials and methods

Classification of the experimental group

The subiects were classified into five groups, with fifteen cases in each. Groups 1, 2 and 3 consisted of patiens with nasopharyngeal cancer from high-incidence areas; groups 4 and 5 were people from low-incidence areas. Routine sampling methods were used to obtain drinking water samples in all groups. Seventy-five samples were collected. The ages of the control group were within a range of ± 5 years. The people from high-incidence areas had a long-term habit of drinking unboiled water. All subjects had lived 20 years or more in these areas.

Metbod of analysis and determination

The obtained water samples were analyzed to determine the contents of the element Cu, Cd, Pb, Zn, Ni, Cr and Mn by the ion-exchange atomic absorption method.

Statistics

We used rank tests for statistical analysis.

Results

The range and madian values for Cu, Cd, Pb Zn, Mn, Ni and Cr in drinking water in high-incidence areas and low-incidence areas are shown in Table 1.

With rank tests, differences, in trace element concentration between the drinking water of high-incidence area people and that of low-incidence ares people are shown in Table 2. The data indicates that there are highly significant differences in the levels of Ni, Zn and Cd in drinking water in high-incidence areas vs the low-incidence areas. Therefore, we hold that the development of nasopharyngeal cancer is directly related to the contents of Ni Zn and Cd in drinking water.

The Ni value corresponds well to that reported in the literature [National Cancer Control Office 1980a, Ou Bao-xiang unpublished].

Table 1 Range of element contents in each group (ppm/l)

Group	Samples n	Cu	Cd	Pb	Zn	Ni	Cr	Mn	PH
1 Range	15	0.5 – 9.9	Tr – 0.97	Tr – 17.6	6.5 – 23.9	0.34 – 5.86	Tr – 72.0	3.1 – 687.9	6.01 – 9.10
Median		2.6	0.42	5.3	13.0	1.03	2.0	7.8	7.30
2 Range	15	0.5 – 5.2	Tr – 1.03	Tr – 20.8	7.4 – 65.2	0.69 – 5.50	Tr – 9.0	0.8 – 31.3	6.40 – 9.10
Median		2.1	0.29	7.2	15.2	1.03	4.0	7.8	7.10
3 Range	15	0.5 – 9.9	Tr – 1.16	Tr – 13.6	5.4 – 21.7	Tr – 4.50	1.0 – 8.0	0.8 – 125.0	6.50 – 8.27
Median		1.6	0.60	6.4	10.9	1.03	5.0	4.7	7.10
4 Range	15	0.3 – 6.3	Tr – 3.42	Tr – 12.8	5.4 – 16.3	Tr – 0.52	Tr – 9.0	0.8 – 511.7	6.20 – 8.20
Median		2.1	0.06	1.6	7.6	0.17	4.0	3.1	6.85
5 Range	15	0.5 – 4.2	Tr – 0.90	Tr – 20.8	3.3 – 54.3	Tr – 0.34	Tr – 74.0	3.1 – 416.7	5.60 – 8.10
Median		2.1	0.03	0.8	8.7	0.34	5.0	7.8	6.50

Tr; Below the limit of detection.

Table 2 Data obtained from drinking water in high and low-incidence areaa with rank test.

Elemnt	Cd	Cu	pb	Zn	Ni	Cr	Mn	pH
Median(high-incidence area)	0.42	2.6	6.4	12.0	1.03	4.0	7.8	7.10
Median(low incidence area)	0.05	2.1	1.6	7.6	0.34	4.0	6.3	6.75
U	2.73	1.31	2.37	4.16	6.61	0.43	1.04	3.028
P	<0.01	>0.05	0.05>P>0.01	<0.01	<0.01	>0.05	>0.05	<0.01

Table 3 Multi-group comparison of M/pH value in drinking water.

M/pH	Cu/pH	Cd/pH	pb/pH	Zn/pH	Ni/pH	Cr/pH	Mn/pH
H	0.54	8.25	5.62	15.60	42.67	4.40	5.60

$X^2 0.01(4) = 13.28$; M = metal element

Table 4 Two-group comparison of Zn/pH, Ni/pH in drinking water among multi-groups

Comparison	1-2	1-3	1-4	1-5	2-3	2-4	2-5	3-4	3-5	4-5
Zn/pH	-	-	*	-	**	**	*	**	*	-
Ni/pH	-	-	**	**	-	**	**	**	**	-

* significant difference; ** highly signifficant difference

In order to determine the relationship between the ratio of the content of trace elements to pH value and the development of cancer, after calculation of M/pH of each gronp, we perfomed mnlti-group comparisons. Statistical treatment of the results are shown in Table 3.

Data from Table 3 indicates that the H value in Ni/pH and Zn/pH surpasses $X^2 0.01(4) = 13.28$; therefore, further two-group comparisons in the multi-group was made. The results are shown in Table 4 The results of Table 4 shows that there are no significant differences of Ni/pH in drinking water in high-incidence areas of nasopharygeal cancer within the two group comparisons of 1, 2, 3 and of 4 and 5 in low-incidence areas. Nevertheless, there are hign significant differences in the two-group comparsions between 1, 2 and 3 in high-incidence areas 4 and 5 in low-

indidence areas. But for Zn/pH this is not the case. This fact indicates the development of nasopharyngeal cancer is not only concerned with the amount of trace element contents but also closely related to the M/pH ratio. It may further suggest that the trace element-cancer relation is a very comprehensive and complicated problem with respect to chemistry and we cannot jump to conclusions purely according to the quantity of a given trace element.

Discussion

The results have shown that Ni, Zn, Cd and pb are present in drinking water in high-incidence areas in higher amounts than in low-incidence areas. Data analyzed by rank tests show that there are highly significant differences between the contents of Ni, Zn and in Cd high-indicence areas and low incidence areas. There are obvious differences in pb contents. The-refore, the incidence of nasopharyngeal cancer is in direct relationship to Ni, Zn, Cd aud pb in drinking water; among these Ni has already been recognized in the literature[Weinstein 1978]. Our study suggests that Zn, Cd and pb are additional foctors which may be related to NPC morbidity.

After further analysis ot M/pH in high-and low-incidence areas by rank tests,the obtained statistical data show that only Ni/pH is is linear relation with incideace nasopharyngeal cancer. This has been confirmed by epidemiology and animal studies [Pan Shi-cheng, unpubl.] . Simultaneously, the obtained statistical data also shows that there are no obvious relationships between the elemental contents of Cu, Cd, pb, Zn, Cr, Mn and NPC. This fact illustrates that trace elements play a very complicated role in the human body.

As mentioned before, to draw conclusions about the relationship with disease based purely on the contents of tarce elements is to examine only part of the problem. Our study points out the relationship between M/pH and NPC, which reflects the complexity of the influence of trace elements on disease and is one of the comprehensive factors to be taken into account.

At present, no conclusive judgement has beed made regarding the carcinogenic mechanism of trace elements from the viewpoint of chemical structure. Any state which trace elements possess (valence, affinity, combination, dissociation, ionization power and configuration to a great extent) depends on the characteristics of the system where they exist (such as the PH value in the system, the chemical

and physical nature of other ions in the system).

No doubt the influence of M/pH in a biological system is obvious. M/pH will influence the absorption degree of a given trace element by the body and as a result, influence the physiological function of the trace element. The views and ideas in this article can only be considered as a study of relationships between trace elements and nasopharygneal cancer.

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TRACE ELEMENT CONTENT IN DRINKING WATER OF NASOPHARYNGEAL CARCINOMA PATIENTS (Ⅱ)

XIA LING-WEI[a], LIANG SHAO-XIAN[a], JIANG JI-WEN[b], ZHOU[a] and LI JIAN[c]

SUMMARY

Chinese in the Xiangxi region of Hunan province in China have a high incidence of nasopharyngeal carcinoma (NPC). For analyzing the relation between NPC and trace elements, the concentrations of 7 trace elements in drinking water(well water)of high-and low-incidence areas were measured (75 samples). The results showed that the concentrations of Ni, Zn and Cd in drinking water of high-incidence areas were significantly higher than those in low-incidence areas. Especially, the Ni level in drinking water had a significant positive correlation with

NPC mortality. These observation are consistent with earlier studies. We also found a highly positive correlation between Ni/PH value in drinking water and NPC mortality. This suggests that only considering the ion concentration in drinking water is not enough, we should also pay attention to the pH of the drinking water when we study the relation between NPC and trace elements. Because the pH of the medium can strongly affect trace element chemical characteristics and its metabolic state in living systems, the M/pH (M, metal concentration) may be an important factor worthy of further research.

Key words:

Trace elements; Nasopharyngeal carcinoma; Nasopharyngeal carcinoma mortality; Carcinogenesis

INTRODUCTION

Previous research on nasopharyngeal carcinoma (NPC)demonstrated that several environmental factors were related to NPC. Ho [4,5] suggested that salted fish,a traditional food of the southern Chinese, might be a risk factor for NPC. Researchers in Malasia and Hong Kong [14] showed a highly significant association between salted fish intake and NPC. Clifford[1] suggested NPC was related to benzopyrene. Pan et al, (The Hunan provincial Data Collections of National ENT Association 1 -10, unpublished data)related NPC to nitrosamines. In recent years, Qu Baoziang et al. ([9] ,Clinical research of national trace elements and collected works of discussion, unpublished data) found the content of Ni in drinking water was related to NPC. A study in Chung shan country also showed high Ni levels in drinkink water[12]. Numerous environmental factors have been found[2, 5]; conclusive results, however, are not available.

Hunan province is one of the high-risk provinces for NPC in southern China[10,11]. Compared with other environmental carcinogenic factors, trace elements in drinking water may be a more important risk factor for NPC. Research on NPC has shown trace element differences between NPC patients and those who do not have this disease.

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*This study was a part of the comprehensive investigation and research program on NPC in Hunan Province, People's Republic of China.

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The purpose of this study was to measure the concentrations of 7 race elements in drinking water of high-and low-incidence areas and the pH value of the samples. The second objective was to analyze the relation between NPC and trace elements and the relation between NPC and M/pH.

MATERIALS AND METHODS

Classification of the experimental group

The experiment was classified into 5 groups, 15 cases in each group. Croups 1,2 and 3 were people with nasopharyngeal cancer in high-incidence areas, 4 and 5 were people in low-incidence areas. Seventy-five samples were collected. The meau ages of control groups were within 5 years. The people from high-inceidence areas had a long-term habit of drinking unboiled water (water All subjects had lived 20 years or more in the high risk areas.

Method of analysis

Method for water sampling and storage. The 5-1 sample containe was made of polythene plastic. After washing with tap water, they were immersed in 4%HNO_3 for at least 24 h and then washed with redistilled deionized water several times and air-dried. Before sampling was begun, the containers were washed with water samples 2–3 times. They were immersed 20–30 cm below water level, then their caps were removed and almost filled with water. Four milliltres of 1 : 1 HNO_3 was added to each 1-1 water sample to make pH<2. These samples were stored at below 4℃ for analysis and determinations were made 36 h after sampling. Before the samples were analyzed, it was necessary to filter them through quantitative filter papers and wash them with 3%HNO_3 several times and then with redistilled deionized water. The filtered water samples were then used for analysis.

Method of determination. The water samples were analyzed to determine the contents of the following elements: Cu, Cd, Pb, Zn, Ni, Cr, Mn by ion exchange-atomic absorption. The instruments used were Atomic Absorption spectrophotometer, Model AAS 5000 (Perkin-Elmer, U.S.A.), AAS WYX-402 (Made in China) and Cation-Exchanger, Model March Exchanger I. Atomic absorption working conditions were as shown in the Table below.

	Wavelength (A)	Lamp current (MA)	Flame condition	Spectral bandwidth (A)
Cn	3247	2	Lean flame	2.0
Cd	2283	2	Lean flame	2.0
Pb	2833	3	Lean flame	2.0
Zn	2139	4	Lean flame	2.0
Ni	2320	4	Lean flame	2.0
Cr	3579	4	Rich flame	2.0
Mn	2795	2	Lean flame	2.0

Fuel: acetylene. Support: Air. Light sources: H.C.L.

Detection limits were as follows:

Element	Cu	Pb	Zn	Cd	Ni	Cr	Mn
D.C. (ppm)	0.002	0.02	0.002	0.001	0.01	0.003	0.002

Statistical analysis

The Rank Test was used for statistical analysis of all data samples [15].

RESULTS

The range of element contents Cu,Cd,Pb,Zn, Mn, Ni, Cr, etc, in drinking water in high-incidence areas and low-incidence areas are given in Table 1.

With the Rank Test, difference in trace element concentrations among the high-incidence cases and the low-incidnce cases are shown in Table 2. The data indicate that there is a highly significant difference in trace element contents between Ni, Zn, Cd, in drinking water in high-incidence areas and low-incidence areas. Therefore, we hold that the development of nasopharyngeal cancer may be directly linkep to the contents of Ni, Zn, and Cd in drinking water. The Ni values correspond well to the literature ([9] Qu Bao-xiang et al., Clinical research of national trace elements and collected works of discussion, unpublished data).

After calculation of M/PH for each group, we performed multi-group comparisons to establish the relationship between the ratio of trace element content to PH value and the development of the cancer. Statistical treatment results are shown in Table 3.

Table 1 Range of element contents in each group (ppm/l)

Group	Samples n	Cu	Cd	Pb	Zn	Ni	Cr	Mn	PH
1 Range	15	0.5－9.9	Tr－0.97	Tr－17.6	6.5－23.9	0.34－5.86	Tr－72.0	3.1－687.9	6.01－9.10
Median		2.6	0.42	5.3	13.0	1.03	2.0	7.8	7.30
2 Range	15	0.5－5.2	Tr－1.03	Tr－20.8	7.4－65.2	0.69－5.50	Tr－9.0	0.8－31.3	6.40－9.10
Median		2.1	0.29	7.2	15.2	1.03	4.0	7.8	7.10
3 Range	15	0.5－9.9	Tr－1.16	Tr－13.6	5.4－21.7	Tr－4.50	1.0－8.0	0.8－125.0	6.50－8.27
Median		1.6	0.60	6.4	10.9	1.03	5.0	4.7	7.10
4 Range	15	0.3－6.3	Tr－3.42	Tr－12.8	5.4－16.3	Tr－0.52	Tr－9.0	0.8－511.7	6.20－8.20
Median		2.1	0.06	1.6	7.6	0.17	4.0	3.1	6.85
5 Range	15	0.5－4.2	Tr－0.90	Tr－20.8	3.3－54.3	Tr－0.34	Tr－74.0	3.1－416.7	5.60－8.10
Median		2.1	0.03	0.8	8.7	0.34	5.0	7.8	6.50

Tr; lower than the limit of detection.

TABLE2

THE DATA OBTAINED IN DRINKING WATER IN HIGH- AND LOW-INCIDENCE AREAS WITH RANK TEST

Element	Cd	Cu	Pb	Zn	Ni	Cr	Mn	PH
Median(high-incidence people)	0.42	2.6	6.4	12.0	1.03	4.0	7.8	7.1
Median (low-incidence people)	0.05	2.1	1.6	7.6	0.34	4.0	6.3	6.75
U	2.73	1.31	2.37	4.16	6.61	0.43	1.04	3.028
P	<0.01	>0.05	0.05>p>0.01	<0.01	<0.01	>0.05	>0.05	<0.01

TABLE3

MULTI-GROUP COMPARISON OF M/PH VALUE IN DRINKING WATER

M/pH	Cu/pH	Cd/pH	Pb/pH	Zn/pH	Ni/pH	Cr/pH	Mn/pH
H	0.54	8.25	5.62	15.60	42.67	4.40	5.60

$X^2 0.01(4) = 13.28$.

M, Metal element.

TABLE4

THE 2-GROUP COMPARISON OF Zn/pH, Ni/PH IN DRINKING WATER AMONG MULTI-GROUPS

	1-2	1-3	1-4	1-5	2-3	2-4	2-5	3-4	3-5	4-5
Zn/pH	–	–	*	–	**	**	*	**	*	–
Ni/pH	–	–	**	**	–	**	**	**	**	–

*Significant difference.

** Highly significant difference.

The data in Table 3 indicate pH values in Ni/pH surpass $X^2 0.01(4) = 13.28$, therefore, further 2-group comparisons in the multi-group was made. The results are shown in Table 4. There are no significant differeces of Ni/pH in drinking waterin high-incidence areas of nasopharygeal cancer within the 2-group comparisos of 1,2, 3, and of 4 and 5 in