

首都师范大学五十周年校庆资源环境与旅游学院
College of Resources, Environment & Tourism, Capital Normal University

论文集



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资源环境与旅游学院论文集

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培养创新的一代

地理系 刘先林

我国改革开放的二十多年,从科学技术的角度看,是为了实现“外国有的我们也要有”。如果要达到这一目标,只能靠大力提升全民族的创造力。过去被蔑视为“黄色蚂蚁”的中国人在当代经济方面取得了巨大成就,震撼了世界。中国如今被称为“世界工厂”,本世纪上半叶将成为全球第一经济大国。而当十几亿中国人的想象力、创造力都发挥出来,才真正是不可思议的!

知识经济时代的竞争说到底人才的竞争。世界各国都把知识的生产放在首要位置。中国古代曾有过许多重大的科技发明,只是在近现代落后了。为了迎头赶上,学习别人的先进科技是必要的,但作为人类的四分之一应该有更大的作为。最然“Made in CHINA”遍及世界,然而其中有知识产权的却是“没得多少”。提高全民族的创造意识、创造能力是我们面前的一个重大课题。其实,在当今知识高速增长的同时,旧知识也在高速消亡。这正是利用后发优势,实现跨越式发展,抢占新的制高点的好时机。关键是要让全社会都来关注“提高全民族的创新能力”。

在崇尚创造这一点上,理工科教育真应该象艺术教育学习。如果导演系、作曲系学生只会模仿别人,那是不能容忍的;而理工科的学生似乎只要理解好已有知识就行了。在创造热情上也应向文学艺术家学习,他们常常因按耐不住创作的热情,夜不能寐、奋笔疾书。

应该把青少年发明创造的欲望激发出来。脑子里总装着一个要解决难题的生活是富有挑战性的、最充实的生活,要坚信解决的办法肯定是有,只是暂时还没找到而已。发明家永无止境的创造热情是一个异常活跃的因素,是它驱使发明家不计名利,总是向往着新的事物,去实现人的最高追求,因为创作是人的高级需要。

多数人都成为发明家的潜能,每个环节都有创造分明的机遇:新理论、新发现、新方法、新材料、新产品、新工艺、新体制、新制度……各路创新好汉都能找到自己的位置。还应该总结那些自发的发明家的发明技巧,来造就一批自觉的发明家。诸如:激情来自何处?如何触发灵感?非常规的大跨度联想的作用等等。也不能样样都从头做起,要站在巨人肩上。看准时机、不怕讥笑,勇敢些、尽早变心动为行动,争取社会支持,要发扬团队协作精神,坚忍不拔,一切为了成功的那一刹那。万事开头难,有志者事竟成。创新成果就象一个新生儿,还要扶上马送一程。

创造发明也要从娃娃抓起,教育创新应该先于其它。被戏称为“坏孩子”的盖茨缔造了世界第二大经济巨人——微软,其成功之道之一是不完全以学历、分数选用人才。而我们的升学考试、教材、教育方法……都有必要来一次创新。科技界忽视创新、以文件大战论英雄的风气也很有必要改一改。

民族的未来取决于每个人的创新能力。社会人是由教师培育出来的,教师又主要是师范大学培养的,决定民族未来的重任历史地落在了我们肩上。

(发表于首都师范大学《高校研究》2001年第2期)

刘先林, 1939 年生于广西桂林, 1962 年毕业于武汉测绘学院。1973-1992 年在国家测绘局测绘科学研究所, 任工程师、高级工程师和教授级高工。1983 年当选第六届全国人民代表大会代表。1984 年, 刘院士作为国家测绘系统第一位应邀到国外讲学的学者赴法国地理院讲学 1 个月, 在法国讲学的讲稿被刊登在法国地理院的刊物上。1986 年被评为测绘系统劳动模范, 同年被国家科委授予有突出贡献的中青年专家。1994 年当选中国工程院首批院士。1995 年任中国测绘科学研究院院长。2001 年 2 月首都师范大学特聘教授、博士生导师、3S 工程中心主任, 资源环境与旅游学院名誉院长, 首都师范大学三维信息获取与应用教育部重点实验室、资源环境与 GIS 北京市重点实验室学术委员会主任。

1989 年被国务院授予全国先进工作者称号。1990 年被评为中央国家机关优秀共产党员, 并被国务院批准为享受政府特殊津贴专家。1992 年当选为中国共产党十四大代表, 同年任中国测绘科学研究院研究员。1994 年当选为中国工程院首批院士, 是建院时信息与电子工程学部 24 位院士之一。1995 年出任中国测绘科学研究院院长, 现为该院名誉院长。

刘先林院士是新中国培养的遥感、地理信息系统专家, 几十年来一直致力于数字摄影测量和遥感图像处理软件、仪器的研制开发。刘院士专业知识宽厚, 理论造诣深, 科研成果显著, 是我国遥感、地理信息系统领域的学术带头人之一。

1963 年, 刘院士研究成功“坐标法解析辐射三角测量”的新方法, 解决了航测内业辐射三角测量平面加密精度低的问题。该方法写入航测技术规范的第一个中国人发明的方法。1965 年, 刘院士完成了微分空中三角测量课题, 使得三维加密坐标可以一次获得, 大大提高了作业效率。

1967 年, 刘院士编制的 DJS-5 航测内业加密程序, 使新型的计算机技术第一次被引进了我国测绘生产领域。该程序从 1967 年到 1978 年, 在我国测绘系统运行了 12 年, 为国家生产了数以千计的地图。1981 年国际摄影测量学会第三委员会专门邀请刘先林院士, 参加国际数字地形模型的共同研究工作。1984 年, 刘院士研制的 ZS-1 正射投影仪以及与之相配套的 80 个程序的软件包, 在数据压缩、等高线软件等方面达到了国际先进水平, 并获国家测绘局科技进步一等奖, 1985 年获国家科技进步三等奖。1988 年, 刘院士相继研制成功集光电计算机技术于一体的 JX-1 解析测图仪、JX-3 解析测图仪和配套软件, 填补了国内该类仪器的空白, 占领了国内市场。该成果获 1992 年国家科技进步一等奖。1998 年, 刘院士研制成功 JX-4A 数字摄影测量工作站及其配套软件, 已销往全国并出口, 获国家测绘局 99 年度科技进步一等奖。2000 年, 刘院士主持开发的 Imatizer-2302 影像扫描仪及其软件, 是国家 863 和国家测绘局“九五”攻关项目“HX-23 影像数字化”的改进产品, 精度和影像质量又上了一个台阶。90 年代以来, 刘先林院士和他的科研集体加强了 3S 高新技术的开发应用, 承担的“国务院综合国情地理信息系统”、“无人驾驶微型航空遥感系统”、“基于测绘数字信息的洪水灾情快速清查技术的研究与应用”等科研项目均取得了重要进展。

刘院士的论文, 曾连续被四年一届的国际摄影测量与遥感大会选为第十四、十五、十六届大会报告论文。刘院士所完成的科研项目, 绝大部分已在全国推广应用, 并产生了很大的社会效益和经济效益。仅 JX-4A DPW 数字摄影测量工作站及其配套软件, 在国内市场就为国家节省外汇 2000 多万美元, 并出口到美国、日本、芬兰、韩国、泰国、巴基斯坦等国。刘院士科学研究与科技成果转化密切结合的工作实践, 在国内外产生了很好的影响, 为国家赢得了荣誉, 为发展我国的遥感、地理信息系统事业做出了突出的贡献。

刘院士在我院主要从事指导学科建设、指导青年教师和培养研究生、科学研究与技术开发等。

(资源学院供稿)



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MANAGEMENT OF GROUNDWATER IN ZHENGZHOU CITY, CHINA

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Abstract—Quasi-three-dimensional numerical simulating and optimum management model was established for evaluating and managing groundwater resources in Zhengzhou city. Based on the coupling of simulating model with a planning model, an optimum management model of groundwater resource was established. Through optimum controlling of the groundwater seepage field, environmental problem caused by unreasonable extraction of groundwater in the study area was decreased to the minimum level, which supply scientific foundation for groundwater resource management in Zhengzhou city. © 1999 Published by Elsevier Science Ltd. All rights reserved

Key words—groundwater seepage field, quasi-three-dimensional numerical simulation, optimum management of groundwater resource, Zhengzhou city

INTRODUCTION

The intense extraction of groundwater in Zhengzhou city has caused groundwater levels to decline; the environmental problems associated with the declination of groundwater levels are: (1) formation and expansion of depression cones, (2) increased pumping lift and pumping cost, (3) deterioration of the quality of pumped groundwater and (4) land subsidence. Based on establishing the numerical simulation model of groundwater seepage field, optimal management model and their coupling model, the extraction management mode of groundwater was optimized by model operating, then the environmental problem associated with the unreasonable extraction of groundwater was solved by controlling groundwater seepage field.

which is mainly composed of Quaternary Holocene series and upper Pleistocene series formation (embedded depth of bottom level is 60 m); (2) intermediate groundwater system, which consists of mid and lower Pleistocene series formation (embedded depth was 80–250 m). The shallow and intermedium aquifer are hydraulically connected to each other by aquitard, which consists of nonhomogeneous isotropic and quasi-three-dimensional groundwater seepage field (shallow and intermedium groundwater system is planar two-dimensional flow, aquitard is a vertical one-dimensional flow). The study area is composed by Dirichlet and Neumann type boundary. Macroscopic input and output water exchange of the system is yielded by actual measurement (Gong and Lin, 1996).

HYDROGEOLOGICAL CONCEPTUAL MODEL

In Zhengzhou city, the groundwater system consists of multilayer aquifer system (about 900 km²). For depth < 250 m, it may be outlined to Anderson (1992): (1) shallow groundwater system,

NUMERICAL SIMULATING MODEL

Based on hydrogeological conceptual model, a mathematical model describing groundwater table distribution in modeling area was built. Without considering the storage capacity of a weak permeable layer, the model is as the following.

The mathematical model of shallow groundwater system (I):

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$$\begin{cases} \mu \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left[K(h-b_1) \frac{\partial h}{\partial x} \right] + \frac{\partial}{\partial y} \left[K(h-b_1) \frac{\partial h}{\partial y} \right] + \frac{K'}{M'} (H-h) + q_1, & (x, y) \in (D), t \geq 0 \\ h(x, y, 0) = h_0(x, y), & (x, y) \in (D) \\ h(x, y, t) = f_1(x, y, t), & (x, y) \in (\Gamma_1^{(1)}), t > 0 \\ K(h-b_1) \frac{\partial h}{\partial n} = q_1(x, y, t), & (x, y) \in (\Gamma_2^{(1)}), t > 0 \end{cases}$$

The mathematical model of intermedium groundwater system (II):

$$\begin{cases} S \frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \left(T \frac{\partial H}{\partial x} \right) + \frac{\partial}{\partial y} \left(T \frac{\partial H}{\partial y} \right) + \frac{K'}{M'} (h-H) + q_2, & (x, y) \in (D), t \geq 0 \\ H(x, y, 0) = H_0(x, y), & (x, y) \in (D) \\ H(x, y, t) = f_2(x, y, t), & (x, y) \in (\Gamma_1^{(2)}), t > 0 \\ T \frac{\partial H}{\partial n} = q_2(x, y, t), & (x, y) \in (\Gamma_2^{(2)}), t > 0 \end{cases}$$

where K is the mean permeability coefficient of the shallow groundwater system (m/d); T the transmissibility coefficient of intermedium groundwater system (m²/d); h, H the groundwater table of the shallow and intermedium groundwater system (m); μ, S the feed water degree and storage coefficient (nondimensional parameter); k', M' the thickness of the interval weak permeable layer and vertical permeability coefficient (m/d); q_1 the algebraic sum of vertical recharge intensity of the shallow groundwater system (l/d), taking positive value; q_2 the algebraic sum of vertical recharge intensity of the intermedium groundwater system (l/d), taking negative value; b_1, b_2 the height of upper and lower boundary of weak permeable layer (m); D the planar seepage area determined synchronal by the shallow and intermedium groundwater system (m²); $\Gamma_1^{(1)}, \Gamma_2^{(1)}$ the known water level boundary of the seepage calculated area D ; $\Gamma_1^{(2)}, \Gamma_2^{(2)}$ the known discharge boundary of the seepage calculated area D and n the inner normal vector of secondary boundary.

Numerical solution of the simulation model

- Discrete of calculated area. Based on the feature of the groundwater seepage field in Zhengzhou city, as well as the structure of groundwater system and boundary condition, the calculated area was divided into 822 triangle units, 286 joints. Among them, there are 78 first type boundary points and 24 secondary type boundary points.
- Simulating phase. Selecting two time-periods from 4-25-1994 to 8-30-1994 and from 8-31-1994 to 2-25-1995, lasting one year, in which water level data was measured by groundwater long-term observation network in study area.
- Basis of parameter and its partition. Basis of selecting initial parameter and partition is: (a) pumping test data of calculated area, including permeable coefficient, coefficient of hydraulic conductivity, storage coefficient, feed water degree and unit inrush quantity, etc; (b) distribution regularities of aquifer, such as thickness, embedded depth and space combination feature of rock character; (c) natural flow field, artificial flow field, hydrochemical field and temperature field of groundwater, difference of geological condition.
- Input and output of the system. Based on precipitation data in the study area from 1951 to 1994, we get the average annual precipitation which is 640.9 mm, maximum annual precipitation is 1041.3 mm and the minimum annual precipitation is 349.3 mm. Wet year (frequency is 25%) precipitation is 584 mm, mean year (frequency is 50%) precipitation is 614 mm, dry year (frequency is 75%) precipitation is 584 mm. The evaporation intensity of shallow groundwater system is measured value in Zhengzhou hydrological budget test site; recharge parameter quoted those data in neighbor area which hydrogeological condition is similar to; the influent recharge of surface water and irrigating water is statistical value of measured data, groundwater production volume too.
- Discretization of numeric simulating model. Using irregular mesh finite difference method, each node is a center of a small equalization area which is outlined by triangle line. In every equalization area, equation and constant-solution condition of mathematical model were discreted, differential quotient is instead of by difference quotient, difference equation of every node was got, then we get these series equation set:

$$\begin{aligned}
 & - \sum_{\beta=1}^p A_i^{\beta} (h_j - h_i) - \sum_{\beta=1}^p B_i^{\beta} (h_k - h_i) \\
 & + \sum_{\beta=1}^p F_{\alpha}(i) q_1^{\beta} + \sum_{\beta=1}^p \frac{K'}{M'} F_{\alpha}(i) (h_i - H_j) \\
 & = \sum_{\beta=1}^p \mu_{\beta} F_{\alpha}(i) (h_i^{t+1} - h_i^t) / \Delta t
 \end{aligned} \quad (1)$$

$$\begin{aligned}
 & - \sum_{\beta=1}^p A_i^{\beta} (H_j - H_i) - \sum_{\beta=1}^p B_i^{\beta} (H_k - H_i) \\
 & + \sum_{\beta=1}^p F_{\alpha}(i) (h_i - H_j) \\
 & - \sum_{n=1}^m Q_n \varphi_n (x_n - y_n) \\
 & - Q_i = \sum_{\beta=1}^p \mu_{\beta}^* F_{\alpha}(i) (H_i^{t+1} - H_i^t) / \Delta t,
 \end{aligned} \quad (2)$$

where

$$A_i^{\beta} = \begin{cases} K_{ij} (H_j - Z_{ij}) \frac{b_i b_j + c_i c_j}{4 \Delta \beta} \\ T_{ij} \frac{b_i b_j + c_i c_j}{4 \Delta \beta} \end{cases}$$

$$B_i^{\beta} = \begin{cases} K_{ik} (H_k - Z_{ik}) \frac{b_i b_k + c_i c_k}{4 \Delta \beta} \\ T_{ik} \frac{b_i b_k + c_i c_k}{4 \Delta \beta} \end{cases}$$

$$F_{\alpha}(i) = \sum_{\beta=1}^p$$

$$\left[\frac{b_k^2 + c_k^2}{16 \Delta \beta} (b_i b_j + c_i c_j) + \frac{b_j^2 + c_j^2}{16 \Delta \beta} (b_i b_k + c_i c_k) \right]$$

$\theta(x_n, y_n)$ are area coordinates; K_{ij} and K_{ik} are harmonic-mean of permeability coefficient between (i, j) node and (i, k) node; K_{ij} , K_{ik} , K_{jk} are permeability coefficient of i, j, k nodes; μ_{β} are specific yield and storage coefficient inside β triangle; Z_{ij} is elevation of the unconfined aquifer bottom between i, j nodes; Q_n is yield of node well located in (x_n, y_n) ; Q_i is yield of node well located in node i ; (β is area of β triangle; t is time step; P is number of triangles whose climaxes are node i).

6. Solution of differential equations. Eqs (1) and (2) are large systems of nonlinear equations whose solution cannot be got directly. For saving memory of computer and reducing computing-time,

we adopt overrelaxation iterative method. An approximate solution series whose rapidity of convergence is faster were added during iteration, it is: $H_{i,k+1}^{t+1} = H_{i,k+1}^t + \omega \cdot \Delta H_{i,k+1}^t$, $1 < \omega < 2$. For any one time-period, the iterating is over only when $\max |H_{i,k+1}^{t+1} - H_{i,k+1}^t| < \varepsilon$ ($10^{-7} < \varepsilon < 10^{-5}$), then enter next time-period.

7. Identification and certification of the simulating model. Initial point of model identification is trend surface analyzing flow filed from groundwater level data of observation network in whole study area at 2-25-1994, the groundwater flow field, at 8-31-1994 and 2-25-1995, is selected as contrast flow field. identification method is inverse simulating level to indirectly readjust parameters. Thirteen parameter areas, five in shallow groundwater system, four in a weak permeable stratum system and four in medium groundwater system, are determined after model identification. During identification time, well points whose absolute error is less than 0.5 m are 70% of 117 wells in a whole observation-network at the end of the first time-period, and are 71% at the end of second time-period, that meet the national standard. Certification time-period of the model is from 2-25-1995 to 7-30-1995 and precipitation data is from the meteorologic bulletin of the Zhengzhou meteorologic bureau; the groundwater yield is from statistical data of the groundwater regime monitoring report of the Zhengzhou water-saving and water-supplying office. Other inflow and outflow items are the same as the identification time-period of model. The result shows that nodes with a relative error less than 5% is above 80% of all level-observing nodes, which meets the national standard (Nation technique supervising bureau, 1994). As showing in Fig. 1:

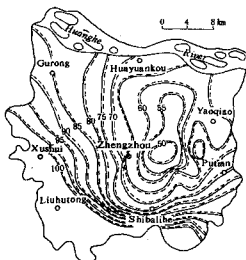


Fig. 1. Groundwater level of intermediate aquifer matched map on July 30th, 1995

OPERATION AND FORECAST OF SIMULATING MODEL

The forecasting result shows that the modeled shallow groundwater system on 7-30-1998 and on 7-30-1999 are similar to the initial flow field. It indicates that factors determining the regime of shallow groundwater are relatively steady during the forecasting time-period. The forecasting flow field of the intermediate groundwater system indicates that, if based on presently extract layout and planning extract yield, the distribution region with an area of 8.96 km² and a water level less than 45 m would appear in the center of the depression cone on 7-30-1998 (Fig. 2). It also indicates that the distribution region with an area of 8 km² and water level less than 40 m would appear in the center of the depression cone at 7-30-1999 (Fig. 3). The average dropping speed of the water level in the center of the drop hopper is 3.5 m/a. So, it is imperative that scientific management of groundwater has to be carried out.

MANAGEMENT MODEL OF GROUNDWATER RESOURCE

Analysing of simulating model

Constant solution problem I may be broken down to constant solution problem I_A (flow field determining by natural recharge-drainage conditions, i.e. uncontrolled condition) and the constant solution problem I_B (flow field determining by artificial recharge-drainage conditions, i.e. controllable condition).

Constant solution problem I_A:

$$\begin{cases} \mu \frac{\partial h'}{\partial t} = \frac{\partial}{\partial x} \left[K(h' - b_1) \frac{\partial h'}{\partial x} \right] + \frac{\partial}{\partial y} \left[K(h' - b_1) \frac{\partial h'}{\partial y} \right] + \frac{K'}{M'} (h' - H) + e_1(x, y, t), & (x, y) \in (D), t \geq 0 \\ h'(x, y, 0) = g_0(x, y), & (x, y) \in (D) \\ h'(x, y, t) = g_1(x, y, t), & (x, y) \in (I_1^{(1)}), t > 0 \\ K(h' - b_1) \frac{\partial h'}{\partial n} = -q_1(x, y, t), & (x, y) \in (I_2^{(1)}), t > 0 \end{cases}$$

Constant solution problem I_B:

$$\begin{cases} \mu \frac{\partial S}{\partial t} = \frac{\partial}{\partial x} \left[K(h' - b_1) \frac{\partial S}{\partial x} \right] + \frac{\partial}{\partial y} \left[K(h' - b_1) \frac{\partial S}{\partial y} \right] + \frac{K'}{M'} (S - S') + P_1(x, y, t), & (x, y) \in (D), t \geq 0 \\ S(x, y, 0) = 0, & (x, y) \in (D) \\ S(x, y, t) = 0, & (x, y) \in (I_1^{(1)}), t > 0 \\ \frac{\partial S}{\partial n} = 0, & (x, y) \in (I_2^{(1)}), t > 0 \end{cases}$$

where: h' is the natural phreatic water level (Anderson, 1992); S' is the falling value of water level caused by only controllable input (Anderson, 1992); $e_1(x, y, t)$ is the uncontrolled input variable [l³/d]; $P_1(x, y, t)$ is the controllable input variable

[l³/d]. So, $h = h' + S$, where: h is the real water level determining by constant solution problem I; h' is water level determined by the constant solution problem I_A; S is the falling value of the water level determined by the constant solution problem I_B. Same argument, formula II may be broken down to constant problem II_A and II_B. Model I_A and II_B are used as mathematical model calculating response matrix.

Formation of response function

In a flow field, if there are N inflow-outflow points which extract and inject water at the same time and affect M observation-points, $M \times N$ unit impulse response coefficients called response matrix may be formed during one time-period. If there are L time-periods, $M \times N \times L$, the three-dimensional matrix is formed, i.e. in the end of time-period n , the total response value of the water level in point i is equal to the total of the level response value for every point individual acting. So,

$$\begin{aligned} S(i, n) &= \sum_{j=1}^N S(i, j, n) \\ &= \sum_{j=1}^N \sum_{k=1}^N \beta(i, j, n - k + 1) Q(j, k), \end{aligned}$$

where, $S(i, n)$ is the total response level value of point i in the end of time-period n ; $S(i, j, n)$ is the unit impulse response efficient; $Q(j, k)$ is the impulse amount of point j in time-period k [l³/T >].

Utilizing the formula above, the level down or up value of any observation point caused by each pumping well or input well during any time-period may be got. The unit impulse response coefficient is $Q_{\text{unit}} = 400 \text{ m}^3/\text{d}$, by means of which the response

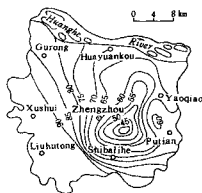


Fig. 2. Predicted groundwater level of intermediate aquifer on July 30th, 1998.

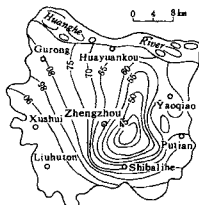


Fig. 3. Predicted groundwater level of intermediate aquifer on July 30th, 1999.

matrix of each management period in the future may be got, and acting as one group constraint condition merging into the optimum model.

Optimum of groundwater yield

It is the main problem to be solved in this program, that adjusting and controlling the shape of the groundwater depression cone through the optimizing yield of an intermediate groundwater system with a layout of existing extract wells and a satisfying condition of the groundwater total yield in the management area.

1. Management target. The target of groundwater management in a study area is not only satisfying water supply but also controlling depression cone expansion and to recover the water level in the center of the groundwater depression cone. So, the management problem becomes seeking a value of the decision index which makes the total value of level-falling of all nodes calculated in the whole area is least and using the yield of each management sub-area as well as the optimal distribution of the groundwater level in the whole area as decision variable, i.e.:

$$\min Z = \sum_{i=1}^m S_i \quad (3)$$

where, S_i is the falling value of the water level of node i (L^3) and m the total number of calculating nodes in the management area.

2. Constraint condition. Water level constraint: this group of constraint conditions assures the falling value of the water level of all calculating nodes in the management area is less than the falling value of the water level being specified. According to the principle of superposition and the response matrix, the falling value S_i of node i should equal the superposition value of the falling value of the water level of node j , caused by

the yield Q_j of each management sub-area j , i.e.:

$$\sum_{j=1}^{NQC} \beta_{ij} Q_j \leq S_{max} \quad (4)$$

where: β_{ij} is the response coefficient of node i caused by extracting in the management sub-area j (L^3); Q_j is the yield of management sub-area j (L^3/T); NQC is the number of the management sub-area.

So, the falling value of the water level of each calculating node:

$$[S] = \begin{bmatrix} \beta_{11} & \dots & \beta_{1NQC} \\ \dots & \beta_{ij} & \dots \\ \beta_{M1} & \dots & \beta_{MNQC} \end{bmatrix} \times \begin{bmatrix} Q_1 \\ Q_j \\ Q_{NQC} \end{bmatrix}$$

The constraint of the total amount of water supply: for satisfying the total amount of water supply in the study area, the sum of yield of each management sub-area should equal the total amount of water the supply.

$$\sum_{j=1}^{NQC} Q_j \geq D(t) \quad (5)$$

where, $D(t)$ is the planning water supply index of different management areas (L^3/T).

Constraint of least water supply of each sub-area: for assuring the property industrial and domestic consumption in each management sub-area, the least water supply amount should be kept in each management sub-area (particularly the center of the depression cones).

$$Q_j \geq Q_{mj} \quad (j = 1, 2, \dots, NQC) \quad (6)$$

where, Q_{mj} is the constraint of the yield in each management sub-area, which is determined by means of "ten-years planning of water-saving and water supply in Zhengzhou city (1991-2000)".

Constraint of positive value: each decision variable should have a positive value:

$$Q_i \geq 0; S_i \geq 0. \quad (7)$$

A linear programming model of optimum management of the groundwater yield in Zhengzhou city is composed by target function formula Eq. (3), constraint condition formula Eqs.(4-7).

OPTIMIZATION RESULT OF YIELD

The optimum yield and optimum distribution of water level in each management sub-area at the end of every management period are found by solving the linear planning model of the optimum of the groundwater yield in Zhengzhou city.

CONCLUSIONS

1. Optimization on yield of each of the sub-areas will obviously recover the shape of the depression cone for intermediate groundwater. The comparison between predicted the flow fields (Figs. 2 and 3) at the end of each management period and optimized flow fields (Fig. 4) shows that, most of the deep and steep depression cones and the smaller cones change into a unitary and steady depression cone in predicted flow fields, which are wide and assuasive. The groundwater level at the center of the cones in the optimized flow fields is 3-5 m higher than that in the predicted flow fields. As the exploitation of groundwater at the center of the cones in optimized flow fields has been transferred to the periphery of the cones, the cones expand their areas but reduce the deepness of groundwater. In results of optimization on groundwater flow, interference of the water-supplying wells at the center of the cones and the shortage of pumps and discharge are lightened greatly. In addition, increasing of the altitude difference between the shallow and the deep groundwater system on the edge of the cones, augments the leakage from the shallow groundwater system to the deeper system; it is advantaged to reduce the incidents such as the filling of water in the underground structure and land subsidence due to the shallow groundwater system.
2. The yield of intermediate groundwater should

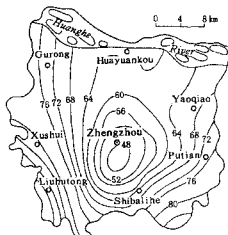


Fig. 4. Optimal head distribution of intermedium aquifer on July 30th, 1999.

- not be larger than $6.5 \times 10^7 \text{ m}^3/\text{a}$ in order to keep the depression cones in deeper groundwater at the present level (i.e. the area circled by a contour of 70 m is about 100 km^2). It based on modeling, predicting, optimizing of groundwater flow field and practicing in exploitation since 1982.
3. Coupling the numerical simulation model of groundwater flow field with the optimization model is effective for managing the groundwater resource. Some factors such as tech-economy, eco-environment and the law of the society are introduced into the management model, it has effective functions for unified planning and supplying of water resource and controlling of groundwater flow field.

REFERENCES

- Anderson M. P. (1992) *Groundwater Modeling*. Academic Press, New York, pp. 16-153.
 Gong H. L. and Lin X. Y. (1996) *Decision support system of urban water resource and environment management*. Xian map publishing company, Xian, China.
 Nation technique supervising bureau (1994) Technical requirement of work on modeling of groundwater resource management. National standard of P.R.C. (GB/T14497-93) 3, 1-15.

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Studies on Stability of ^{109}Cd , ^{65}Zn Complex with Humus Acids

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Abstract: The radioactive isotope tracer and ion exchange balanced method was used to study the stability of ^{109}Cd , ^{65}Zn complexes with humus acids. In the ^{109}Cd and ^{65}Zn single existing system with humic acids, the stability constants of humic- ^{109}Cd (^{65}Zn) complex compound was higher than fulvic- ^{109}Cd (^{65}Zn) complex compound. The stability constant of humic (fulvic) - ^{65}Zn was higher than that of humic (fulvic) - ^{109}Cd . In ^{109}Cd and ^{65}Zn coexisting system, stability constant and co-ordination number of humic (fulvic)- ^{65}Zn complex obviously increased, but stability constant and co-ordination number of humic (fulvic)- ^{109}Cd complex obviously decreased. The result showed that the humus matter with higher molecular weight could more effectively reduce plant availability of heavy metals than the humus matter with lower molecular weight in polluted soil, and that humus matter could more effectively reduce plant availability of Zn than that of Cd. Application of humus-acid increased harm of Cd and decreased harm of Zn to plant with Cd-Zn coexisting.

Key words: Humus acid; complex; Cadmium; Zinc; Stability of complex; Isotope tracer technique

The stability of heavy metals complexes with humus acids in soil affected the its ion's transformation, the transference and its plant availability directly. The stability of complex compound is indicated by the stability constant and co-ordination number. Many reports on the stability of complex compound by the single metal ions with humus acids were observed in 1980's^[1~4]. However, the contaminations by heavy metal in natural environment consist always multiply with another metals, for example, cadmium and zinc have same geo-chemical characteristics in environment respectively, so the contamination by cadmium always occurred with the zinc pollution, for the zinc mineral always associating with 0.1%-0.5% cadmium^[5]. Few reports were observed on the stability of Cd, Zn complex compound with humus acids in the soil conditions of Cd, Zn coexisted condition. The advantage of measuring the stability constants and co-ordination numbers of heavy metal complex with soil humus acids by radioactive isotope were that: (1) more coincided with the Schubert's principle of ion exchange balanced method, e.g. the concentration of complex ion was $10^2 \sim 10^3$ times more than heavy metal ion; (2) could avoid the disturb of metal ions in humus acids, simplify experimental processes, shorten the experimental time and improve the precision of the experiment; (3) could measure the stability constants and co-ordination numbers of more than two metals ions complexes with soil humus acids simultaneously and simplify the measure processes.

This paper mainly studied the stability of HA-Zn (Cd) complexes with Zn, Cd separated and coexisted conditions by using radioactive isotope tracer technique, so as to provide scientific basis for decreasing Zn and Cd in soil-plant system by using organic complex method.

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1 Materials and Methods

1.1 Materials

1.1.1 Soil samples: The soil used for the study is light color drab soil in north China originated from the forth diluvium-alluvial mother material, the soil samples were taken from the experimental farm of the Institute for Application of Atomic Energy, Chinese Academy of Agriculture Science, with the depth of 30 cm, the main minerals were montmorillonites, the basic chemical characteristics were: pH8.0, organic matter 1.76%, CaCO_3 2.46%, CEC 40.12 me / 100g, total Cd 0.10 mg / kg, total Zn 79.90 mg / kg, available P 15.7 mg / kg.

1.1.2 Humic acids for this study: The humic acids for this study were extracted and purified according to the method recommended by International Humic Acids Association (IHSS), e.g. extracted humic acids from soil by 0.1 mol / L $\text{Na}_2\text{P}_2\text{O}_7$ / NaOH and got the fulvic acids (yellow upper liquid) and humus acids (sediment) by acids treatment with 1:1 HCl, the humus acids were purified by ratio 1:1 of 0.1 mol / L HCl and 0.3 mol / L HF and translucening, and the fulvic acids by flowing through active charcoal column, H-ion exchange resin and then dried at 50°C vacuum.

1.1.3 The radioactive isotope used for this study: ^{65}Zn (ZnCl_2 solution), ^{109}Cd (CdCl_2 solution)

1.2 Analysis and test Methods

1.2.1 The stability constants and co-ordination numbers of cadmium (Cd), zinc (Zn) complex with humus acids and fulvic acids were tested by using radioactive isotope ^{65}Zn and ^{109}Cd tracer technique and the ion exchange balanced method recommended by Schuber^[6].

1.2.2 The methods of measuring the concentration of metal ions in balanced solution: drew some concentration-known humus acids solution (3 g / l, pH 8.0) as 0.1, 2, 4, 8, 16 ml, and put it in beaker with volume of 100ml, added some distilled water to 25ml in total, then 5 ml 1 mol / l NaCl (G.R) solution, 1 ml ^{109}Cd (CdCl_2), ^{65}Zn (ZnCl_2) solution with radioactive specific activity 2.6×10^4 Bq / ml (Cd: 7×10^4 μ g, Zn: 0.5 μ g), modulated the solution to pH8.0 and volume 45 ml, transferred the solution to centrifugal tube in volume 100 ml, added distilled water to 50 ml in total, then put 1.00 g Na-ion exchange resin in each centrifugal tube, vibrated one hour in thermostatic chamber, put the solution into beaker after balanced 24 hours for measuring radioactive specific activity by HPGe-gc-3018- γ meter.

1.2.3 Metal ions adsorbed by per unit resin after balance: washed the filtrated resin with 1-2 ml 2 mol / l HCl (G.R) and then 2-3 ml 0.1 mol / l, added distilled water to solution volume 50 ml. The radioactive specific activity of ^{109}Cd , ^{65}Zn were tested by HPGe-gc-3018- γ meter on condition of pH8.0, $\mu = 0.2$, T = $25 \pm 1^\circ\text{C}$.

2. Result and Discussion

The experiment data of the stability of Cd, Zn complex with humus acids and fulvic acids were listed as table1 and table2.

Conversed the data into equation as:

$$\text{Log} (\lambda_0 / \lambda - 1) = \text{Log } K + \text{Log } [A]^{[6]}$$

Among which: λ_0 : distributive coefficient of metal ion with absence of complex ion, here $\lambda_0 = [\text{MR}] / [\text{M}]$, λ : distributive coefficient of metal ion with presence of complex ion, here $\lambda = [\text{MR}] / [\text{M}] + [\text{MA}_x]$. The cut length in y-axis of the equation equaled to the stability constant and the slope of the curve equaled to the co-ordination number. We could get the stability constants and the co-ordination numbers of the ^{109}Cd , ^{65}Zn complex with humus acids and fulvic acids in soil with Cd, Zn separated and coexisted condition on the basis of the equation (table 3).

In the Cd and Zn single existing the stability constant (4.32) and the co-ordination number (1.65) of Zinc complex with humus acids (HA-Zn) were higher stability constant (3.93) and co-ordination number(1.56) of Cadmium complex with humus acids (HA-Cd), the stability constants and the co-ordination numbers of HA-Zn, HA-Cd were higher than that of zinc, cadmium complex with fulvic

Table1 Measurement of stability of HA-Zn(Cd) complexes with Cd, Zn separated and coexisted conditions

Added HA volume *(ml)	HA		Metal initial specific activity **(Bg/ml) [Mf]	Metal ion specific activity after balance (Bg/ml)			
	Solution volume 50 ml			In solution		On resin	
	Concentration [A](g/L)	Log[A]		Absence of HA [M]	Presence of HA {M}+[MAx]	Absence of HA [Mf]- [M]	Presence of HA [Mf]-[M]-[MAx]
Separated Zn HA-Zn							
0			302	57		245	
1	$3.0 \cdot 10^{-3}$	-2.5229	302		121		181
2	$6.0 \cdot 10^{-3}$	-2.2218	302		158		144
4	$1.2 \cdot 10^{-2}$	-1.9208	302		233		69
8	$2.4 \cdot 10^{-2}$	-1.6198	302		275		27
16	$4.8 \cdot 10^{-2}$	-1.3188	302		294		8
Coexisted Zn and Cd HA-Zn							
0			282	97		185	
1	$3.0 \cdot 10^{-3}$	-2.5229	282		144		138
2	$6.0 \cdot 10^{-3}$	-2.2218	282		199		83
4	$1.2 \cdot 10^{-2}$	-1.9208	282		244		38
8	$2.4 \cdot 10^{-2}$	-1.6198	282		264		18
16	$4.8 \cdot 10^{-2}$	-1.3188	282		280		2
Separated Cd HA-Zn							
0			1359	498		861	
1	$3.0 \cdot 10^{-3}$	-2.5229	1359		681		678
2	$6.0 \cdot 10^{-3}$	-2.2218	1359		975		384
4	$1.2 \cdot 10^{-2}$	-1.9208	1359		1114		245
8	$2.4 \cdot 10^{-2}$	-1.6198	1359		1290		69
16	$4.8 \cdot 10^{-2}$	-1.3188	1359		1320		39
Coexisted Zn and Cd HA-Zn							
0			1308	521		787	
1	$3.0 \cdot 10^{-3}$	-2.5229	1308		814		494
2	$6.0 \cdot 10^{-3}$	-2.2218	1308		1013		295
4	$1.2 \cdot 10^{-2}$	-1.9208	1308		1147		161
8	$2.4 \cdot 10^{-2}$	-1.6198	1308		1210		98
16	$4.8 \cdot 10^{-2}$	-1.3188	1308		1255		53

*Concentration of prepared HA solution: 3.00g/L **Metal ion s radioactive specific activity in solution volume 50 ml [A]:HA concentration; [Mf]:Metal initial radioactive specific activity in the solution; [M]-[Max]:Metal ions all specific activity in balance solution with presence of HA; [M]-[Mf]: Metal ions specific activity adsorbed by resin without HA; [Mf]-[M]-[Max]:Metal ions radioactive specific activity adsorbed by resin with presence of HA

acids (FA-Zn, FA-Cd), it meant that the stability of HA-Zn was higher than that of HA-Cd and the stabilities of HA-Zn, HA-Cd were higher than that of FA-Zn, FA-Cd, the co-ordination numbers of HA-Zn, HA-Cd and FA-Zn, FA-Cd all ranged from 1.11 to 1.88, that indicated the complex compound of HA-Zn, HA-Cd and FA-Zn, FA-Cd were the mixture of 1:1 and 1:2 complexion, but the proportion of 1:2 complexion in HA-Zn, FA-Zn was higher than that of HA-Cd, FA-Cd, e.g. the proportion of chelate

compound of HA (FA)-Zn was higher than that of HA (FA)-Cd. For the affinity of humus acids to metal ions was relative to the atomic number and the ion radius, the shorter the ion radius was, the stronger affinity of humus acids to metal ions appeared^[7],

Table2 Measurement of stability of FA-Zn(Cd) complexes with Cd, Zn separated and coexisted conditions

Added HA volume *(ml)	FA		Metal initial specific activity ** (Bg/ml) [Mf]	Metal ion specific activity after balance (Bg/ml)			
	Solution volume 50ml Concentration [A] (g/L)	Log[A]		In solution		On resin	
				Absence of HA [M]	Presence of HA [M]+[MAX]	Absence of HA [Mf]- [M]	Presence of HA [Mf]-[M]-[MAX]
Separated Zn FA-Cd							
0			296	64		232	
1	3.0*10 ⁻³	-2.5229	296		78		218
2	6.0*10 ⁻³	-2.2218	296		106		190
4	1.2*10 ⁻²	-1.9208	296		145		151
8	2.4*10 ⁻²	-1.6198	296		193		104
16	4.8*10 ⁻²	-1.3188	296		246		50
Coexisted Zn and Cd FA-Cd							
0			291	84		207	
1	3.0*10 ⁻³	-2.5229	291		104		187
2	6.0*10 ⁻³	-2.2218	291		143		148
4	1.2*10 ⁻²	-1.9208	291		196		95
8	2.4*10 ⁻²	-1.6198	291		235		56
16	4.8*10 ⁻²	-1.3188	291		266		25
Separated Cd FA-Cd							
0			1316	515		801	
1	3.0*10 ⁻³	2.5229	1316		572		744
2	6.0*10 ⁻³	-2.2218	1316		673		644
4	1.2*10 ⁻²	-1.9208	1316		801		515
8	2.4*10 ⁻²	-1.6198	1316		945		372
16	4.8*10 ⁻²	-1.3188	1316		1131		186
Coexisted Zn and Cd FA-Cd							
0			1347	515		859	
1	3.0*10 ⁻³	-2.5229	1347		558		816
2	6.0*10 ⁻³	-2.2218	1347		615		759
4	1.2*10 ⁻²	-1.9208	1347		701		673
8	2.4*10 ⁻²	-1.6198	1347		887		487
16	4.8*10 ⁻²	-1.3188	1347		1016		358

*Concentration of prepared FA solution: 3.000g/L **Metal ions radioactive specific activity in solution volume 50 ml [A]: FA concentration; [Mf]: Metal initial radioactive specific activity in the solution; [M]-[Max]: Metal ions all specific activity in balance solution with presence of FA; [M]-[Mf]: Metal ions specific activity adsorbed by resin without FA; [Mf]-[M]-[Max]: Metal ions radioactive specific activity adsorbed by resin with presence of FA

the atomic number and the ion radius of zinc were less than that of cadmium, so the affinity of humus acids to zinc was stronger than that to cadmium, and the stability constants of zinc complex with humus acids

Table 3 Stability constants (logK), co-ordination numbers (X) of Cadmium-humus acids and Zinc-humus acids(pH 8.0 $\mu = 0.2$ T = 25±1°C)

Humus acids	Stability constant(logK)				Co-ordination number(x)			
	Cd, Zn Separated		Cd, Zn Coexisted		Cd, Zn Separated		Cd, Zn Coexisted	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn

Humus acid	3.93	4.32	3.05	4.69	1.56	1.65	1.11	1.88
Fulvic acid	2.64	3.08	2.19	3.42	1.31	1.42	1.20	1.50

($\log K_{Zn}$) was larger than the stability constants of cadmium complex with humus acids ($\log K_{Cd}$) according to the same humus acids, that meant the stability of HA-Zn was higher than that of HA-Cd and HA-Zn was not easy to hydrolysis in soil solution. The affinity of humus acids to metal ions were stronger than that of fulvic acids to metal ions because of their chemical characteristics, luminous flux, molecular weight, function ions and negative electric charge, the affinity of complex ions to metal ions were relative to the negative electric charge, the stronger the negative electric charge was, the stronger the affinity appeared^[6], the affinity of humus acids to metal ions were stronger than that of fulvic acids to metal ions, so the stability constants of metal ions with humus acids ($\log K_{HA-M}$) were larger than that with fulvic acids ($\log K_{FA-M}$), for those reasons, fulvic acids could increase the transportability of zinc, cadmium in soil section, fulvic acids mainly acted as transmission of cation ions in soil, this had been confirmed by Schnizer^[9] and Tan's^[10] experiments. The main processes of fulvic acids assembling metal cation ions were that fulvic acids accumulated metal cation ions from inorganic mineral and resulted in water-soluble complexion, however, humus acids accumulated metal ions from the complexion of fulvic acids-metal ion (FA-M) by complexion competition and resulted in humus acids-metal ion (HA-M), the results above indicated that the stabilities of HA-Zn(Cd) complexion compound were higher than that of FA-Zn(Cd) which had been confirmed by Schnizer's^[9] experiments. So there existed much difference between the stability of HA-M and FA-M complexion, but the stabilities of FA-M complexion were lower than that of HA-M complexion due to the higher acidity and lower molecular weight, so the FA-M complexion always had higher plant availability and were easier to transport in soil environments than that of HA-M complexion. Besides the concentration of ions, the extent of humification, the pH, the stability of humus acids-metal ion complexion were affected by the competition of co-existed ions.

The results above showed the stability constants and co-ordination numbers of HA-Zn complexion were larger than that of HA-Cd with Zn, Cd co-existed conditions, the stability constant (4.69) and co-ordination number (1.88) of HA-Zn complexion were larger than that with Zn, Cd separated condition (4.32, 1.65 resp.) while the stability constants of HA-Cd complexion decreased from 3.93 to 3.05 and the co-ordination number from 1.56 to 1.11 with Zn, Cd co-existed, this indicated that the stability and the proportion of chelate compound of HA-Zn increased with cadmium co-existed but this reacted with HA-Cd complexion, the stability constants and co-ordination numbers of FA-Zn complexion were larger than that of FA-Cd with Zn, Cd co-existed, compared to that with Zn, Cd separated conditions, stability constant of FA-Zn went up from 3.08 to 3.42, and co-ordination number from 1.42 to 1.50. However, stability constant of FA-Cd went down from 2.64 to 2.19 and co-ordination number from 1.31 to 1.20, that indicated the stability and the proportion of chelate compound of FA-Zn increased with cadmium co-existed, while the stability and the proportion of chelate compound of FA-Cd decreased with zinc co-existed.

From the above we could conclude that the stability of humus acids-metal ions complexions were affected by the co-existing metal ions, so as the transportation, transformation and plant availability of the heavy metal ions. The result of this study showed that the humic matter with higher molecular weight could more effectively reduce plant availability of heavy metals than the humic matter with lower molecular weight in polluted soil, and that humic matter could more effectively reduce plant availability of Zn than that of Cd. So it could only achieve the aim of decontaminating soil polluted by heavy metal by applying humic matter which formed the HA (FA)-M complex compound with high stability when used organic complexion as the method of decontamination of soil.

3. Conclusion

- 3.1 The result showed the stability constants of humus acids-Cd (Zn) complex compound were higher than that of fulvic-¹⁰⁹Cd (⁶⁵Zn) complex compound; the stability constant of humus acids-Zn was higher than that of humus acids-Cd;
- 3.2 In Cd and Zn coexisted system, humic (fulvic)-⁶⁵Zn complex stability constant and co-ordination number obviously increased, but humic (fulvic)-⁶⁵Cd complex stability constant and co-ordination number obviously decreased. The stability constants and co-ordination numbers of HA-Zn (Cd) were higher than that of FA-Zn (Cd) and the stability of HA-Zn was higher than that of HA-Cd.
- 3.3 The stability constants and co-ordination numbers of HA (FA)-Zn obviously increased with Zn, Cd co-existing, on the contrary, The stability constants and co-ordination numbers of HA (FA)-Cd obviously decreased.
- 3.4 The humic matter with higher molecular weight could more effectively reduce plant availability of heavy metals than the humic matter with lower molecular weight in polluted soil. and that humic matter could more effectively reduce plant availability of Zn than that of Cd. Application of humic-acid increased harm of Cd and decreased harm of Zn to plant with Cd-Zn coexisting.

References:

- [1]. Xia R J. Humus Chemistry [M]. Beijing: *Beijing Agricultural University Press*, 1994, 258.
- [2]. Bao X M, Yu T R. Stability constant of soluble Fe^{2+} complexes in soil. [J]. *Acta Pedologica Sinica*, 1984, 23: 4~10.
- [3]. Zhu Y W Lu C Q. Stability constant of Zn complex with humus acid [J], *Acta Pedologica Sinica*, 1982, 19(1): 56~61.
- [4]. Lu C Q, Zhu Y W. Stability constant of Cd complex with humus acid [J], *Environmental Chemistry*, 1982, 1(5): 365~368.
- [5]. Adriano D C. Trace elements in the terrestrial environment[M]. New York, *Springer-verlag Inc.*, 1986, 517.
- [6]. Wen Q X. Research method of organic matters in soil [M]. Beijing: *Agricultural Press*, 1984, 237~249.
- [7]. Backwith R S. Metal complexes in soils[J]. *Aust. J. Agr.*, 1955, Res. 6: 685~695
- [8]. Yan Z X. chemistry of Complexes [M]. Beijing: *People Education Press*, 1960.
- [9]. Schnitzer M. and Kadama H.. The dissolution of micas by fulvic acid [J]. *Geoderma*.1976, 15: 381~391.
- [10] Tan D E. The release of Silicon, Aluminum and Potassium during decomposition of soil miner minerals by humic acid [J]. *Soil Sci.*1980, 129: 5~11.
- [11] Kuiters A.T and Mulder W. Gel Permeation chromatography and Cu-binding of water-soluble organic substances, from litter and humics layers of forest soils [J]. *Geoderma*.1992, 52: 1~15.

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