



## *Online Journal*

**Southern California Chinese American  
Environmental Protection Association  
(SCCAEPA)**

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## **Southern California Chinese American Environmental Protection Association (SCCAEPA)**

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## **A Few Words from Editor**

Dear SCCAEPA Online Journal Readers:

In this issue of the Southern California Chinese American Environmental Protection Association (SCCAEPA) Online Journal (ISSN 1944-8945), we published two peer-reviewed papers, one in English on freshwater lake water quality management and one in Chinese on new nano technology for environmental pollution remediation. In addition, this issue, I wrote a commentary on a book in the subject of environmental solutions, published in Chinese and the commentary written in English. Finally, we include a poem for water in both English and Chinese language.

To sustain the journal, we need members' contributions. I invite you to submit your work and written materials from your experience. To make things easier, I would like to suggest short articles that can be modified from your conference presentations and slides. The Journal is also open to outside of our association.

Enjoy!

Sincerely,

Yue Rong, Ph.D.  
Editor-in-Chief  
SCCAEPA Online Journal  
March 2011  
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## **Disclaimer**

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# 水頌

葉向東

紀念 3 月 22 日世界水日並獻給所有熱愛自然和環保事業的人

## ODE TO WATER Xiangdong Ye

English Translation by Kylie Hsu  
California State University, Los Angeles

Commemorating World Water Day on March 22, 2009, and Dedicated to All Nature  
Lovers and Those Involved in Environmental Protection

你從太空下來，  
匯成江河湖海。  
為了孕育生命，  
不辭艱辛，  
日夜兼程。  
你是生命之源，  
你是地球母親的血脈。

You descend from the heavens,  
Forming rivers and lakes.  
So as to nurture life,  
Day and night you work,  
Overcoming difficulties and hardships.  
You are the source of life,  
You are the blood stream of Mother Earth.

你是天下之至真，  
無色無味，  
質樸純潔。  
表裡如一，  
清澈透明。

You are the universal truth,  
Colorless and tasteless,  
Simple and pure.  
True to yourself,  
Clear and transparent.

你是天下之至善，  
滋潤萬物，  
從不自傲。  
甘居低處，  
無我無畏。

You are the universal virtue.  
Never arrogant,  
You nourish all things.  
Selfless and fearless,  
You lower yourself.

你是天下之至柔，  
柔中有剛，  
穿岩破壁。  
循環往復，  
自強不息。

You are the universal gentleness.  
Soft but strong,  
You penetrate rocks and walls.  
Moving in a perpetual cycle,  
You strive to become stronger.

你是天下之至美，  
美的使者，  
無處不在。  
美的化身，  
無時沒有。

你在晶瑩的露珠中，  
你在絢麗的朝霞中，  
你在朵朵的白雲中，  
你在綿綿的細雨中，  
你在潔白的雪花中，  
你在七色的彩虹中，  
你在奔騰的瀑布中，  
你在動人的淚花中...

不知從何時開始，  
你擁抱的星球不再那麼蔚藍，  
江河開始斷流，  
綠地變成沙漠。  
但你沒有怨言，  
沒有悲傷。  
你依然如故，  
盡你所有，  
滋潤萬物。  
竭你所能，  
孕育生命。

你雖默默無語，  
但我知道，  
你的每一顆結晶，  
都有一顆心。  
我能感受到，  
你心靈的呼喚。  
你無時不在提示人們：  
關愛和珍惜每一滴水吧，  
因為這，  
就是關愛和珍惜每一個生命，  
就是關愛和珍惜—  
我們自己和我們的子孫後代，  
就是關愛和珍惜—  
我們賴以生存的大自然！

You are the universal beauty.  
As the envoy of beauty,  
You are ever present.  
As the embodiment of beauty,  
You exist at all times.

You are present in the crystalline dew,  
You are present in the splendid dawn,  
You are present amongst the clouds,  
You are present in the drizzling rain,  
You are present in snow white flurries,  
You are present in colorful rainbows,  
You are present in roaring cascades,  
You are present in one's enchanting tears ...

I never knew when it started,  
No longer as blue, is the planet you embrace,  
Rivers have ceased to flow,  
Greens have become deserts.  
Yet without complaints,  
Nor sorrow,  
You remain as before.  
With your entirety,  
You nourish all things.  
To your very best,  
You nurture life.

Though you are silent,  
Yet I know,  
Each of your crystals,  
Carries a heart.  
I can sense,  
Your soul's calling.  
You are always reminding us:  
To love and cherish every drop of water,  
Because,  
This is loving and cherishing each and every life,  
This is loving and cherishing—  
Ourselves and generations to come,  
This is loving and cherishing—  
Mother Nature upon which our existence relies!

# APPLICATION OF WATER QUALITY MODELS TO CHARACTERIZE EUTROPHICATION PROBLEMS IN YUQIAO RESERVOIR, TIANJIN, P.R.C.

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## Abstract

This paper summarizes the application of multiple water quality models to characterize eutrophication problems in Yuqiao Reservoir, a drinking water source for the City of Tianjin, northeastern China. The paper describes the monitoring program, multiple eutrophication models used to analyze water quality data from Yuqiao Reservoir, and results of the modeling analysis. The BATHTUB model was used to predict the phosphorus and nitrogen load reductions needed to meet the current water quality standards for Yuqiao Reservoir. Results show that significant reductions in phosphorus and nitrogen loads from watershed sources (e.g. fish ponds, nonpoint source runoff from farmlands and villages, and tributaries to the Reservoir) are needed in order for Yuqiao Reservoir to meet existing water quality standards for phosphorus, nitrogen, chlorophyll and Secchi depth. Recommended strategies for phosphorus and nitrogen load reduction include converting manure from animal feedlots to biogas, improving practices at fishponds, and public education and outreach activities.

**Keywords:** Chlorophyll, Eutrophication, Models, Nitrogen, Phosphorus, Watershed Protection

## 1. INTRODUCTION

Yuqiao Reservoir is located in Ji County, in the northern portion of Tianjin City, along the Li/Zhou River. The Yuqiao Reservoir was built in 1956 for agricultural irrigation and flood control purposes. In the 1980s, the reservoir was enlarged to store water diverted from the Luan River as a source of drinking water for the City of Tianjin.

The three major tributaries to the reservoir are the Lin, Sha, and Li He rivers. The Luan River diversion flows into the Li He in Hebei province. The area surrounding Yuqiao Reservoir, Ji County, has a population of 171, 000, and 96.3 percent of households are engaged in farming.

Yuqiao Reservoir is designated as Class III surface water, suitable for public water supply with conventional treatment, fish preservation, and swimming. Monitoring data

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from the Tianjin Environmental Monitoring Center (TEMC) showed the reservoir is eutrophic and does not meet water quality standards, especially in summer and fall. Nutrient sources (phosphorus and nitrogen) include local industrial and agricultural sources, discharges from fish ponds, and nonpoint source surface runoff.

In 2003, Civil Engineering Research Foundation and US EPA entered into a Cooperative Agreement for a project entitled Clean Water for Sustainable Cities in China – To Improve Drinking Water Quality and Increase Access to Safe Drinking Water in the Hai River Basin in China. One of the approaches of the project was to promote watershed best management practices (BMPs) to improve and preserve water quality in Yuqiao Reservoir. These BMPs included nutrient load reduction and public education and outreach. Water quality modeling was conducted to evaluate the impact of management practices on reservoir water quality. Objectives of model analysis were to identify the limiting nutrient for algal growth in Yuqiao Reservoir and to predict the reservoir water quality in response to nutrient load reductions.

Water quality modeling has been used extensively in the US watershed planning process to aid decision-making in implementing water quality control measures. Water quality models provide a framework to analyze observed data and understand mechanisms and interactions among various parameters. Mathematic models can be useful tools to predict how receiving water will respond if a range of control measures are implemented. Modeling techniques vary in complexity, but in general can be classified in two groups, steady state or dynamic. Steady state models use constant inputs for flow, concentration and meteorological conditions. Dynamic models consider time dependent variation of inputs. Selection of models depends on system complexity, objectives of model analysis, and availability of input data.

Considerable effort has been expended in the past 20-30 years to develop empirical and theoretical models for lake eutrophication problems. Simple eutrophication models have been valuable in first estimates of the probable effects of reduction of nutrient input (Thomann and Mueller 1987).

The present study utilized several simple eutrophication models developed for lakes and reservoirs (Walker 1999; Dillon and Rigler 1974; Jones and Bachman 1976)<sup>2, 3, 4</sup> to analyze the water quality data collected by TEMC to assess the relationship between nutrients and algal growth in Yuqiao Reservoir. Another empirical steady state model, BATHTUB, was used to predict reservoir water quality after nutrient load reduction. This is the first effort to apply water quality models in Yuqiao Reservoir. Dynamic model analysis can be conducted in the future to simulate nutrient dynamics and to predict the response of the reservoir over time.

## **2. METHODOLOGY**

### **2.1 Yuqiao Reservoir Watershed Monitoring Program**

A monitoring program was designed to quantify nutrient loads and characterize the conditions of Yuqiao Reservoir. Sampling sites were located at the mouths of major

tributaries (i.e., Lin He, Sha He and Li He), and along representative small drainages that flow directly to the Reservoir. Both flow and water quality data were collected. Samples were collected during rainy season only because the drainages are dry otherwise. Sampling stations are shown in Figure 1.



Figure 1. Yuqiao Reservoir Watershed, Principle Features and Monitoring Stations

Five sampling stations were located on Yuqiao Reservoir. Water quality parameters analyzed included pH, dissolved oxygen, COD, BOD, nitrogen, phosphorus, chlorophyll, and Secchi depth. Water samples were collected monthly at surface from four stations, but from two depths (surface and bottom) at the center sampling station (The reservoir is quite shallow, with an average depth of 4.6m. Only one station (center) was sampled at surface and bottom to see if there is stratification) (see Figure 1, monitoring station #10 Kuzhongxin). Precipitation and Reservoir inflow and outflow data were also collected. Model analysis covers monitoring data collected from 1999-2003.

## 2.2 Evaluation of the Role of Nutrients in Algal Growth

In order to identify the relative influence of nutrients on algal growth, diagnostic parameters were calculated and compared to criteria developed by Walker (1999). Definitions and criteria of the parameters are shown in Table1, where  $Z_{SD}$  is the Secchi depth (m) and  $Chl a$  is the chlorophyll *a* concentration ( $\mu\text{g/L}$ ). Low  $T$  values ( $<0.4$ ) indicate low nonalgal turbidity, thus suspended sediment and other particulates are unimportant and the light is not a limiting factor, thus algal response to nutrients should be high. Conversely, when  $T > 1$ , the nonalgal turbidity is high, suspended sediment and other particulates and algal response to nutrients should be low.

Light availability ( $L$ ) is an index calculated from  $T$  and mixing depth. A value of  $L < 3$  indicates that light availability is high; nonalgal turbidity is unimportant and there is likely to be high algal response to nutrients. A value of  $L > 6$  implies low light availability; nonalgal turbidity is important and the algal response to nutrients will be low, indicating the system will be at least partially light-limited.

Table1. Criteria Used to Evaluate the Role of Nutrients in Algal Growth in Yuqiao Reservoir

Symbol	Diagnostic Parameter	
	Name	Criteria
$T$	Nonalgal turbidity ( $\text{m}^{-1}$ ) $T = 1/Z_{SD} - 0.025Chl a$	$T < 0.4$ algal response to nutrient is high; $T > 1$ nonalgal turbidity is high
$L$	Light availability $L = Z_{mix} * T$	$L < 3$ light availability is high $L > 6$ light availability is low
$F_{chl}$	Relative chlorophyll concentration factor $F_{chl a} = Chl a / TP$	$F_{chl} < 0.13$ low phosphorus response $F_{chl} > 0.4$ lake is phosphorus limited

A relative chlorophyll concentration factor (Fchl) was defined by the ratio of chlorophyll and phosphorus concentrations. Fchl less than 0.13 indicates low phosphorus response and thus, chlorophyll production is limited by another factor. Conversely, Fchl > 0.4 indicates high phosphorus response by phytoplankton .

### 2.3 Simple Model Calculations

Simple empirical relationships previously developed for other lakes and reservoirs were applied to available water quality data from Yuqiao. These equations link concentrations of chlorophyll *a* (Chl, in mg/m<sup>3</sup>) and total phosphorus (TP, mg/m<sup>3</sup>) (Table 2).

**Table 2. Empirical Equations between Chlorophyll and Phosphorus Concentrations Used for Yuqiao Reservoir**

Author	Equations
Walker	$\text{Chl} = \text{TP}^{1.37}/4.88$
Dillon and Rigler	$\text{Log chl} = -1.136 + 1.449 \log \text{TP}$
Jones and Bachmann	$\text{Log chl} = -1.09 + 1.46 \log \text{TP}$

### 2.4 BATHTUB Model

The BATHTUB model was developed for use at US Army Corps of Engineers reservoirs by William Walker (1999). The model relates eutrophication symptoms to external nutrient (nitrogen and phosphorus) loadings, hydrology, and reservoir morphometry, and provides a framework for interpreting water quality monitoring data and predicting effects of future changes in external nutrient loadings.

Required input data include reservoir morphometry (surface area, mean depth, lengths of major reservoir segments and width), flow and nutrient concentrations of tributaries, and reservoir mean Secchi depth and mean concentrations of phosphorus, nitrogen, chlorophyll, and conservative substances.

Nutrient data collected by TEMC in 1999 were used in the BATHTUB model because that year had the most complete dataset. Model output was compared with measured water quality in Yuqiao Reservoir. Reservoir morphometry data are shown in Table 3. Tributary and nutrient budget data are shown in Table 4.

**Table 3. Yuqiao Reservoir Morphometry Input Data to BATHTUB Model**

<b>Parameter</b>	<b>Values</b>	<b>Unit</b>
Drainage Area	2060	(km <sup>2</sup> )
Reservoir Surface Area	86.8	(km <sup>2</sup> )
Length	30	(km)
Mean Depth	4.6	(m)
Volume	386x10 <sup>6</sup>	(m <sup>3</sup> )
Precipitation	344.2	(mm)
Evaporation	1733.6	(mm)
Storage Change	- 61.37x10 <sup>6</sup>	(m <sup>3</sup> )

*Table 4. Tributary Input data for Yuqiao Reservoir for 1999*

		<b>Values</b>	<b>Unit</b>
<b>Lin He</b>			
	Drainage Area	252	(km <sup>2</sup> )
	Flow	4.9	(hm <sup>3</sup> /yr)
	TP	39.75	(ug/L)
	TN	6771.5	(ug/L)
	IN	5191.88	(ug/L)
<b>Li He (including Luan He)</b>			
	Drainage Area	488	(km <sup>2</sup> )
	Flow	582.5	(hm <sup>3</sup> /yr)
	TP	60	(ug/L)
	TN	3783.33	(ug/L)
	IN	3359.17	(ug/L)
<b>Sha He</b>			
	Drainage Area	887	(km <sup>2</sup> )
	Flow	27.2	(hm <sup>3</sup> /yr)
	TP	64.67	(ug/L)
	TN	6413	(ug/L)
	IN	4953.5	(ug/L)
<b>Nonpoint Source- Local Runoff</b>			
	Runoff	0.172	(m/yr)
	TP	478	(ug/L)
	TN	2269	(ug/L)
<b>Fishponds</b>			
	Area	14.043	(km <sup>2</sup> )
	Water Discharge	69.50	(hm <sup>3</sup> /yr)
	TP	374	(ug/L)
	TN	2060	(ug/L)

A relative chlorophyll concentration factor (Fchl) was defined by the ratio of chlorophyll and phosphorus concentrations. Fchl less than 0.13 indicates low phosphorus response and thus, chlorophyll production is limited by another factor. Conversely, Fchl > 0.4 indicates high phosphorus response by phytoplankton .

After the model was run using the 1999 input data, a scenario analysis was conducted to determine the phosphorus and nitrogen load reduction required in order to meet the existing water quality standard for Class III Lakes and Reservoir for which Yuqiao Reservoir is classified (Table 5).

**Table 5. Surface Water Quality Standards for Class III Lakes and Reservoirs**

Parameters	Standard Values
Total Phosphorus (mg/L)	0.025
Total Nitrogen (mg/L)	0.3
Chlorophyll a (mg/L)	0.01
Transparency (m)	2.5
Dissolved Oxygen (mg/L)	5

(Source: State Environmental Protection Agency, PRC, 1999).

### 3. RESULTS AND DISCUSSION

#### 3.1 Diagnostic Parameter Values for Yuqiao Reservoir

Annual average values of the diagnostic parameters for Yuqiao Reservoir for 1999, 2000, and 2003 are shown in Tab. 6. Parameters were defined in Table1. T values for 1999 and 2000 are less than 0.4, indicating that the algal response to nutrients was high in those two years. The T value for 2003 is greater than 0.4, but less than 1, indicating suspended sediments and other particulates increased in 2003, but nonalgal turbidity was still less than 1, and thus the algal growth in response to nutrients was still high in 2003.

**Table 6. The Annual Average Values of the Diagnostic Parameters for Yuqiao Reservoir**

Calendar Year	T	L	Fchl
1999	0.20	0.80	0.42
2000	0.20	0.82	0.60
2003	0.45	1.79	0.16

L values for all three years were less than 3, indicating that light availability and

algal response to nutrients were high for all three years. Fchl values for 1999 and 2000 were greater than 0.4, indicating that phytoplankton growth in Yuqiao Reservoir responded to phosphorus. Fchl for 2003 was less than 0.4 but still greater than 0.13, indicating other factors, in addition to phosphorus, affected phytoplankton growth in Yuqiao Reservoir in 2003. Higher nonalgal turbidity in 2003 may have affected algal growth, but other factor(s) need to be considered as well. In order to understand the other factors that may have affected the algal growth, the ratio of total nitrogen to total phosphorus (N:P) was determined. The N:P ratio has been used to estimate the limiting nutrient for algal growth. If the ratio is greater than 20:1, phosphorus is limiting. When the ratio is between 20:1 and 10:1, both nitrogen and phosphorus are limiting. When the ratio is less than 10:1, nitrogen is limiting. The N:P ratios in Yuqiao Reservoir are mostly greater than 20:1 suggesting that phosphorus is usually the limiting nutrient (Redfield, 1958). However, during the summer/fall months of 1999, 2000, and most months in 2003, the ratios were less than 10:1, suggesting that nitrogen was limiting (non-detected results were not included in the analysis). It is not common for freshwater lakes to be N limited. Therefore, both phosphorus and nitrogen need to be controlled in order to reduce algal biomass.

### **3.2 Empirical Model Results and Discussion**

Predicted chlorophyll *a* concentrations from the three equations in Table 2 are graphed in Figure. 1. All three models seem to predict the chlorophyll concentrations generally well, particularly the seasonal trend in 1999-2000. However, chlorophyll concentrations in 2003 were overestimated. As discussed in section 2.1, factors other than phosphorus significantly affected phytoplankton growth in 2003. Nitrogen was limiting to algal growth at times during 1999, 2000 and 2003. This may explain why the models overestimated chlorophyll concentrations in 2003. Another possibility is that phosphorus may have entered the reservoir as particulates and algae could not uptake the phosphorus until it was converted into soluble forms.

### **3.3 BATHTUB Model Results and Discussion**

Estimated water quality data are compared with observed data (TEMC, 2003) for Yuqiao Reservoir in Table 7. The model seems to simulate the phosphorus, nitrogen, and Secchi depth fairly well, but under-predicted chlorophyll *a* concentration by 37%. The reason that chlorophyll *a* was under-predicted is that the algal growth was affected by other factors besides phosphorus. The BATHTUB model used a correlation between chlorophyll *a* and phosphorus. The BATHTUB model will be used to calculate phosphorus and nitrogen load limits so that Yuqiao Reservoir can meet water quality standards (Table 4), with the understanding that when new information become available, the model can be refined to improve its prediction accuracy.

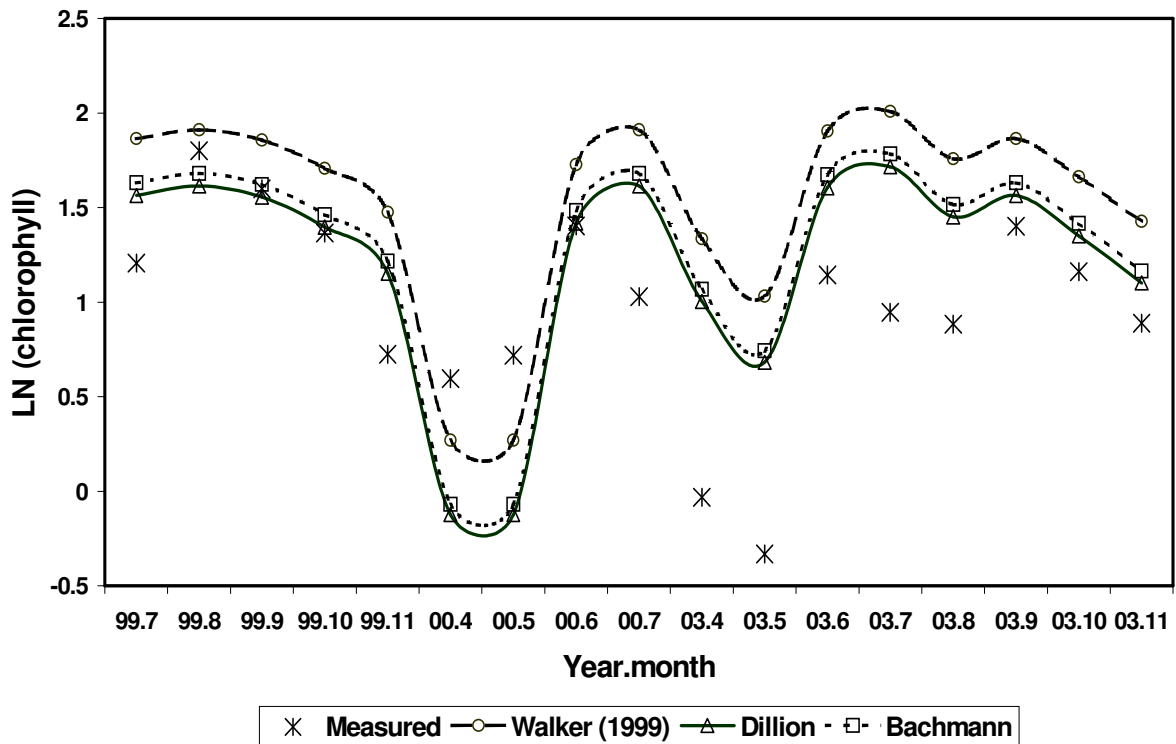


Figure 2. Predicted chlorophyll concentrations compared to the measured values during 1999-2003 period

Table 7. Comparison of Observed Water Quality Data for Yuqiao Reservoir in 1999 and the Estimated Results from BATHTUB Model Analysis

Parameter	Unit	Observed	Estimated
Total P	Mg/m <sup>3</sup>	44.6	46.7
Total N	Mg/m <sup>3</sup>	1283.40	1345.7
Chlorophyll a	Mg/m <sup>3</sup>	29.52	21.6
Secchi	M	1.56	1.4

It is known that 1999 was a dry year since the average precipitation from 1991 to 1999 was 747 mm, with a maximum of 1050 mm and minimum of 344.2 mm, which just happened to be measured in 1999. Therefore, the 1999 measurement is the lowest in the past 8 years, and condition will be a baseline for dry years and model predictions only apply to dry years. The required nitrogen and phosphorus annual load reductions are significant (Table 8).

Table 8. Reduction for Phosphorus and Nitrogen Loads Needed for Yuqiao Reservoir to Meet the Water Quality Standards

Source	Phosphorus	Nitrogen
Lin He	50%	99%
Li He	50%	99%
Sha He	50%	99%
Fishponds	87.5%	87.5%
Nonpoint Source	87.5%	87.5%

#### 4. CONCLUSION AND RECOMMENDATIONS

Several diagnostic parameters indicated that eutrophication in Yuqiao Reservoir was caused by excessive phosphorus and nitrogen. Phosphorus was the limiting nutrient for algal growth in Yuqiao Reservoir most of the time. Nitrogen was limiting at times, particularly in 2003. Both nitrogen and phosphorus loads need to be reduced to control eutrophication. Simulation by the BATHTUB model suggested that significant reductions from all sources are needed (Lin He, Li He, Sha He, nonpoint source runoff from farmlands and villages surrounding the reservoir, and fish ponds).

The BATHTUB model's analytical ability for Yuqiao Reservoir can be improved by additional data collection, e.g., concentrations and loads of ortho-phosphorus, inorganic and organic nitrogen, a conservative substance such as chloride, reservoir area and depths in different hydrologic conditions, and seasonal segmentation of reservoir water quality data. Since the model was calibrated to a dry year (1999), additional data for dry and wet years are needed to enhance the model's predictive ability.

Extensive macrophytes can be seen in the shallow areas of Yuqiao Reservoir. The function of macrophytes in nutrient cycling needs to be better understood. Studies of other reservoirs with dense macrophytes have shown that macrophytes can be a significant sink (during growing season) and source (during senescence) of nutrients (Landers, 1982). A survey of macrophytes in Yuqiao Reservoir to identify major species and evaluate distribution, density, and biomass will help understand nutrient dynamics and control eutrophication.

Another potentially significant source of nutrients is internal loading from reservoir sediment. Studies of other shallow lakes and reservoirs have shown that internal nutrient loading can be the dominant source of nutrients (Anderson, 2002, Li, 2004)<sup>6,7</sup>. Studies to

evaluate nutrient loading from permanent reservoir sediments and annually flooded farmlands will help to understand the contribution. Should the sediments prove to be significant source of nutrients, in-lake treatments can be considered, such as alum treatment to sequester phosphorus release by binding phosphorus with aluminum salt, or dredging to remove the nutrient-rich sediments. Aeration systems have proved to be effective in increase dissolved oxygen and sequester phosphorus and ammonia release.

Several control measures can be implemented in the watershed to control nutrient loads. One such measure is the construction of biogas facilities in the surrounding villages. Many villagers raise animals in their courtyards. Untreated manure from animal feedlots is washed to the Reservoir during rainy seasons. Human wastes are not treated either. These wastes carry nutrients and pathogens to the reservoir. Villagers can organize their animal feedlots to a centralized location and collect the manure to be used as fuel for a biogas facility. Anaerobic digestion technologies have been widely used in China and can be easily adapted for these rural villages. The methane gas generated by the biogas facility can be used for cooking and heating.

Nutrient runoff control measures need to be applied to the private and commercial fishponds neighboring the reservoir. Every year, fishponds discharge wastewater directly to the reservoir. The nutrient budget for 1999 showed that 44% of the phosphorus inputs to Yuqiao Reservoir were from fishponds (see Figure 1). Fishpond operators need to make sure not to fertilize ponds in excess, to recycle wastewater, or to divert wastewater away from the reservoir, and apply to the crop fields.

Another control measure is public education and outreach. Farmers who live nearby the reservoir feel that the water is for Tianjin, not for them; therefore they do not see the need to protect its water quality. These farmers need to be aware that the water in the reservoir is also used to irrigate their crops. When the irrigation water percolates to the ground, it affects the water of the groundwater they drink. In fact, some well water samples show high nitrate concentration (TEMC unpublished data). The quality of the Reservoir affects their quality of life as well (e.g., fishing and recreation). Protecting water quality is in everyone's interest.

Lastly, it is important to develop a watershed management plan that identifies all potential sources of nutrients and control measures. The plan can prioritize the most cost-effective projects to restore reservoir water quality. Funding sources need to be identified and aggressively pursued. The watershed planning process also provides a forum for all interested/affected parties to look at the watershed as a whole and to look at water quality issues from all perspectives.

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# 納米單質鐵在環境修復中的研究及應用進展

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## 摘要

納米單質鐵是一種具有很大潛力的環境修復技術，用於處理土壤和地下水中的污染物。納米單質鐵體積小，比表面積大，反應活性強，可以降解多種環境污染物。由於其獨特的物理和化學性質，納米單質鐵可以被直接注入地下，對受污染的地下水和土壤進行原地處理，從而免去污染物異地處理所涉及的挖掘、填埋等工序，降低環境修復成本，同時減少污染物對人體和環境的危害。本文簡要介紹了納米單質鐵在環境修復中的研究及應用進展，包括污染物降解機理，納米單質鐵的製備，納米單質鐵的穩定化，示範工程，以及該技術面臨的問題和挑戰。

## 1 背景

納米單質鐵是一種新型的環境污染治理技術。通常所指的納米單質鐵，其顆粒大小在1-100納米之間。單質鐵是一種還原性很強的還原劑，其電極電位為-0.44 V，氧化時釋放電子，能夠降解多種污染物。與大顆粒單質鐵(顆粒直徑大於一微米，10-6米)相比，納米單質鐵具有以下顯著的特點：1) 比表面積(單位質量單質鐵的表面積)大，為降解污染物提供更多的反應場所；2) 表面活性強，對污染物的降解速度快；3) 可以被直接注入地下，用於去除地下水和土壤中的污染物。據報導

(Wang and Zhang, 1997)，納米單質鐵降解含氯有機污染物的反應速率是傳統大顆粒單質鐵降解含氯有機污染物反應速率的10到100倍。在過去十幾年中，該技術正受到越來越多研究人員的關注。並且在工程實踐中逐步得到應用。大量的實驗研究和有限的示範工程應用表明，該技術能有效的去除或降解受污染地下水中的污染物，包括含氯有機物、重金屬、砷、硝酸鹽、高氯酸鹽等。目前，納米單質鐵的製備過程，微觀結構，性能表徵等方面的研究已經趨於成熟。本文討論了納米單質鐵在環境修復方面的研究及應用進展，包括污染物降解機理，納米單質鐵的製備，納米單質鐵的穩定化技術，在工程應用上的現狀及面臨的問題和挑戰。

## 2 納米單質鐵在環境修復中的研究進展

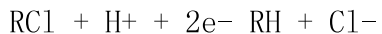
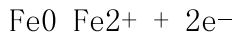
### 2.1 可降解的污染物及反應機理

大量的實驗研究證明納米單質鐵是一種有效的還原劑，可以有效地處理大量常見的環境污染物，包括含氯有機物及重金屬 (Zhang, 2003; He and Zhao, 2005; Xiong等, 2007; 2009)。表1列出文獻中報導過得可以被納米單質鐵降解的常見的污染物。

如表1所示，目前文獻中所報導的能被納米單質鐵降解的污染物很大一部分是有機污染物，包括含氯有機溶劑，含氯有機殺蟲劑，多氯聯苯等。由於含氯有機物是地下水和土壤中最常見的污染物之一，納米單質鐵對含氯有機物的降解尤其受到關注，其降解機理也逐漸被發現及確認。納米單質鐵作為電子供體能有效地提供電子，而含氯有機物能接受電子而脫氯，該反應能通過下面的反應方程式表示（Li等，2006）。

表1 - 可以被納米單質鐵降解的常見污染物(Zhang, 2003)

甲烷氯化物	有机染料	重金属离子
四氯化碳(CCl <sub>4</sub> )	橙II (C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> NaO <sub>4</sub> S)	汞
氯仿(CHCl <sub>3</sub> )	橘红(C <sub>12</sub> H <sub>13</sub> ClN <sub>4</sub> )	镍
二氯甲烷(CH <sub>2</sub> Cl <sub>2</sub> )	金莲橙 (C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> NaO <sub>5</sub> S)	银
氯甲烷(CH <sub>3</sub> Cl)	酸性橙	镉
<b>氯化苯</b>	酸性红	<b>三卤甲烷</b>
六氯代苯(C <sub>6</sub> Cl <sub>6</sub> )	<b>氯化乙烯</b>	溴仿(CHBr <sub>3</sub> )
五氯代苯(C <sub>6</sub> HCl <sub>5</sub> )	四氯乙烯(C <sub>2</sub> Cl <sub>4</sub> )	二溴氯甲烷 (CHBr <sub>2</sub> Cl)
四氯代苯 (C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> )	三氯乙烯(C <sub>2</sub> HCl <sub>3</sub> )	二氯溴甲烷 (CHBrCl <sub>2</sub> )
三氯代苯(C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> )	顺式-二氯乙烯(C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )	<b>其他多氯碳水化合物</b>
二氯代苯(C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> )	反式-二氯乙烯(C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )	多氯联苯
氯苯(C <sub>6</sub> H <sub>5</sub> Cl)	1,1二氯乙烯(C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )	二恶英
<b>杀虫剂</b>	氯乙烯(C <sub>2</sub> H <sub>3</sub> Cl)	五氯酚(C <sub>6</sub> HCl <sub>5</sub> O)
DDT(C <sub>14</sub> H <sub>9</sub> Cl <sub>5</sub> )	<b>无机离子</b>	<b>其他有机污染物</b>
林丹(C <sub>6</sub> H <sub>9</sub> Cl <sub>5</sub> )	重铬酸盐(Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> )	亚硝基二甲胺 (C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O)
	砷(AsO <sub>4</sub> <sup>3-</sup> )	三硝基二甲胺 (C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub> )
	高氯酸盐(ClO <sub>4</sub> <sup>-</sup> )	
	硝酸盐(NO <sub>3</sub> <sup>-</sup> )	



單質鐵降解三氯乙烯的反應系統中可能存在著三種還原劑，即單質鐵(Fe<sup>0</sup>)，亞鐵離子(Fe<sup>2+</sup>)，氫氣(H<sub>2</sub>)。單質鐵表面的電子能夠直接轉移到含氯有機物進行脫氯反應，反應過程中生成的亞鐵離子能進一步提供電子使部分含氯有機物脫氯，納米單質鐵與污染物及水反應生成的氫氣以及納米單質鐵製備過程中可能產生的氫氣同樣能使含氯有機物脫氯。

納米單質鐵降解污染物的另一個反應機理是產生氧化態自由基，將污染物氧化成無害的物質(Joo 等, 2004; Lee 等, 2008)。在有氧條件下，納米單質鐵被水中的溶解氧(DO)氧化，生成雙氧水(H<sub>2</sub>O<sub>2</sub>)，後者通過Fenton反應(H<sub>2</sub>O<sub>2</sub>和二價鐵[Fe<sup>2+</sup>]之間的反應)生成羥自由基(.OH)、四價鐵離子(Fe<sup>4+</sup>)、過氧化自由基(O<sub>2</sub><sup>-</sup>)等高級氧化劑。通過這些氧化劑，納米單質鐵可以氧化降解被污染水體中的有機污染物(Joo 等, 2004; Lee 等, 2008)。

納米單質鐵也能夠修復被重金屬污染的地下水和土壤。納米單質鐵可以通過電子轉移將重金屬的離子價態降低，促使其通過沉澱或吸附反應得到去除。另外，納米單質鐵表面通常覆蓋著一層氧化鐵，後者能吸附某些重金屬污染物，降低其在環境中的遷移，實現固定化的目的。研究表明(Zhang, 2003)，納米單質鐵能夠有效處理和修復被鉻，砷，鈾等污染的地下水。

## 2.2 納米單質鐵的製備

以下簡要介紹文獻中報導過的比較有代表性的幾種納米單質鐵的製備方法，包括硼氫酸鈉還原法、高溫氫氣還原法、機械碾磨法、和碳熱解法。實驗室研究中使用的納米單質鐵大多是通過硼氫酸鈉還原法和高溫氫氣還原法製備的納米單質鐵。工程應用中使用的納米單質鐵大多是通過高溫氫氣還原法和機械碾磨法製備納米單質鐵，少數工程中也採用通過硼氫酸鈉還原法製備的納米單質鐵。這一節也簡單介紹了鐵/鈮雙金屬納米顆粒的製備方法。

在實驗室研究中，人們通常採用化學還原法製備納米單質鐵，即利用硼氫酸鈉(NaBH<sub>4</sub>)還原鐵離子(Fe<sup>2+</sup>或者Fe<sup>3+</sup>)來生成單質鐵。Wang and Zhang (1997)報導，將1.6M NaBH<sub>4</sub>溶液緩慢(一滴一滴地)加入1.0M FeCl<sub>3</sub>溶液中，混合溶液在常溫條件下以磁力攪拌器進行攪拌，使之混合併且反應。納米單質鐵能通過如下反應式生成：



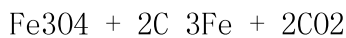
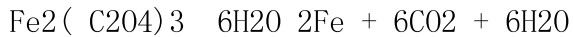
通過該方法製備的納米單質鐵，顆粒直徑在1 nm到100 nm之間，比表面積約為33.5 m<sup>2</sup>/g (Wang and Zhang, 1997)，顆粒中含有約5%(重量比)的硼(Liu 等, 2005)。

另一種通常運用在實驗室研究中的活性納米鐵顆粒(RNIP)是由日本Toda Kogyo公司開發並商業化生產。該納米單質鐵是在高溫(450°C)氣態條件下使用氫氣還原氧化鐵而生成。通過該方法製備的納米單質鐵，其比表面積在5 m<sup>2</sup>/g到60

m<sup>2</sup>/g 之間，20% (體積比) 的單質鐵直徑在 50 nm 到 500 nm 之間，80% (體積比) 的單質鐵直徑在 500 nm 到 5000 nm 之間 (Uegami 等, 2003)。

Zhang (2006) 採用機械碾磨的方法把微米級 (<10 μm) 的鐵顆粒碾磨成納米單質鐵。微米級鐵顆粒被投加到高能球磨機中，經過長時間運轉 (>4 小時)，微米級鐵顆粒在高能球磨機內受到反復的擠壓和破碎，使之成為納米鐵顆粒 (<100 nm)。

Hoch 等 (2008) 採用碳熱解法製備納米單質鐵。該方法採用吸附或者浸泡的方式將鐵鹽溶液中的鐵離子 (Fe<sup>2+</sup> 或者 Fe<sup>3+</sup>) 附著在炭黑上 (炭黑的比表面積為 80 m<sup>2</sup>/g)，常溫條件下風乾後，附著有鐵離子的炭黑在氬氣保護下在熔爐內加熱 (溫度為 800 °C) 3 小時，鐵離子通過以下反應式生成單質鐵：



通過該方法製備的納米單質鐵直徑在 20 nm 到 100 nm 之間，比表面積在 38 m<sup>2</sup>/g 到 130 m<sup>2</sup>/g 之間。

研究表明，通過在納米單質鐵的表面添加第二種單質金屬 (如鈀)，從而形成鐵/鈀雙金屬納米顆粒，可以進一步提高納米單質鐵的反應活性 (Wang and Zhang, 1997; He and Zhao, 2005)。鐵/鈀雙金屬納米顆粒可以在納米單質鐵的基礎上，經過下列反應生成單質鈀顆粒：



通過以上反應生成的單質鈀附著在單質鐵顆粒的表面上，從而生成鐵/鈀雙金屬納米顆粒。

### 2.3 納米單質鐵的穩定化

納米單質鐵在顆粒間的磁力、范德華力等的作用下容易聚合形成較大的顆粒，從而失去其比表面積大、反應活性強等優點。而且聚合生成的大顆粒容易沉澱，難以在地下水及土壤中移動，限制其在環境修復中的使用。所以，研究開發穩定納米單質鐵的穩定劑，使其能保持持久的反應活性、分散的顆粒結構、並且能夠在土壤及地下水中移動，成為近年來有關納米單質鐵研究的重點之一。一般而言，高分子聚合物或者表面活性劑被用作納米單質鐵穩定劑 (He 等, 2007; Saleh 等, 2005; Tiraferri 等, 2008)。在納米單質鐵製備過程中或者使用前，將穩定劑與納米單質鐵反應材料混合，在納米單質鐵生成後，表面附著一層穩定劑薄膜。有的穩定劑薄膜帶有負電荷，納米顆粒在帶電薄膜的作用下，通過顆粒間的靜電排斥力和空間位阻斥力，使得納米單質鐵顆粒保持分散狀態，防止納米單質鐵顆粒聚合，從而保持其較大的比表面積和較高的表面活性。表 3 列出了近年來文獻中報導的各種納米單質鐵穩定劑的信息，包括各種穩定劑的來源、分子量，穩定後形成的納米鐵顆粒的顆粒直徑、比表面積等信息。各種穩定劑有其各自的優缺點，在選擇使用時可以考慮以下幾個因數 1) 穩定納米單質鐵的效果，如使用穩定劑後產生的納米單質鐵顆粒的大小、比表面積、穩定化持續時間；2) 穩定劑是否被環境監管部門接受；3) 穩定劑的生物可降解能力，即穩定劑被釋放到環境中後是否能被環境中的微生物降解；4) 穩定劑的成本。

表3. 納米單質鐵穩定劑

穩定劑		來源	納米單質鐵表征			鐵濃度 (g/L)	穩定劑濃度 (g/L)
名稱	分子量		顆粒直徑 (nm)	比表面積 (m <sup>2</sup> /g)	Z電位 (mv)		
PolyFlo	--	PureSyn	10-30	24.4 ± 1.5	--	--	--
Poly(acrylic acid)	2000	Aldrich		20-30	--	21	61
Carbon	--	Cobat	30-100	--	--	21	61
Starch	--	Alfa Aesar,	14±11	55	--	0.1-1	2-8
Carboxyle methyl cellulose	90,000	Acros Organics	4.3±1.8	--	--	0.1	2
Sodium Hexametaphosphate	612	--	306-1131	38-54	--	2.1	0.2
Triblock polymer	--	Lab synthesis	212±21	--	-50±1.2	0.8	2
Sodium Polyaspartate	2000-3000	Toda Kogyo	--	--	-39±1		
Sodium docecyl benzene sulfonate	348.5	Acros	190±15		38.3±0.9	3	2
Poly(styrene sulfonate)	1000, 1000000	Sigma Aldrich	--	--	--	3	0.005-1
Sodium polymethacrylate and ammonia polymethacrylate	1000-50,000	Darvan	10-50	5.2-20	--	300	10-20
Polyvinyl alcohol-co-vinyl acetate-co-itaconic acid	4300-4400	Sigma Aldrich	15-105	--	-80	--	--
Guar Gum	800-5000k	Sigma Aldrich	200-500	--	--	1.5	1.3-4.0

### 3 納米單質鐵在環境修復中的應用進展

#### 3.1 工程應用

目前，納米單質鐵在北美和歐洲已經運用於數十個示範工程中，用以降解地下水或者土壤中的污染物。本節討論幾個具有代表性的並且相關技術細節在文獻中報導過

的工程案例。

### 3.1.1 美國新澤西州 Trenton 市的製造工廠

Elliott 和 Zhang (2001) 運用鐵/鈀雙金屬納米顆粒去除地下水中的含氯有機污染物，進行了中試研究。工程所在地是一個地位於美國新澤西州 Trenton 市的製造工廠，當地的地下水受到四氯乙烯 (PCE)，三氯乙烯 (TCE) 等含氯有機物的污染。地下水水位在地表以下 1.8 到 2.1 米。鐵納米顆粒通過  $\text{FeCl}_3$  與  $\text{NaBH}_4$  反應生成，納米單質鐵與鈀離子 ( $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$ ) 反應生成鐵/鈀雙金屬納米顆粒。鈀/鐵的重量比為 1:300。鐵/鈀雙金屬納米顆粒混合液在重力作用下被注入地下。

注射系統包括一個上游的原來用作地下水監測之用的注射水井和三個位於下游的原來用來測量水壓的監測水井。注射水井和下游的監測水井之間間隔為 1.5 米。鐵/鈀雙金屬納米顆粒注射進行了兩天。第一天，大約 890 升濃度為 1.5 克/升的鐵/鈀雙金屬納米顆粒混合液 (總共 1.34 公斤納米顆粒) 在重力作用下被注入地下。注入持續時間為 6.3 小時。第二天，大約 450 升濃度為 0.75 克/升的鐵/鈀雙金屬納米顆粒溶液 (總共 0.34 公斤納米顆粒) 在重力作用下被注入地下。注入持續時間為 4 小時。納米顆粒注入過程進展順利，注射流速從第一天最開始幾個小時的 7.5 升/分鐘逐漸降低並且穩定在 3.7 升/分鐘。

注射完成後 6 週，在注射井進行的水力學測試表明，注射井附近區域的水力傳導率在注射納米顆粒前後基本相當。這表明納米顆粒注射沒有造成含水層滲透率的變化。注射完成之後的監測數據表明，不同檢測井中的 TCE 去除效率在 1.5% 到 96.5% 之間。值得注意的是，本案例只提供了短期 (四周) 的監測數據。而且在這期間的後期，TCE 濃度出現反彈。總鐵 (FeT) 和溶解性鐵 ( $\text{Fe}^{2+}$ ) 的監測數據表明，鐵流到注射井下游 4.5 米以外的地方。根據最大總鐵濃度計算的納米顆粒遷移速度為 0.8 米/天。其他監測數據表明地下水 pH 受納米顆粒的影響升高，氧化還原電位 (ORP) 下降。

### 3.1.2 美國佛羅里達州 Jacksonville 市的海軍航空基地

Henn 和 Waddill (2006) 報導了一個運用聚合物包裹的鐵/鈀雙金屬納米顆粒降解地下水污染物的中試工程案例。工程所在地是一個地位於佛羅里達州 Jacksonville 市的海軍航空基地，當地的地下水受到四氯乙烯 (PCE)，三氯乙烯 (TCE) 等含氯有機物的污染。納米單質鐵由 PARS Environmental 公司提供，納米單質鐵的表面附著有鈀及聚合物，用來提高納米單質鐵的表面活性和在地下水中的流動性能。採用的聚合物是一種無毒的常用聚合物，並且被美國食品及藥品管理局許可用作食品添加劑。

納米單質鐵的注射通過兩種不同的注射方式完成，即直接注射和地下水循環注入。直接注射的優點是可以將注射液注射到受污染最嚴重的區域，而地下水循環注入的優點包括促進納米顆粒在地下水中的遷移、增加注射液與地下水和土壤的混合、同時提高污染物的溶解速度，以利於污染物的降解。在本示範工程中，10 克/升的納米鐵顆粒混合液通過 10 個直接注射孔注入污染最嚴重的區域。地下水循環系統將地下水從下游抽出，在地表與納米單質鐵混合後，通過注射水井注入地下。地下水循環注入進行了兩次。第一次，納米鐵顆粒濃度從開始時的 2 克/升增加到 4.5 克/

升，注射流速為 12.1 升/分鐘，總共 132475 升納米鐵溶液被注入地下。第二次，納米鐵顆粒濃度為 4.5 克/升，注射流速在 11.4 升/分鐘到 17.0 升/分鐘之間，總共 15897 升納米鐵溶液被注入地下。在本工程中，總共 150 公斤納米鐵顆粒被注入地下。

納米單質鐵注射完成後近一年的監測數據顯示，土壤中的污染物濃度的下降幅度在 8%到 92%之間，地下水中污染物的濃度最高下降了 99%。監測數據同時顯示，納米單質鐵注射不但提供了污染物的非生物降解，而且促進了污染物的生物降解。根據地下水中污染物，副產物濃度，地質化學參數推斷出，納米單質鐵注射完成後的六到九個月，污染物的非生物降解占主導地位，之後生物降解占主導地位。另外，在注射井和監測井進行的水力學測試表明，注射井和監測井附近區域的水力傳導率比納米單質鐵注射前下降了約 45%。這可能是由於納米單質鐵沉澱或者被土壤吸附，從而降低土壤中的空隙率所造成。

### 3.1.3 美國加利佛尼亞州 Palo Alto 市製造工廠

He 等(2009)在工地現場採用硼氫酸鈉還原法製備納米單質鐵和鐵/鈮雙金屬納米顆粒，並將現場配備的納米顆粒用於治理一個受 PCE 等含氯有機物污染的場地。現場製備納米單質鐵的目的在於保持”新鮮”納米顆粒的活性和顆粒大小，防止納米顆粒在運輸過程中的所造成得氧化消耗或者聚合。現場製備納米單質鐵採用 NaBH<sub>4</sub> 還原 Fe<sup>2+</sup>的方法，在製備過程中，反應溶液中添加了纖維素(carboxymethyl cellulose)作為納米單質鐵穩定劑，用來抑制納米顆粒的聚合。通過該方法在工地現場製備的納米單質鐵和鐵/鈮雙金屬納米顆粒未出現聚合現象。製備好的納米單質鐵和鐵/鈮雙金屬納米顆粒溶液被運用於注射-抽出(Push-Pull)測試中，用來測試納米顆粒在地下的遷移狀況及其對污染物的降解能力。測試結果表明：1) 通過該方法在工地現場製備納米單質鐵和鐵/鈮雙金屬納米顆粒是可行的，製備成的納米顆粒能立即被注射到地下，從而降低納米顆粒的失活；2) 納米單質鐵和鐵/鈮雙金屬納米顆粒能夠在地下移動，但是移動的距離有限，注射完成後 12 小時內即失去其移動能力。

以上幾個工程案例顯示 1) 納米單質鐵技術逐漸在環境修復工程中得到應用，主要運用於被含氯有機物污染的場地； 2) 納米單質鐵能夠有效的降解地下水和土壤中的污染物； 3 ) 通過使用穩定劑，納米單質鐵能夠在地表以下移動一定的距離。

### 3.2 納米單質鐵注射/應用方法

納米單質鐵注射/應用方法的選擇通常是由工程所在地的具體條件決定，取決於受污染區域的地質情況，納米單質鐵的表徵等。最常見的納米單質鐵注射/應用方法是利用現有的監測井，測壓井，或者注射井，通過重力或者泵將納米單質鐵注射到地下。水力循環是另一種注射/應用方法。通常是在下游將地下水抽取出來，在地面與納米單質鐵混合後，再通過注射井打入地下。

其他納米單質鐵的注射/應用方法還有，直接注射，脈沖壓力技術，液體霧化注射，水力壓裂注射。直接注射通過將直接注射管打入地下，然後將納米單質鐵通過直接注射管注入地下。脈沖壓力技術利用高強度的脈沖壓力將納米單質鐵溶液擠入土壤中的空隙。液體霧化注射通過載氣將納米單質鐵-液體混合物注入地下，促使

納米單質鐵-液體-氣體混合物形成微小顆粒，實現納米單質鐵在地下的有效傳遞。水力壓裂注射利用高壓氣體，或者高壓下黏度很高的水-砂混合物，使得地下土壤出現裂縫。納米單質鐵通過裂縫傳遞（USEPA，2008）。

### 3.3 商業化供應商

隨著納米單質鐵技術在環境修復中逐步受到人們關注，市場上出現了一些納米單質鐵的生產和供應商。表 4 列出了一些納米單質鐵供應商及其產品。

表 4 - 納米單質鐵供應商（USEPA，2008）

供應商	納米鐵名稱	供應商網站
Crane Polyflon	PolyMetallix	<a href="http://www.polymetallix.com">www.polymetallix.com</a>
Lehigh University	Fe/B	<a href="http://www.lehigh.edu/nano/environmental.html">www.lehigh.edu/nano/environmental.html</a>
Environmental Restoration Services LLC	Nano-Ox	<a href="http://www.ersllccorp.com">www.ersllccorp.com</a>
OnMaterials LLC	ZLoy	<a href="http://www.onmaterials.com">www.onmaterials.com</a>
PARS Environmental Inc.	NanoFe <sup>TM</sup> and NanoFe Plus <sup>TM</sup>	<a href="http://www.parsenviro.com">www.parsenviro.com</a>
Toda Kogyo Corporation	RNIP	<a href="http://www.todakogyo.co.jp/docs/english/products/efm.html">http://www.todakogyo.co.jp/docs/english/products/efm.html</a>
VeruTEK Technologies, Inc.	G-nZVI	<a href="http://www.verutek.com">www.verutek.com</a>

## 4 納米單質鐵技術面臨的問題與討論

納米單質鐵用於修復地下水和土壤中的污染物是一項比較新的技術，在工程應用中面臨著以下這些問題和挑戰。

1) 納米單質鐵的成本：目前納米單質鐵的市場價格大約為\$60 - \$150/公斤。對於大規模的地下水和土壤修復工程，納米單質鐵的成本相對於傳統環境修復技術的成本較為昂貴。表 5 列出了幾個運用納米單質鐵示範工程的成本結構。單位成本費用為\$235 - \$352/立方米受污染土壤。所以，找到更為簡便，廉價的納米單質鐵製備技術，降低納米單質鐵的成本是推廣該技術的重要挑戰之一。

2) 納米單質鐵的失活和在地下的遷移：納米單質鐵活性強，不但能與污染物反應，也可以與空氣中的氧氣、水、以及水中的溶解氧反應。當納米單質鐵曝露在空氣中時，納米單質鐵會被氧氣氧化，降低其反應活性。在納米單質鐵的運輸過程中，部分納米單質鐵會與水以及水中的溶解氧反應，從而失去部分反應活性。如Liu等（2005）報導，Toda Kogyo提供的納米單質鐵，其中單質鐵的成分僅為26.9%±0.3%，

其餘部分在運輸或者儲藏過程中被氧化。同時，納米單質鐵顆粒在顆粒間的磁力，范德華力等的作用下容易聚合成較大的顆粒，從而失去其反應活性。而且，大顆粒很難被注入地下，或者注入地下後，在地下水或者土壤中遷移非常有限的距離。

表 5 - 運用納米單質鐵修復環境污染示範工程的成本及費用 (USEPA, 2008)

工程名称及地址	成本结构			
	污染修复成本(总)	资本成本	运行及维护费用	单位成本
Naval Air Engineering Station, Lakehurst, NJ, USA <sup>1</sup>	\$255,500	--	\$213,000	--
Naval Air Station, Jacksonville, FL, USA <sup>2</sup>	\$260,000	--	\$110,000	\$352/立方米
Patrick Air Force Base, FL, USA <sup>3</sup>	\$4,000,000	\$2,000,000	\$70,000	\$235/立方米

1. 运行及维护费用：安装监测水井:\$24,400, 采样及分析:\$58,400, 技术报告:\$18,100。

2. 纳米单质铁成本: \$37,000。运行及维护费用：安装监测水井:\$52,000, 采样及分析: \$110,000。740立方米受污染土壤被处理。

3. 资本成本: 纳米单质铁成本: \$1,000,000, 注射分包商: \$1,000,000, 17000立方米受污染土壤被处理。

3) 納米單質鐵顆粒壽命：如上所述，納米單質鐵活性強，易與污染物，水，和水中的溶解氧反應。另一方面，納米單質鐵顆粒體積小，單個顆粒的鐵含量低。使得納米單質鐵顆粒的壽命只能維持幾個星期或者幾天。而地下水和土壤中的污染物濃度卻能保持幾年或者數十年，尤其是被吸附到土壤中的污染物，需要很長時間才能夠從土壤中滲透出來。因此，納米單質鐵顆粒相對較短的壽命可能限制其在土壤和地下水修復中的使用。

4) 納米單質鐵的環境毒理性：近年來，納米材料的毒理性受到越來越多的關注。由於納米顆粒極小，納米顆粒可能被微生物攝入體內，造成對生物體的毒害(Karn等；2009)。逸今為止，人們對納米單質鐵的環境毒理性知之甚少。這可能會限制納米單質鐵技術的應用和推廣。不過，根據本文作者的了解，納米單質鐵在被注射到土壤和地下水以後，在環境中的遷移距離非常有限（在3-5米以內），對注射井下游的環境或者人體的影響將是有限的。另外，納米單質鐵在環境中的存活壽命比較短（幾天到幾個星期）。因此，本文作者認為，納米單質鐵對環境的毒性跟其被用來降解有毒環境污染物的功效比起來是微乎其微的。

## 5 結論

納米單質鐵自上世紀90年代中期被提出以來，其作為一種環境修復技術的潛力逐漸

受到人們關注。由於其獨特的物理和化學性能，納米單質鐵能有效、快速的降解許多種類的環境污染物，尤其是對含氯有機物的降解非常有效。而且納米單質鐵可以被直接注入地下，對受污染地下水和土壤進行原地修復，可以省去處理所需要的昂貴的挖掘，填埋等工序。另外，納米單質鐵在地下水和土壤中被消耗後，使得地下水和土壤中的氧化還原電位降低，為微生物的生長創造了良好的條件，有利於後續的生物處理過程。目前有關該技術的研究主要是實驗室研究，同時，該技術在北美和歐洲應用到數十個示範工程中。隨著納米單質鐵生產成本的降低以及人們對納米單質鐵降解污染物機理的進一步提高，該技術可能會在環境修復中得到更多的應用。

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### 作者簡介

熊忠博士：

現任職於AMEC Geomatrix工程諮詢公司位於美國加利福尼亞州Newport Beach市的分公司，是土壤和地下水修復項目經理和項目工程師。具體工作包括污染場地調查、土壤和地下水修復設計和實施、土壤和地下水修復技術的研發等。熊忠博士參與設計和實施了多個土壤和地下水修復工程項目，目前正作為項目負責人主持一個由美國國防部資助的項目，採用穩定化的納米單質鐵修復受含氯有機物污染的土壤和地下水。同時，作為主要研究人員，開發了幾項新型環境修復技術，持有美國專利兩項（其中一項待批），在專業期刊雜誌上發表論文多篇。熊忠博士分別在2000年和2003年畢業於重慶大學獲環境工程專業學士和碩士學位，2007年畢業於美國Auburn University獲環境工程專業博士學位。擁有美國加利福尼亞州政府核發的“職業工程師”執照。

何鋒博士：

現為美國能源部橡樹嶺國家實驗室研究員，致力於研究持久性有機物及重金屬污染物的環境修復技術以及汞的環境行為變化。何鋒博士1999和2002年畢業於浙江大學環境工程專業，分獲學士和碩士學位。2007年畢業於奧本大學（Auburn University）土木（環境）專業，獲博士學位。2007至2010年在Golder Associates擔任修復工程師，從事地下水和土壤修復，以及垃圾填埋場沼氣發電的設計施工。2005和2007年，在Environmental Science & Technology和Industrial & Engineering Chemistry Research上分別發表了食品級澱粉和羧甲基纖維素穩定化的納米鐵應用於地下水處理的三篇論文，被獨立研究認為是真正能在地下水中傳遞1米以上的納米鐵材料，論文已被同行應用200次以上。2008年曾獲美國化學學會環境化學分會研究生最高獎The C. Ellen Gonter Environmental Chemistry Award.

## **Commentary: Deep Thought from a Book**

Looking East and Peeking West (东张西望) (Dong Zhang Xi Wang) (2010)

Author: XiaoYi Liao (廖晓义), Publisher: San Chen,  
[www.sunchime.com.cn](http://www.sunchime.com.cn)

Reviewed by Yue Rong, Ph.D., Editor-in-Chief, SCCAEP Online Journal

(March 2011)

I am recommending a good book entitled “Looking East and Peeking West” (东张西望) (2010) by XiaoYi Liao (廖晓义). Usually, “东张西望” in Chinese means “looking around in all directions.” However, the title of this book has given more implications underneath the superficial meaning. Subtitled “Environmental solution formula”, the book is about discussions among people beyond environmental professionals from “East” and “West” culturally across the globe. The author, a philosopher turned environmental advocate and practitioner, interviewed 20 people who represented a wide range of cultural and professional spectrums with the subject of current global environmental challenges and solutions. Among people who participated in the discussions include a world renowned physics scholar, professors in history, religion and philosophy, a traditional Chinese herbal medicine doctor, editor-in-chief in the World Cultural Forum, an executive director of the Environment and Ecology Protection Association, Vice Minister of Environmental Protection of China, and former Under-Secretary General of the United Nations.

The book is about “the East meets the West” perspective to re-think the solutions to current environmental problems, challenges, and solutions. The author and the people in the discussion believe that the solution to the global environmental problems should be a holistic approach based on not only modern science and technology (hardware), but also on people’s conscience, mentality, recognition, determination, behavior, and cultural traditions (mental power).

For last two hundred years or so, humans have been proud and joyful with our revolution of industrialization. More than ever in human history, we have enjoyed an increase in the quality of modern life. We have enough food to eat, modern house to live, computers, and modern transportations. We also have technologies to send humans to the moon and knowledge of decoding DNA. The capitalist system developed in the West has driven people to strive for the best and for the most.

It seems human abilities and resources are unlimited and improving with time. However, what we do not have is the unlimited natural resources on earth commensurate to the human resources. We are using out our natural resources to pay for “the best and the most.” The current global environmental crisis is actually a clash between human desire to get the best and the most and the limited natural resources. “China uses 30 years time to finish what the West had developed in the last 100 years, but ironically, the 100 years pollution due to modern industrialization in the West all showed up in the past 30 years in China.” Said one of the people in the book. Should today’s China also follow the experience of last 100-year pollution and remediation path in the West?

The author believes that the current thinking to deal with the global environmental problems is too linear and too compartmental. People only see the piece of the puzzles instead of the whole picture. Using the global climate change as an example, the author thinks we often misconstrue the deep-rooted social and economical problems as environmental problems, then simplify comprehensive environmental problems as a climate change problem, then make the climate change problem into energy problem, which then becomes energy development issues and energy demand issues, then the energy development problems further lead to reusable energy strategy, which leads to new technology and capital investment, and so on. All of sudden in the cascade, we lost the full picture in the global environmental and natural resources problems.

Then, what is the solution suggested? The answer is to see the whole picture, so we can find the balance between human and the nature. The author suggests we re-think and re-visit what the deep-rooted Chinese culture which our ancestor left for us to strike a balance between human desire to want a better life and consideration of environmental harmony. Using the analogy of Western medicine versus traditional Chinese herbal medicine, the author suggests the Western medicine is a surgical method for a quick solution to remove the problem (relatively fast), while the traditional Chinese medicine is a systematic approach to tune the whole body into a harmonious working system (relatively slow). Each approach has its philosophy behind it and its way to reach the ultimate goal of curing a disease. Relatively fast solution may leave a long term repercussion. Relatively slow solution may not be able to stop the bleeding. However, if we can be smart enough to use strength of both, we certainly will be better off. Therefore, why can we do that with our environmental problems? People on earth all have professions and are doing different kind of work. Now, they all come together to face the global environmental crisis. The West has modern industrialization and pollution remediation technologies, and the East can offer 5000 years culture of harmony between human and the earth. Now, it is the time for the West to meet the East, or vice versa, for the sake of environmental protection.

The East can offer a traditional perspective on the harmony between the mankind and the nature. The Chinese traditional philosophy believes that the

earth (地) represents the physical world that we can see and feel, the heaven (天) is the “invisible” world that we cannot see, but can produce mental power and energy. The human is the one connecting the “earth” to the “heaven.” Then, the solution should be with the human, with each one of us.

Therefore, the material things we strive for everyday (money, big house, beautiful cars, etc.) may not be the only thing that matters. Maybe there is something invisible and intangible that also matters to us. We may need to think that way when dealing with our environmental problems which may relate to the “heaven” as Chinese defined it. The Chinese traditional religion “Daoism” says that “dao” is a way of life, and can be understood, but cannot be articulated in a regular layman’s way. Human behaviors follow this line. Indeed, sometimes, we do something that we cannot explain, rather just follow the instinct.

So, let’s follow the instinct. The solutions of the environmental problems lay among each one of us. That is our mental power, mentality, understanding, recognition, determination, actions, and behavior. Maybe we should recognize that our current popular thinking and mentality of capital values is not right for the environment. Maybe we should change the way of our life and re-evaluate our personal benefit and value in the benefit of the environment. The best and the most the Western capitalist strives for may not be the best after all.

Maybe next time we enjoy a recreation like skiing or scuba diving (disturbing the nature), we should also think to play a game of chess (less disturbing the nature). Maybe next time we put our laundry into electrical dryer, we should also think to hang the laundry under the sun and let the sun dry them. Maybe next time we get into our automobile, we should also think to use a bicycle instead. Maybe we should recycle the bottles after we drink the beverages. Maybe we should not have so many pair of shoes and so many shirts? Maybe our modern life is very wasteful in many ways? Maybe, and maybe . . . .

So, what do you do for the environment today?

(Acknowledgment: The author would like to thank Mr. Gensen Kai for his review and comments.)



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***Fourth Symposium on Global Emerging Environmental  
Challenges and Government Responses  
Global Chinese Scientists Environment Forum - Special Session***

Presented By

Southern California Chinese American Environmental Protection Association (SCCAEPA)  
Professional Association for China's Environment (PACE)  
Global Chinese Scientists Environment Forum (GCSEF)

Support and Co-organizer Agencies: Chinese Society for Environment Sciences, Overseas Chinese Environmental Engineers and Scientists Association, Chinese Environmental Scholars & Professionals Network  
U.S. EPA Region IX, Cal EPA-Los Angeles Regional Water Quality Control Board, San Diego Regional Water Quality Control Board, and California State University at San Bernardino,

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**225 West Valley Boulevard**  
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You are cordially invited to the Symposium on Global Emerging Environmental Challenges Government Responses. Preliminary session topics are listed below. The symposium will include two days of technical sessions and a one day technical tour.

Forum topics: Green Industry, Low Carbon Economy, Alternative Energy,  
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Symposium topics:

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- US National Pollutant Discharge Elimination System (NPDES) Program
- Lake and Reservoir Management for Eutrophication
- Low Carbon Economy, Green Industry, and Alternative Energy
- Soil and Groundwater Remediation
- Brownfield Redevelopment and Land Use Management
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Please send the abstract to:

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### **Invited Speakers (preliminary)**

Dr. Paul Bishop, Program Director of Environmental Engineering Chemical, Bioengineering, Environmental and Transport System Division (CBET), US National Science Foundation (NSF)

Dr. Stephen Shu-hung Shen, Administrator of Taiwan EPA

Dr. Chung Liu, Deputy Executive Officer, South Coast Air Quality Management District

Prof. Jiming Hao, Tsinghua University, member of Chinese Academy of Engineering

Prof. Shu Tao, Dean of College of Urban and Environmental Sciences, Peking University, member of Chinese Academy of Science

Prof. Zhong Ma, Dean of School of Environment and Natural Resources, Renming University of China

Prof. Zhifeng Yang, Dean of School of Environment, Beijing Normal University

Prof. Yanqing Wu, Dean of School of Environmental Science & Engineering, Shanghai Jiao Tong University

Ms. Lida Tan, Director of China Initiative, U.S. EPA Region 9

### **Symposium Highlights**

- Excellent speakers (high rank government officers, world class environmental experts, well-known university professors, executive officers of international corporations).
- Contemporary environmental topics that most developed countries are currently challenged with.
- Most of the materials presented in the symposium are from State of California, which has the most stringent environmental regulations among 50 states in the USA and well-developed environmental industry (over 100 environmental consultant companies and numerous environmental equipment manufacturers)

- All presentations and site visit guides will be in Chinese.
- Great opportunity to network with the US environmental community, i.e., governmental agencies, universities, and environmental consultants.
- Symposium is organized by a non-profit professional organization

***Site Visit Trips (subject to change)***

Trip one - City of Los Angeles Hyperion Waste Water Treatment Plant, West Basin Municipal Water District - Advanced Recycled Water Facility

Trip two - Southern California Edison New Technology Center, Miller Beer Factory — Waste to Electricity Project

Trip three - Brownfield project one — Douglas Park Development, Brownfield project two — Campus Playa Vista Development and Fresh Water Wetland Restoration

**Guided local city tours for spouse and family members**

**Golf tournament (optional if enough interest)**

**Tour visit to other cities in the US**

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- Chinese regulators in government environmental protection agencies
- Environmental professionals in major Chinese corporations
- Professors and researchers from Chinese universities
- Chinese professionals from US governmental agencies, universities, and environmental consulting companies

**Registration fee: US\$300 / person (Fee includes lunches for 8/18, 19, and 20, and dinners for 8/18 and 8/20, symposium materials, site visit transportation)**

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- Guangyu Wang, Ph.D., Deputy Director, Santa Monica Bay Restoration Commission
- Jason Wen, Ph.D., P.E., Assistant Utility Manager, City of Downey
- Yu Yang Gong, Ph.D., P.E., Managing Director, ESD China Limited

# Call for Best Student Research Awards Papers

## Deadline for submission: July 7, 2011

You are invited to submit a research paper for 2011 competition for Best Student Research Awards sponsored by the Southern California Chinese-American Environmental Protection Association (SCCAEPA). There will be one (1) \$1000 award for the 1<sup>st</sup> prize winner, and up to three for 2<sup>nd</sup> and 3<sup>rd</sup> prize winners.

### Topics and Eligibility

Topics are limited to research work related to environmental protection issues. The research work may include on-going research or published after **January 2010**. All levels (Bachelor, Master, Doctorate, J.D. or other professional degrees) college students are eligible in the environmental related fields, including environmental engineering (environmental, civil, chemical, and engineering geology) and sciences (chemistry, geology, hydrogeology, ecology, biology, toxicology, climatology, atmosphere science, earth science, soil science, air quality, water quality, and hazardous wastes), public health, environmental studies, environmental laws and economics, urban planning and studies. Individuals may submit only one paper. The applicant must be the primary author of the paper.

### Submission and Format

Submission shall include: 1) a presentation in PowerPoint slides format that may be used for a Poster presentation, 2) a cover letter or e-mail to describe the student's education background and updated resume, specific role and contribution to the research.

All required materials shall ONLY be submitted by e-mail to [sccaepa2011@gmail.com](mailto:sccaepa2011@gmail.com) by **July 7, 2011** for evaluation. The selected presentations will be displayed as Posters at SCCAEPA Annual Meeting on August 20, 2011 at Hilton San Gabriel, 225 West Valley Blvd, San Gabriel, CA 91776.

### Review Process and Judging Criteria

Research project will be reviewed by a student award committee. All corresponding authors will be notified by **August 12, 2011** of the result on their submittals. The selected paper will be eligible for Poster presentation and receipt of the awards. The authors of the selected papers will be responsible to prepare their posters on 3 ft by 4 ft project display boards (up to three per presenter) and present them in the designated area during the 2011 SCCAEPA Annual Meeting.

The research project will be reviewed and judged on the basis of the following criteria:

- Relevance to the theme of environmental protection and significance of the work to a broad audience
- Application of the academic research to the real world problems
- Originality of the work, including new concepts, innovations, or data
- Scientific and technical merit
- The completeness of the project, clarity of presentation and quality of the slides
- Student's specific role and contribution to the project.

### Contact

*Please contact Student Award Committee via e-mail at [sccaepa2011@gmail.com](mailto:sccaepa2011@gmail.com) if you have any questions.*