Origin and tracing techniques of high ^{15}N nitrogen compounds in industrial environments

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Abstract

Effluents and process waters from various industrial plants were investigated for the ^{15}N/^{14}N isotope ratio in nitrate and ammonia. It was found that large isotope fractionation occurs in cases where ammonia is involved in gas-liquid phase changes. This feature was found to occur in two coke oven plants where ammonia gas is removed from a gas stream by solution in water, in an ammonia sulphate plant where ammonia gas is absorbed in sulphuric acid and in a water treatment plant where ammonia is removed from (high pH) water by blowing air through the process water. In all these cases ^{15}N isotope enrichments (in the range of 10 to 30 ‰) occurred. These enrichments are in excess of those found naturally. Ammonia in such wastewaters essentially retains this high ^{15}N content when it is converted to nitrate underground: which occurs rapidly under well-oxidised conditions. Nitrate is a fairly conservative tracer and its contamination in water can be followed readily. In the low recharge environment in the central parts of South Africa evidence of waste management practices of 10–20 years earlier were still quite evident using this isotopic label. The high ^{15}N nitrate signal could be used to distinguish industrial nitrogen pollution from pollution by local sewage disposal systems. Vegetation that derives its nitrogen from such high ^{15}N sources retains the isotope signature of its source. Grass and other annual plants then exhibit the isotope signature of the water of a specific year. Trees exhibit the isotope signature of deeper water, which shows the effects of longer term pollution events. The use of high ^{15}N as tracer enables the source apportionment of nitrogen derived pollution in these specific circumstances.

1. INTRODUCTION

Inorganic nitrogen pollution of groundwater is becoming a matter of increasing concern in South Africa. This manifests itself usually as nitrate since most of our groundwater is well-oxidised, the soils are low in organic content and recharge rates are low. The origins of nitrate in groundwater are diverse (Tredoux 1993) and can generally be formulated as a consequence of some disturbance of the natural nitrogen cycle in the soil.

Water pollution due to excessive fertilizer use is probably not very common in the country. South African farmers are fairly conservative with the use of inorganic fertilizers and at this

stage there is not much evidence that significant water sources are polluted by nitrate from agricultural runoff (Conrad et al 1999). Nitrate production in soils is enhanced by tilling and ploughing of soils; both during the conversion of natural vegetation into agricultural lands and during the continuous exploitation of such lands. The nitrate accumulation in groundwater is probably due to the rapid conversion of organically bound N to nitrate which then drains towards the water table (Heaton 1985). Organic pollution from livestock and city, town or rural sewage disposal is however becoming more common. Water supply boreholes close to dwellings and within villages with animal drinking troughs close to boreholes, have led to the abandonment of many boreholes due to rising nitrate contents of the pumped water. In the more arid areas of the country elevated nitrate content of water is associated with the occurrence of nitrogen fixing plants (certain grasses, legumes, acacia trees, etc) (Heaton et al 1983, Heaton 1984). In (semi-) arid areas one therefore frequently finds a baseline nitrate value in groundwater (typically 2–20 mgN/L) above which pollution (usually manure or faecal) can then be identified. These nitrate sources have characteristic ^{15}N values and they can be identified by this means with reasonable success (Heaton 1986, Conrad et al 1999).

Industry is increasingly influencing groundwater in the urban environment. Past practices of less rigorous water management are now reflected in the quality of groundwater. This is particularly noticeable in the more arid parts of the country where recharge rates are low (seldom more than 100 mm/a) and the water table can be up to 100 meters deep. Pollution then appears many years after the event. In our laboratory various isotopic and chemical 'tracers' are being used in studies to follow water plumes from pollution sources (mine dumps, landfills, industrial sites, etc). These techniques are used to identify likely sources, assess the time frames involved and aid in possible remediation efforts.

Heaton (1987a) found 'condensate' from a coking plant with an anomalously high ^{15}N values (δ^{15}N= +21‰ AIR). In 1995 similar high ^{15}N values (>30‰AIR) were found in ammonia and nitrate in wastewaters of a steel plant in Vanderbijlpark, South Africa. These ^{15}N values are higher than those found in natural compounds. It was deemed useful to investigate the origin and occurrence of such anomalous nitrogen isotope compositions in industrial environments in more detail and explore the possible uses that could be developed from this phenomenon. IAEA supported this project from 1998 to 2000. Additional funding was provided by the CSIR. This report presents the data generated during this project and includes the data obtained prior to 1998.

2. AIMS OF THE PROJECT

- To identify the source of high ^{15}N (δ>+25‰AIR) nitrate and ammonia compounds in industrial settings and investigate the mechanism of their formation.

- To establish the extent of cases where high ^{15}N compounds are introduced in the environment and follow their transport underground.

- To assess the usefulness of this approach to other similar situations.

3. METHODOLOGY

- Sampling of nitrogen compounds in the process lines of suitable industries in South Africa for chemical and isotope analyses (^{15}N and ^{18}O in nitrate and ammonia).

- Sampling and analysis of water from waste and evaporation ponds of these industries as well as seepage and groundwater likely to be influenced by such ponds.

NO_3 and NH_4 analyses are reported as mgN/L. Nitrogen isotope contents in water are determined on nitrogen gas prepared by distillation from water, either direct (NH_4) or in the presence of Devarda's alloy (NO_3), followed by oxidation with LiOBr (Heaton & Collett 1985). ^{15}N analysis of organic material was done on nitrogen prepared by Dumas combustion. Subsequent samples were analyzed at the Institute of Geological & Nuclear Sciences (K Rogers: Lower Hutt, New Zealand) using EA-CF-MS. Deuterium and oxygen-18 analysis of water was done after equilibration of hydrogen gas (with Hokko beads as catalyst) and carbon dioxide at constant temperature in a VG Isoprep-18 preparation system. Isotope analysis is in all cases done on a SIRA 24 mass spectrometer at the CSIR in Pretoria. ^{18}O analysis of nitrate was done at Hydroisotop (A Voropaev: Schweitenkirchen, Germany) by ion exchange purification of the sample, conversion to CO_2 with graphite and MS analysis. Isotope results are reported relative to AIR (nitrogen), SMOW (hydrogen and oxygen) and PDB (carbon).

Based on the initial data from Vanderbijlpark we had intentions to sample at least four more sites. The investigation at Vanderbijlpark produced so many different aspects that most of the effort was expended on this study area, especially when the sampling of vegetation proved very useful. Less intensive sampling was only done at two other sites.

4. ISCOR STEEL WORKS PRETORIA

4.1. Coke plant

During a study of atmospheric nitrogen emissions, Heaton (1987a) collected a sample of 'first condensate' from a coke oven extraction system at the Pretoria steel works of Iscor Ltd. This is the first fraction of water sprayed into the coke oven gas stream with the aim of cooling the gas and extracting ammonia. Ammonia in this sample had $\delta^{15}N$ of +21.4‰AIR (Table 1). The equilibrium fractionation between gaseous NH_3 and NH_4^+ in solution has been experimentally determined as -33‰ and between gaseous and dissolved NH3 as –5‰ (Kirshenbaum et al 1947, Heaton et al 1997); the gaseous phase is depleted in ^{15}N with respect to the liquid phase. $\delta^{15}N$ of the first dissolved fraction (a mixture of NH_3 and NH_4^+) of +20‰AIR different from the source material (coal +2 to +4‰AIR) can therefore be expected. The ammonium sulphate product, which presumably represents the bulk of the nitrogen derived from coal, has an isotope composition close to that of the coal (Table 1). These data indicate that large fractionations, in the order of 20‰ or more are likely to occur in coke plants when ammonia is removed by water solution from a gas stream. The large isotope difference is caused by fractionation during nitrogen transfer between gas and liquid phases where maximum fractionation is known to occur.

4.2. Subsurface samples

The coke plant at the Pretoria steel works has since closed down and has been dismantled, as were the blast furnaces and mills on this site. The groundwater on the site is however still locally contaminated with high ammonia and nitrate. Seepage water is being collected at the lowest point of the site, the water is recycled and the pollution of the environment effectively managed.

Two groundwater samples were obtained from boreholes (5 and 13) that are located downslope of two different relict waste dumpsites. These dumps were used to deposit slag and (unknown) other materials from the past activities of the steel factory. There are no possible sewage water sources upstream of these boreholes and the only source of nitrogen is drainage from the waste dump. Isotope analysis of the two borehole samples (Table 1) indicate similar high ^{15}N isotope ratios as found in the Vanderbijlpark steel works for

groundwater just downstream of evaporation ponds with a few hundred mgN/L (Table 4). No ammonia is present in these borehole waters. The ^{18}O of these samples (Table 1) is above that of local rainfall (-4‰SMOW) and local municipal water (-5 to 0‰SMOW) and indicates some evaporation during re-use of this water. The nitrogen isotope data indicates that the pollution in the borehole water is similar to that of the high ^{15}N ammonia from the coke ovens that has been oxidized to nitrate.

A sample of 'process water' from the site was also analysed for comparison (Table 1). This sample represents the cumulative drainage from the entire site and mainly consists of seepages from various sources. The high nitrate content represents an average value of the total drainage and so does the ^{15}N content (of +15.4‰AIR). The ^{18}O content of this sample (+7.7‰ SMOW) is much higher than local rainfall or the local water supply and indicates excessive evaporation during re-cycling of the process water on this site.

Table 1. Analytical data for samples from the Pretoria steel plant

Source	Description	Date	$\delta^{18}O$	NO₃		NH₄		Source
				mg/L	$\delta^{15}N$	mg/L	$\delta^{15}N$	
NT474	Coke oven: first NH₃ condensate	1983	-	-	-	7860	+21.4	Heaton (1987a)
NT331	Coke oven: NH₃ Liquor	1983	-	-	-	9640	+1.6	Heaton (1987a)
NT321	(NH₄)₂SO₄ product	1983	-	-	-	-	-0.5	Heaton (1987a)
G4920	Borehole 5	2000	-2.5	162	+19.5	<1	-	This study
G4921	Borehole 13	2000	+1.2	73	+28.0	<1	-	This study
G4922	Process water	2000	+7.7	6528	+15.4	<1	-	This study

5. ISCOR STEEL WORKS VANDERBIJLPARK

This factory was established in the early 1950's and has been in operation since then. It houses three batteries of coke ovens and gas handling plants, blast furnaces, steel mills and associated activities. In the course of years the management has had to take increasingly stringent steps to limit the effects of present day pollution and to correct the influences of past water management.

Water management of the entire plant involves significant recycling of water and eventual release of a portion of the water after treatment. One of the steps in the water system is the collection of water in ponds for evaporation. These ponds also serve to hold excess water that drains from the entire site during heavy rainfall episodes. They contain water with high

sulphate, chloride and ammonia content. Wiid and Meyer investigated leakage from these ponds into the surrounding groundwater since 1993. It was found that chloride- and sulphate-rich water seeped through the soils beyond the boundaries of the works into groundwater of the adjoining populated areas to the west of the site. When nitrate was also found in some boreholes in this area, ^{15}N isotope analysis was used to indicate the likely source of nitrate. In the course of this investigation it became clear that the high ^{15}N signal of Heaton's (1987a) 'first condensate' was also evident in these waste ponds and in some of the boreholes adjacent to the ponds. This observation sparked off the present project.

The present study at this site investigated the isotope content of condensate water in the coke plant, the variations of the nitrogen species in waste ponds, in leakages from the ponds and in adjacent boreholes. The investigation extended to include isotope analysis of plants growing in this high ^{15}N water and its potential for monitoring of this effect.

The main water features relevant for this discussion are (Figure 1):

- The two **evaporation ponds** EV4 and EV10,

- A **line of boreholes** downstream of the evaporation pond EV10 that were drilled along the western boundary of the site in an approximate north-south direction,

- A group of boreholes (IPS, IPD, MJ) in the **northeast** of the site that is located in an area that had been utilized for irrigation disposal of high NO_3 water in the past,

- **Steel Valley** area to the west of the site, where high salinity has been observed in groundwater and pollutant transfer in a westerly direction is known to be occurring.

5.1. Coke plant

Coal is heated in the coke ovens under anoxic conditions. This drives gas off and leaves coke (very pure carbon) behind. The hot gas is a mixture of ammonia and a range of hydrocarbons (from methane to heavy tars and creosotes). Water is sprayed into the gas lines to cool the hot gases. This so-called 'condensate' (which is actually a solvent extract) contains ammonia and some organic compounds.
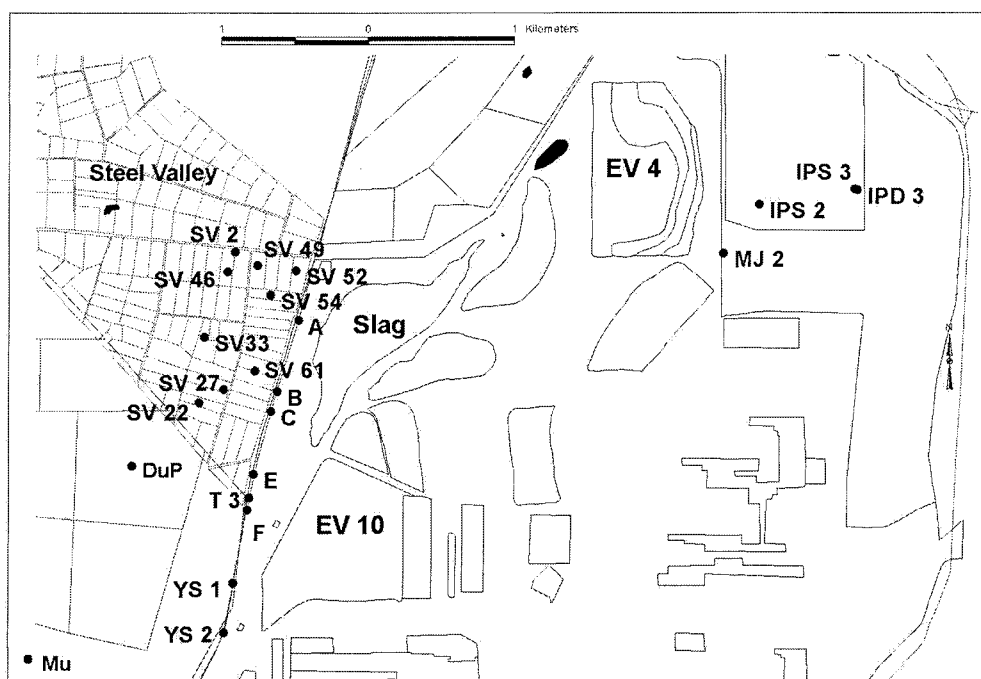
Figure 1. Map of the steel works in Vanderbijlpark. Note the evaporation ponds, the line of boreholes along the western boundary of the site, the boreholes on the Steel Valley smallholdings to the west of the site and those in the northeastern corner of the site.

At various stages organic solvent scrubbers are used to remove additional organic components from the gas stream and further water extracts are recovered. The combined ammonia solution ('liquor') is collected in one container and transferred to the ammonia sulphate plant. In this plant ammonia gas is driven off the liquor with steam and transferred to a sulphuric acid tank. Ammonia sulphate in solid form is recovered by heating and centrifugation and is sold to agriculture and industry.

In order to identify the source of high ^{15}N water to the evaporation dams, samples of these process waters from the coke plant extraction process were taken. The samples were collected from selected different parts of the plant tapping different parts of the process. The plant has three separate extraction lines, called 'batteries' which are fed by different combinations of ovens. Battery 3 was sampled in as much detail as possible in 1998 and a limited number of samples of the combined ammonia liquor of both battery 2 and 3 were obtained later. The samples consist of ammonia solutions drained from parts of the process line (Table 2). Ammonia concentrations in these extracts range from 2000 to 16 000 mgN/L.

Fractions A, B and C are subsequent fractions of ammonia extracted from the gas stream by absorption in water, the sum total of which accumulate in the ammonia liquor tank, D. This

liquid is acidified, purified and dried to eventually produce product G. E and F are the liquid and gaseous fractions that are lost during the conversion of D to G (Table 2). The first fraction, A, is similar to the 'first condensate' sampled by Heaton at the Pretoria coke oven plant (Table 1).

Table 2. Isotope analysis from the Vanderbijlpark coke plant

	Sample	$\delta^{15}N$		
		Battery 3		Battery 2
		Oct-98	Jun-00	Jun-00
	Single coal sample at battery 3	+4.8	-	-
	9 differently sourced coal samples used in batteries 2 and 3	-	+1.4 to +2.2	
A	First NH$_3$ fraction	+26.6	-	-
B	Second fraction	-	-	-
C	Benzol scrubber: final fraction	-23.4	-	-
D	Ammonia liquor tank	+14.1	+9.3	+11.0
E	Ammonia sulphate plant: effluent water	+26.6	-	-
F	'Devil' gas (condensate)	+1.8	-	-
G	Ammonia sulphate product	+4.2, +3.9, +2.5	-	-

As expected, the different fractions of ammonia from the gas line have ^{15}N contents from positive to negative in accordance with a classical Rayleigh condensation process. The plant operating staff was not able to provide mass balance data with which one might quantify the fractions A, B and C. While concentrations of NH$_4$ in the various liquids can be measured, their time weighted averages and quantities of the liquids are not known. Access to the actual ammonia gas from the process stream was not possible; only the water extracts could be sampled and not even all of them.

The cumulative ammonia liquors, D, derived from both batteries have $\delta^{15}N$ higher than that of the original coal (+1 to +4 ‰) and also from the final product (+2 to +4 ‰). This implies that there are significant ammonia losses that are not evident from the simple mass flow, or that the information given on the plant details and the sample locations might be incorrect or wrongly interpreted. More effort in obtaining such data was not justified in the present context.

The data confirm that $\delta^{15}N$ values in excess of +20 ‰ of ammonia solutions are quite common and are likely to be encountered if leakage or spillage of some of these process waters enters the water drainage system of the plant. Ammonia solutions with high ^{15}N such as those that are found in the waste ponds can certainly originate from specific parts of the coke plant extraction lines. For the purposes of the management of water around the waste ponds the source of the high ^{15}N in ammonia has been sufficiently established.

5.2. Isotope evaporation signals in the water

^{18}O and a few deuterium analyses were done on the pond and groundwater samples collected in the course of this project. The ^{18}O content of the different water sources show some grouping (Figure 2):

- The evaporation ponds have ^{18}O content in excess of +3‰ as expected from water subject to long term evaporation.

- The Steel Valley boreholes (SV) have ^{18}O between –4 and –2 ‰. Local rainfall results in groundwater with ^{18}O of –4‰. The Steel valley boreholes therefore contain essentially locally recharged water with local evaporation effects or small amounts of leakage from the ponds.

- The line boreholes ($\delta^{18}O$=-4 to +2‰) show more evaporation effects, which can be due to recharge from the marsh west of EV 4 and EV10, or to direct leakage from these ponds.

- The northeast boreholes have a wide range of ^{18}O contents, which is consistent with their former use as irrigation areas together with local rainfall recharge.

The D-^{18}O relation (Figure 3) is located along a slope of 5.4, which is typical for water that evaporates in our climate. It indicates that the different water sources are to various extents, evaporated. The plant derives it operating water from Rand Water, the local water utility that derives its water from the Vaal Dam of which the isotope content is known to vary considerably from time to time (Butler & Verhagen 1997). Within the time span of this project the water source (as judged from the extrapolation of EVL against MWL) must have remained stable.
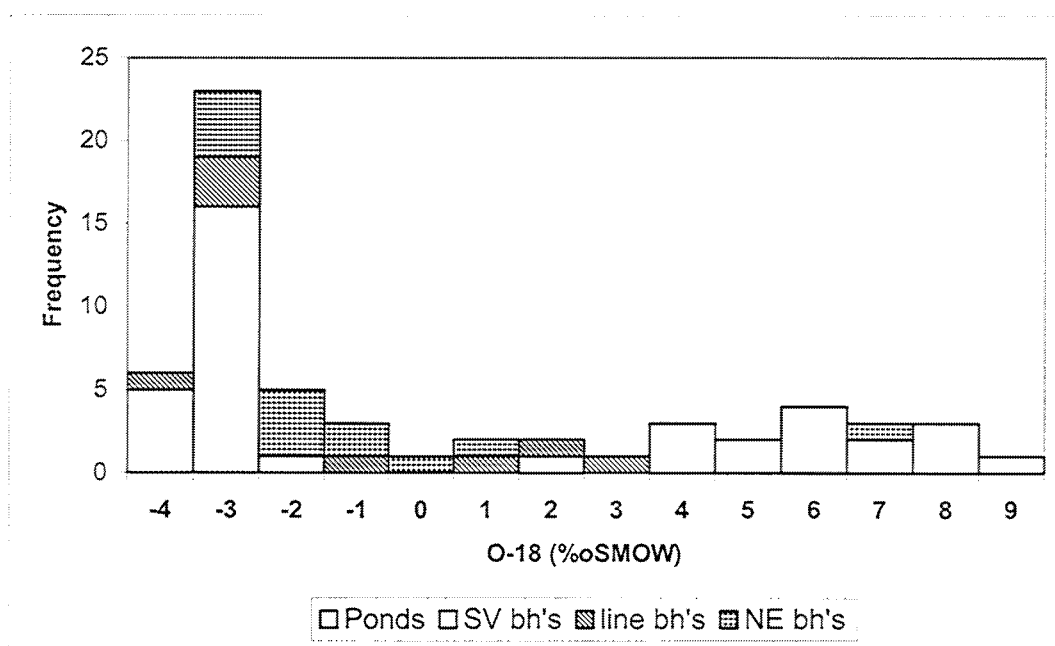
Figure 2. Frequency distribution of ^{18}O data of water at the steel works and surroundings. The evaporation effects are noticeable in the pond waters, and the line boreholes as well as boreholes in the northeast.
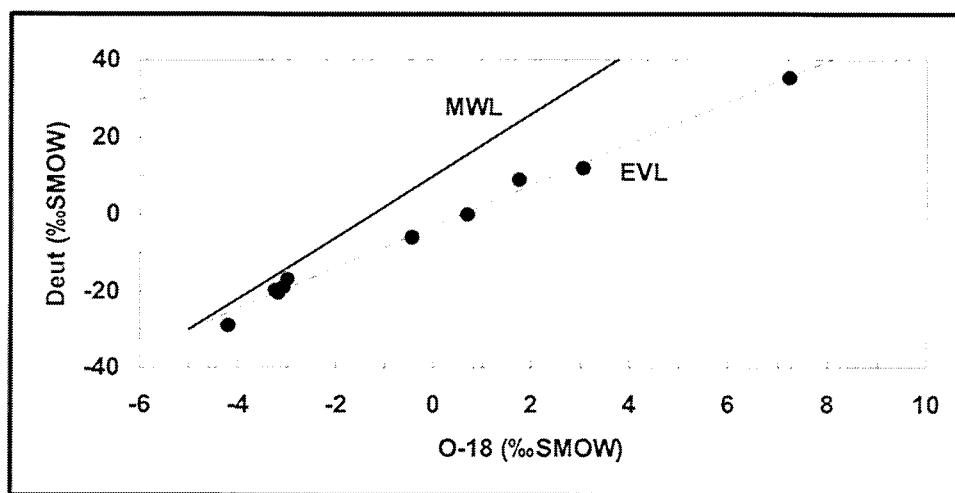

Figure 3. ^{18}O-deuterium correlation for the water samples from the steel works. All samples are on a common evaporation line (EVL) with slope 5.4, which is typical for the area. The Meteoric Water Line (MWL: slope 8) represents the variation that is found in rain (IAEA 1992).

5.3. ^{15}N in evaporation ponds

The water in the two evaporation ponds (EV4 and EV10) has been sampled a number of times in the course of the project specifically for nitrate and ammonia content and its ^{15}N content. A few associated parameters (pH and EC) are presented here of the samples collected (Table 3).

The data confirm that the ammonia content in the water remained within the range of a few hundred mgN/L in both ponds. Nitrate content remains low, never exceeding 13 mg/l. The steel works environmental management obtains more regular analyses of pond water, which indicate NO_3 and NH_4 variations of similar magnitude. The ^{15}N content of ammonia in EV10 ranged between +24 and +32 ‰AIR while in EV4 values between +36 and +58‰ were found. EV10 is considered to be the main source of groundwater pollution to the west of the site (see the next section). Nitrate has a similar ^{15}N content as ammonia, but the data are too limited and variable to establish the existence of fractionation between nitrate and ammonia. The kinetic fractionation factor (if such exists) is probably in the order of –10‰, which is considerably less than the –15 to –35‰ that has been found for nitrification by *Nitrosomonas europaeus* (review by Handley & Raven 1992). While the ^{15}N content of nitrate less than that of ammonia in this water supports the idea that the nitrate is derived from the ammonia and the isotope difference due to kinetic fractionation during nitrification it is also likely that the ponds may derive some nitrate from another source on the site. These aspects were not further investigated.

Table 3. Isotope analysis results from evaporation dams EV4 and EV10

Pond	Date	Sample	Ammonia		Nitrate			Water		
			mgN/l	$\delta^{15}N$	mgN/L	$\delta^{15}N$	$\delta^{18}O$	pH	EC	$\delta^{18}O$
EV 4	11/96	S4650	472	+36.6	10.9	+43.7	-	6.2	1760	+7.2
	05/98	S4719	73	+58.5	10.9	+33.9	+30.4	6.1	1350	+6.1
	10/98	S4787	105	+52.5	0.7	-	-	6.0	1423	+8.4
	08/99	S4844	137	+40.9	2.8	-	-	4.5	1188	+8.0
	06/00	S4986	125	-+44.7	2.7	-	-	4.3	1358	+5.1
EV4 wall seepage	10/98	S4785	72	+43.7	9.7	-	-	7.4	688	+4.7
EV 10	11/96	S4649	168	+32.1	0.8	-	-	7.7	630	+3.1
	05/98	S4707	235	+27.3	12.8	+16.3	+28.3	4.5	723	+5.0
	10/98	S4788	200	+26.5	4.0	-	-	6.9	746	+6.7
	08/99	S4845	229	+24.8	1.9	-	-	7.9	738	+5.8
	06/00	S4989	141	+25.2	0.8	-	-	4.2	585	+1.8
EV10 Halley beacon marsh	05/98	S4718	41	+35.9	1.8	-	-	-	-	+2.6

Chemical differences exist between water of the two ponds. These are a reflection of water management practices on the site. The water in the pond EV4 consistently shows higher EC, ^{15}N and [18]O than EV10. These data suggest that EV4 is a later phase than EV10. If this were so, then the higher [15]N(NH$_4$) content in EV10 suggests that some ammonia was released from either of these ponds. There are no indications that large scale ammonia release from these ponds occurs: there is no ammonia smell detectable at the ponds and the pH of the water is normal. Nevertheless, small losses of ammonia cannot be ruled out.

The two [18]O analyses of nitrate in pond water are higher than found in the groundwater samples elsewhere in the area (Figure 4) and higher than can be imagined even if all the oxygen were derived from the atmosphere (+23‰). High [18]O in nitrate is known to occur in denitrifying groundwater (Kendal 1998). This is unlikely to occur in the Iscor ponds since there has to be an oxygen-rich environment to form nitrate from ammonia in the first instance. Nitrate in the atmosphere, in rain or as dry deposition, is known to have [18]O contents greater than +30‰AIR (Kendall 1998). The hypothesis can therefore be made that the nitrate in the ponds could be derived from atmospheric precipitation. This nitrate precipitation would then be the product of oxidation of ammonia gas released from the nearby plant. The nitrate levels in the ponds are low enough to make this a reasonable hypothesis, but proper measurements of fallout and the actual inflow to the ponds would have to be made to check this idea.
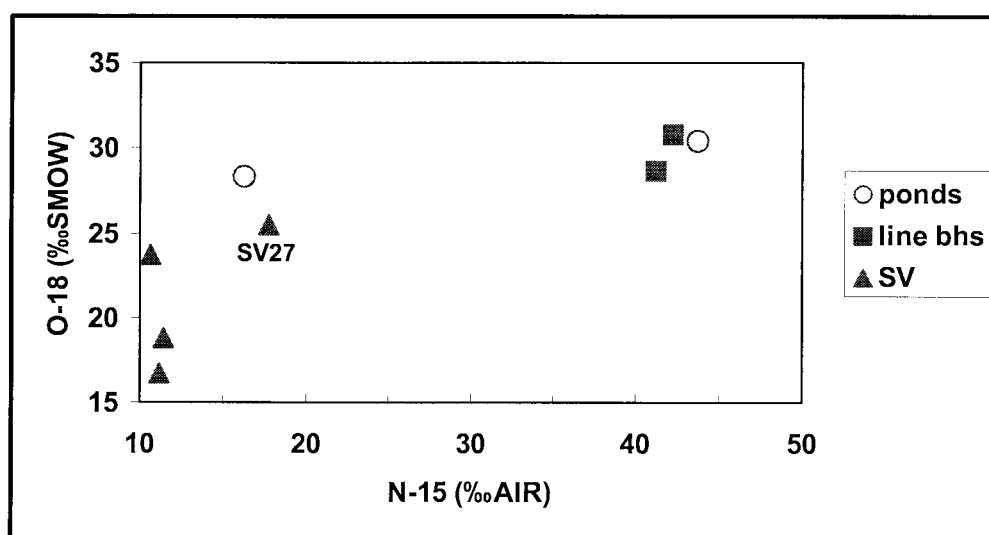

Figure 4. Relation between $\delta^{18}O$ and $\delta^{15}N$ in nitrate of different water in Vanderbijlpark. The Steel Valley samples (SV) are distinctly different from the other samples that are directly derived from evaporation ponds. SV27 tends towards the evaporation pond values.

Seepage through the wall of pond EV4 was sampled in October 1998 (Table 3). This sample had EC, NH_4 and ^{18}O values that can be attributed to some dilution with rainwater or other local water.

5.4. Line boreholes

A number of boreholes are available in a line running roughly north-south along the western perimeter of the factory site (Figure 1). The southern-most part of this line is parallel to the western wall of pond EV10. The boreholes were established to monitor groundwater leakage from the steel works site towards the west. Stable isotope data of these waters ($\delta^{18}O$ –2 to +1‰ SMOW) show evaporation effects in these boreholes (Figure 2) consistent with containing leakage water from pond EV10 and EV4.

The boreholes are monitored regularly for their chemical composition. Samples for which ^{15}N isotope analyses were done are shown in Table 4. In all cases the boreholes were sampled by submersible pump and the boreholes were purged before sampling. The ^{15}N data of +33 to +44‰ for these boreholes clearly show the influence of leakage of water from pond EV10. Note that no ammonia is present in all but two of the boreholes sampled in 1996, and neither is it present in any of the other boreholes along this line that are regularly sampled by the steel works pollution group. Leakage is therefore very localized and in the course of leakage nitrification occurs readily.

The elevated nitrate levels and specifically the associated high ^{15}N content unmistakably points to the fact that the nitrate is derived from the evaporation ponds. There appears to have been sufficient time for the ammonia to be oxidized to nitrate, so there may be a time delay involved. The distance between pond wall and the borehole line is a minimum of 200 meters (Figure 5). It is not possible to assess the quantities of pond water contributing to the borehole water. Ammonia is not a conservative tracer and one does not know how much nitrogen is lost during the conversion to nitrate. The dynamic nature of the water in these boreholes is testified by its variable chemistry and isotope content.

Table 4. Chemical and isotope data from the line boreholes along the perimeter of the steel works site

Borehole	Date	Lab No	NH$_4$ mg/L	NO$_3$			EC mS/m	$\delta^{18}O$
				mg/L	$\delta^{15}N$	$\delta^{18}O$		
T3	Oct-98	G4835	<0.1	10.5	+43.9	-	327	-3.4
YS1	Oct-98	G4836	<0.1	7.1	+41.2	+28.6	579	+2.0
YS2	Nov-96	G4031	1.6	7.0	+43.0	-	570	+1.7
YS2	Oct-98	G4837	<0.1	23.7	+36.8	-	261	-4.0
B	Nov-96	G4032	0.5	9.7	+33.8	-	300	-3.2
B	Oct-98	G4834	<0.1	3.1	+42.2	+30.8	321	-3.0

5.5. Steel Valley boreholes

The Steel Valley area is located to the west of the steel works boundary (Figure 5). The area contains a large number of private boreholes. These are low yielding water supply boreholes that serve the homes and small gardens of smallholdings. The smallholdings are 2½ hectare pieces of land on which 2 to 5 families live, practicing limited agriculture and livestock that is supported by these boreholes. Sewage disposal on these smallholdings is done through underground septic tanks of which the effluent is bound to reach the groundwater some or other time. Some boreholes in this area have high salinity water due to pollution of chloride- and sulphate-rich leakage from the steel works that has leaked through from the plant during its 50 years of operation.

The ^{18}O and D analyses of these ground waters show less effects of evaporation than the line boreholes closer to the steel works site (Figure 2). Some boreholes also show elevated nitrate levels. The nitrogen isotope investigation was undertaken to establish the influence of N compounds from the evaporation ponds to the groundwater of this area.

Samples were taken from boreholes in the eastern part of Steel Valley adjacent to the steel works perimeter fence. 19 boreholes were sampled in October 1998 of which 15 showed high chloride (>100mg/L) and 6 high sulphate (>100mg/L). Only 7 boreholes had NO$_3$ or NH$_4$ levels greater than 4 mgN/L (Figure 5). Nitrate in Steel Valley borehole water is therefore not all that common nor are they necessarily associated with high Cl and/or SO$_4$. Data from earlier surveys have shown that high nitrate in groundwater is not limited to boreholes adjacent to the steel works.

The nitrogen isotope data (Table 5) suggest two groups of boreholes:

- The boreholes from the south and western part of Steel Valley (2, 22, 33, DuP and Mu) that have low $\delta^{15}N$ (+11 to +16‰) which is well within the known range of sewage related nitrate. They group together on the nitrate-^{18}O and ^{15}N plot (Figure 4) where the low ^{18}O indicates that nitrification occurred from water with low ^{18}O, in contrast to the situation in the evaporation dams. DuP borehole (20 mg/L NO_3; $\delta^{15}N$=+11.2‰) is a typical faecally contaminated borehole: it has a shallow water table, it is equipped with a handpump, the wellhead is unprotected and surrounded by muddy pools of water in which pigs and chicken wallow. Bacterial counts of *E coli* have been found in this water. Borehole Mu (NO_3=16 mgN/L; $\delta^{15}N$=+16.0‰) is close to a milk stable with a few dozen cows and the likelihood of faecal contamination is large.

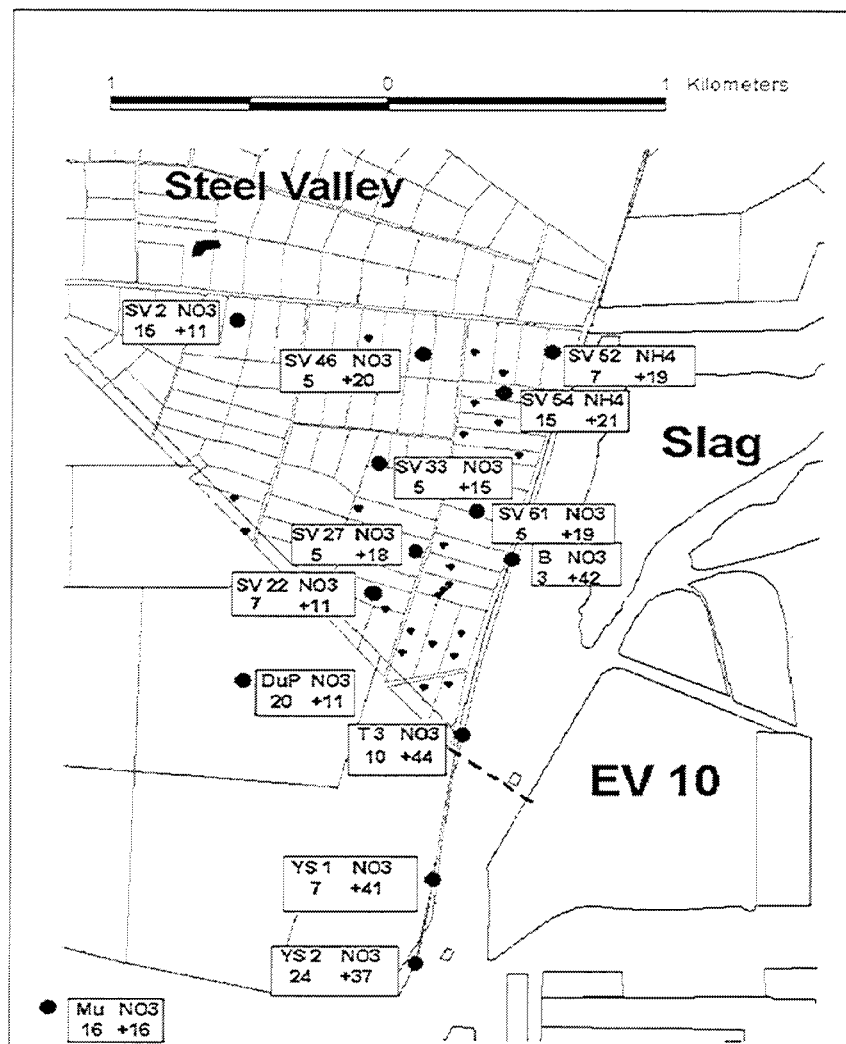*Figure 5. Map of the Steel Valley and adjacent areas. Small solid circles show boreholes with NO_3 <4mgN/L. Large solid circles show boreholes having significant NO_3 and NH_4 contents (>4mgN/L). The rectangles represent the borehole number, NO_3/NH_4, mgN/L, $\delta^{15}N$. The dashed line between T3 and EV10 represent the cross-section shown in Figure 6.*

Table 5. Analytical data from the Steel Valley boreholes

| Borehole | Date | Lab No | NH₄ | | NO₃ | | | EC mS/m | pH |
			mg/L	$\delta^{15}N$	mg/L	$\delta^{15}N$	$\delta^{18}O$		
RK Mu	Feb-96	G3861		-	16.0	+16.0	-	-	-
SV DuP	Nov-96	G4038	0.1	-	20.0	+11.2	+16.7	-	-
SV02	Feb-96	G3862	0.1	-	15.2	+11.4	+18.8	-	-
SV22	Oct-98	G4639	0.1	-	6.6	+10.6	+23.7	112	7.9
SV27	Oct-98	G4640	0.2	-	5.0	+17.8	+25.5	129	7.7
SV33	Oct-98	G4641	0.2	-	4.8	+15.0	-	62	7.8
SV46	Oct-98	G4642	0.1	-	4.9	+19.9	-	130	7.6
SV52	Oct-98	G4643	7.1	+18.7		-	-	79	7.0
SV54	Feb-96	G3864	0.1	-	6.7	+16.6	-	-	-
SV54	Oct-98	G4644	15.0	+21.2		-	-	126	7.1
SV61	Nov-95	G3863	0.1	-	7.0	+26.8	-	-	-
SV61	Mar-96	G3899	<0.1	-	6.5	+16.4	-	-	-
SV61	Oct-98	G4645	0.1	-	4.9	+19.3	-	162	7.4

- The boreholes in the Northeastern sector consisting of SV 27, 46, 52, 54 and 61 have $\delta^{15}N$ in the range of +17 to +21‰. This range is just within the usually quoted range (+10 to +20‰) for sewage effluent nitrate water (Heaton 1986). The single sample of this group for which nitrate ^{18}O is available ($\delta^{18}O$ = +25.5‰) plots not far from the other sewage derived groundwaters of Steel Valley but way below the group of pond-derived nitrates as typified by line borehole B (Figure 4). The likely contribution from pond-derived nitrate cannot be more than 10%. The significant NH₄ content of SV52 and SV54 does bear the ^{15}N signal of pond-derived nitrate. The only clear indication of possible pond-derived nitrate in Steel valley is the sample of SV61 taken in November 1995 with $\delta^{15}N$=+26‰ (Table 5). This is beyond the range for sewage derived nitrate and but could not be reproduced when re-sampled 4 months and 23 months later.

Apart from the northeast corner, the nitrogen isotope analyses therefore do not indicate any significant nitrogen pollution in Steel Valley that can be attributed to the steel works. The nitrate that is found in local groundwater has the character of that produced by faecal pollution. During the past year the pollution issue in this area became the subject of legal

action. Despite scientific evidence that the steel works was responsible for contamination in boreholes of only the first row of smallholdings, the legal action was settled after the steel works agreed to purchase the entire area of smallholdings and other private land immediately west of the plant.

5.6. NE irrigation field

The northeastern boreholes (Figure 1) show similar high ^{15}N content in both ammonia and nitrate as is found in the ponds of the steel works (Table 6). Concentrations in the order of hundreds of mg/L are the highest levels found in groundwater on the site.

From 1978 to 1988 this area had been used for disposal of water from pond EV4 by spray irrigation. Application rates were in the order of 3 mm/day. This rate is less than the normal evaporation rate (even in winter) and it can be expected that all of the water, except for the excess during heavy rainfalls, would have evaporated. The nitrogen in that water would however have migrated towards the water table eventually. In the boreholes of this area we are dealing with an historical isotope signature that has not been flushed out of the system yet. Annual recharge rates in the range of 20–70 mm ensure that many years will be required to flush this high nitrate load from the system.

Table 6. Isotope data from the northeastern boreholes

Sample	Date	Lab No	NH$_4$		NO$_3$		EC	pH
			mgN/L	$\delta^{15}N$	mgN/L	$\delta^{15}N$	mS/m	
BH IPD3	May-98	G4522	<0.1	-	246	+28.6	-	-
BH IPS2	May-98	G4520	160	+37.3	135	+27.3	-	-
BH IPS3	May-98	G4521	<0.1	-	160	+37.2	-	-
BH MJZ (deep)	Nov-96	G4036	0.3	-	75	+38.1	148	6.1
BH MJZ (shallow)	Nov-96	G4037	2.1	-	260	+46.7	1035	6.2

As is the case in Steel Valley, these boreholes have predominantly nitrate rather than the ammonia found in the evaporation ponds. Most of the ammonia in the irrigation water has therefore been oxidised. It is not certain where this oxidation could have occurred: during recharge or later while the water was below the water table already. It is consistent with the fact that ammonia is hardly ever found in local groundwater. The low flow rate and well-

aerated nature of the deep soils are probably factors that ensure complete oxidation of nitrogen compounds to nitrate.

5.7. Plants growing in pond water

Most of the edges of the ponds are bare of vegetation. In the east where the gradient is flat, some plants grow in the water, but access is limited. Samples were obtained from plants that were growing in shallow water along a wall extending into pond EV4 on the northern end (Table 7). Grass (sample M3649) was growing on the embankment 1 meter above the water level of the pond at the time of sampling.

The ^{15}N content of vegetation growing in the water is significantly above that of the background (+2.9‰) and also higher than that of other plants found in the southern African environment (0 to +8%o: Heaton et al 1987b).

Table 7. Isotope analyses of plants growing in pond EV4

Date	Lab No	Description	Location	Δ^{15}N	%N	δ^{13}C
May-98	M3061	Phragmites	Pond 4 north wall, wet	+29.6	3.0	-26.7
Jun-00	M3652	Phragmites	Pond 4 north wall, wet	+24.7	4.1	-27.2
Jun-00	M3650	Rushes	Pond 4 north wall, wet	+31.9	1.5	-25.4
Jun-00	M3651	Scirpus seeds	Pond 4 north wall, wet	+22.1	1.9	-26.9
Jun-00	M3649	Grass, kikuyu	Pond 4 north wall, dry	+29.5	1.9	-14.2
Oct-98	M3103	Eucalypt leaves	100 m east of dam 4	+12.5	1.0	-29.1
Feb-99	M3205	Eucalypt leaves	Background, 2km west	+2.9	2.5	-27.2

The effect of the water with high ^{15}N content is obvious since ammonia in the water is the sole source of nitrogen for these plants and the isotope signal of the source is passed on to the plants (Robinson et al 1998). The ^{15}N content of the plants is however considerably lower than the range of ^{15}N in water that we have analysed (+36 to +50‰). There may be more fractionation processes at work here relating to nitrogen recycling.

The Eucalyptus tree growing 100m to the east of the pond may be influenced by leakage of pond water flowing east, or some residual effect of the irrigation practices that operated even further east in the past (see section 5.8 below). *E grandis* generally has deep roots and it can be expected that this particular tree will draw deep water and therefore sample events of a

decade or more ago. The lower ^{15}N content suggests less (10–20%) polluted water influence in this tree.

The data show that vegetation sampling can be a powerful means of long term monitoring of the ^{15}N content of pollution sources. More work needs to be done regarding the relation between source and vegetation and the effect that turnover times or growth periods can have on the eventual ^{15}N content of the plant. This approach ignores the subtler isotope differences between ammonia and nitrate as nitrogen source, which seem relatively small here. It also overlooks the isotopic differences that are known to exist between different plant organs and various compounds in plants (these intra-plant effects are usually less than 5‰: Handley & Raven 1992), which are not significant in the present situation where isotope differences of 10 to 30 ‰ are considered. Attempts to use the approach to use the ^{15}N content of plant to indicate effluent from sewage sites, where the ^{15}N may be elevated by only 5 to 10‰, will require more control over intra-plant isotope variations.

5.8. Vegetation growing downstream of pond EV10

The area on which this site is located slopes towards the west. Ponds EV4 and EV10 therefore each have extensive (unlined) earth walls on their west side. In the course of time leaks have developed in these walls and various measures have been, and are being, undertaken to contain and recycle the water leaking through the walls. In October 1998 such seepage water had formed a small marsh just on the southwest side of pond EV10 (location site: Halleys Beacon). Water from this marsh showed the same characteristic high ammonia content as in the pond itself (Table 3). To monitor this effect samples of plants growing in this marsh and nearby areas were collected at that time. Green plants were considered to be growth of that season (summer 1998/9) while dry plants were assigned to the previous season (1997/8). The locations were taken as South Pump House (close to wall), Halley Beacon and Road (further west) (Figure 6). The resulting ^{15}N data provide a pattern of nitrogen leakage at this site over the few seasons. During 1999 remediation measures were taken to recycle the dam leakage water and the marsh had dried up by the time of the last sampling (June 2000).

δ^{15}N of the grasses and weeds below the wall of EV10 form a fairly consistent pattern (Figure 6.) At the pump house (just below the wall) δ^{15}N of grasses and weeds is high (+33‰) during the first summer, decreasing to +14‰ during the next two summers. This is consistent with

the fact that the first sample set was obtained while the area was flooded with ammonia-rich water and had virtually dried out during the last summer (1999/2000). This last summer was wetter than usual and the extra high rainfall would have diluted much of the remaining leakage effect. By that time the plants would be obtaining nitrogen from other sources.
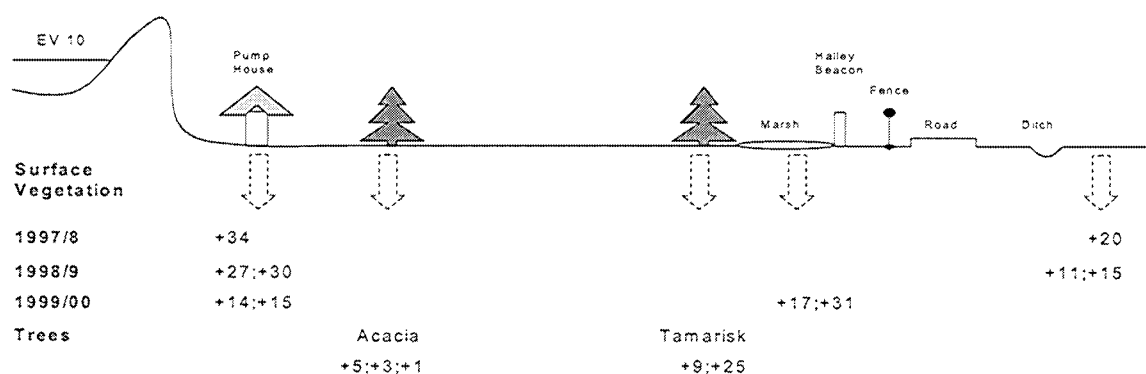

Figure 6. Cross-section along a line from pond EV10 to beyond Halley Beacon in the west showing location of the marsh, pump house and location of the trees that were sampled. $\delta^{15}N$ obtained for each season is shown for the surface vegetation.

At Halley Beacon ^{15}N of grass and weeds is variable and probably still subject to high leakage water. Across the road the ^{15}N effect in weeds is smaller and more variable. There is anecdotal evidence that there have in the past been floods from the marsh across the road into the ditch and this could have caused the increased ^{15}N content.

The Tamarisk tree close to the pump house (Figure 6) had ^{15}N content close to normal, which rose to a high +24.6 ‰ in the last summer. It would suggest that during the first season the high ammonia water had not reached the roots of this tree yet. The Acacia tree located slightly more west, maintained low $\delta^{15}N$ throughout the study period. The roots are likely to be deeper or the tree's habitat is slightly different. The Eucalypt standing on the west side of the road showed a small (+11.9‰) influence from ammonia pollution.

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Table 8. Isotope data from plants sampled west of pond EV10

Date	Lab No	Sample	Location	$\delta^{15}N$	%N	$\delta^{13}C$
Oct-98	M3104	Reeds, green leaves	South Pump House	+29.6	2.3	-
Oct-98	M3105	Reeds, dry leaves	South Pump House	+33.5	2.4	-
Jun-00	M3642	Grass, dry	South Pump House	+14.3	1.1	-14.1
Jun-00	M3643	Kakiebos, dry seeds	South Pump House	+14.9	2.8	-28.4
Feb-99	M3207	Acacia, seeds	South Pump House	+4.6	2.4	-29.1
Jun-00	M3647	Acacia, seeds	Halley Beacon	+3.2	6.7	-29.9
Jun-00	M3648	Acacia, leaves	Halley Beacon	+1.5	2.3	-31.3
Jun-00	M3645	Grass, dry	Halley Beacon	+16.9	1.4	-13.8
Jun-00	M3646	Weeds, dry leaves	Halley Beacon	+31.0	3.0	-29.1
Feb-99	M3206	Tamarisk, leaves	Halley Beacon marsh	+8.7	2.4	-
Jun-00	M3644	Tamarisk leaves	Halley Beacon	+24.6	2.9	-25.8
Oct-98	M3109	Grass, green	West road @ Halley	+10.8	0.8	-
Oct-98	M3110	Grass, dry	West road @ Halley	+19.7	0.7	-
Feb-99	M3204	Reeds, dry leaves	West road @ Halley	+14.9	1.5	-
Sep-99	M3473	Eucalyptus leaves	East road @ Halley	+11.9	2.0	-28.7

Overall these samples indicate the influence of ammonia seepage on the plants that are growing below the pond wall. The different pattern exhibited by short living plants and trees with roots is quite noticeable.

6. MMC NELSPRUIT

In this plant manganese ore is dissolved in sulphuric acid, treated and the metal subsequently recovered by electrolysis (Figure 7). Large amounts of ammonia are being used to neutralise the acid and adjust the pH of the electrolyte to about 11. pH control is critical for the efficiency of the electrolysis process and the quality of the metal product. A large part of the water consumption of the plant is used for washing the floor of the electrolysis hall and for cleaning of the metal product. Wastewater from the site is treated in the Effluent Plant (cheap method) and in the more efficient MVR plant (more expensive process).

The plant is located on a steep slope. Water draining the site is intercepted in a few seepage channels a few meters deep at the lowest end of the plant. This water is acid, contains grams per litre quantities of ammonium and small amounts of nitrate. The origin of the nitrate is

uncertain, since no obvious nitrification occurs anywhere on the site. The low pH of the drainage water suggests a major contribution from acid wash water.

The plant is 30 years old and increasingly stricter environmental regulations motivate the operators to refine the water management in order to improve the quality of the effluent from the plant. An audit of NO_3 and NH_4 compounds in the various water streams of the plant was done in 1998 and indicated the presence of some nitrate in the cooling water for the cell house as well.

The water flow in the plant is rather complex (Figure 7). The available data are not sufficient to follow the flow of either ammonia or nitrate through the process: there seem to be too many variables. In particular is it difficult to establish the response time of different units of the system to process changes, of which there are many. The sampling was not frequent enough to establish the dynamics of the flow system. The chemical and isotope data (Table 9) show the main features of the nitrogen flow through the plant.
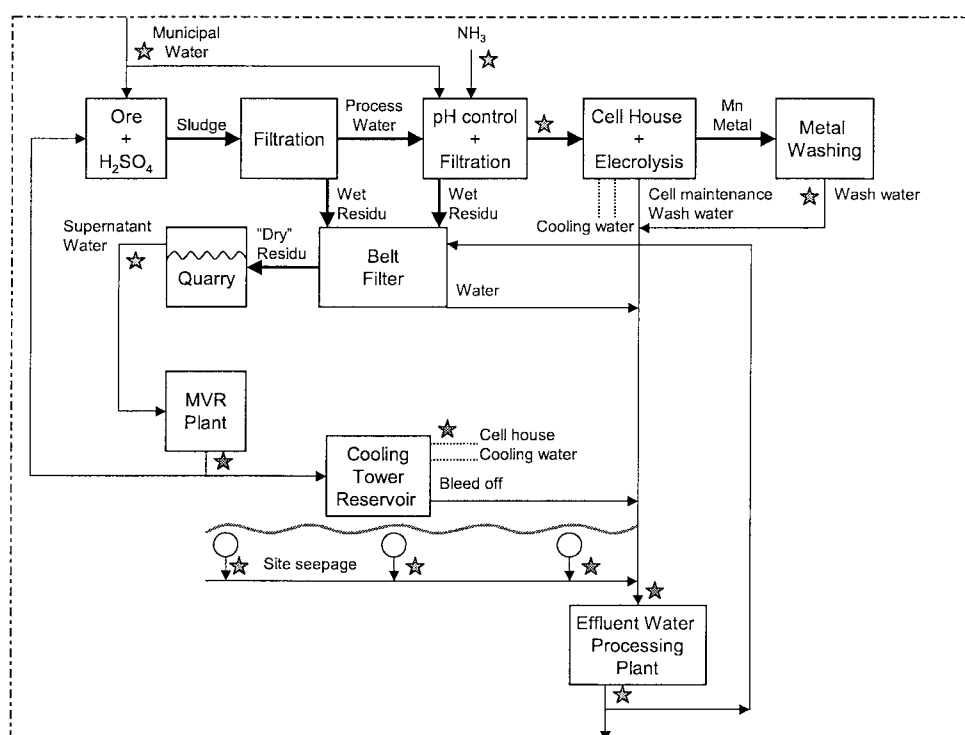

Figure 7. Water flow diagram for the electrolysis plant in Nelspruit. Thick lines indicate metal flow; thin lines indicate water flow; stars indicate sample points.

Table 9. Isotope data from the manganese electrolysis plant

SAMPLE	Date	Lab No	pH	Ammonia mgN/L	Ammonia $\delta^{15}N$	Nitrate mgN/L	Nitrate $\delta^{15}N$	Nitrate $\delta^{18}O$
Municipal water	04/98	E1154	7	<0.1	-	0.3	-	-
Ammonia input solution to the plant	04/98	E1143	-	130 000	-	-	-	-
Process water	11/98	E1228	8	24 000	-	4.5	-	-
Electrolysis solution	04/98	E1155	-	21 900	-	-	-	-
Cooling tower water	04/98	E1151	5	257	+8.7	184	-17.1	-
	11/98	E1229	5	482	+9.8	273	-17.5	+22.2
Metal wash water	04/98	E1145	1	23 800	-	1.2	-	
Quarry water: input to MVR plant	11/98	E1230	8	8100	+16.3	23	-	
Output from MVR	11/98	E1232	10	185	-3.3	<0.1	-	
Seepage below ground		E1146	3	2980	+12.0	35	-2.1	-
	04/98	E1147	2	12400	-	17	-	+21.3
		E1148	3	11500	-12.2	20	+3.5	-
Effluent plant input	04/98	E1149	4	1430	+13.9	42	+6.3	-
Effluent plant output	04/98	E1152	12	304	+23.3	33	-13.4	-

Points that are relevant for the purposes of this project are where isotope ratios change significantly through a specific process and there is no mixture with other water:

- Input water into the main effluent treatment plant has $\delta^{15}N$ (NH_4)=+13.9 and output of +23.3‰. Ammonia removal in this plant is done by increasing the pH of the water and blowing the resulting NH_3 into the atmosphere with air. The isotope enrichment during this process is +9.4‰ for a concentration reduction of 4.7X. As Rayleigh fractionation this implies a fractionation, ε, of only -6.3 for the ammonia release and suggests that the fractionation is related to the gaseous removal of NH_3 and not the NH_3-NH_4 relation; in which case larger fractionations would have occurred. The large change of ^{15}N content of the nitrate through this plant (from +6.3 to –13,4‰) for a concentration reduction for only 42 to 33 mgN/L is unexpected, since the plant is not designed for nitrate treatment at all.

- Reduction of ammonia by a factor 40 in the MVR plant changes the ^{15}N value by –19.6‰. Details of the process in this plant are not available.

- Production of nitrate in water at this site probably occurs in the cooling tower water reservoir. The cooling effect is reached by circulating water through a porous medium, well ventilated (i.e. oxygen rich), in the dark. These are all conditions favourable for bacteria to settle and grow. The isotope fractionation of -26 ‰ between nitrate and

ammonia is of a magnitude that can be expected for such a process where ^{14}N will be more reactive than ^{15}N would be (Handley & Raven 1992). The ^{18}O of nitrate is identical of that of atmospheric oxygen (+23) and suggests that atmospheric oxygen is the sole source of oxygen for nitrification. This is contrary to the situation in groundwater where generally the ^{18}O content of the nitrate suggests that oxygen from the water and from atmosphere are both used (Kendall 1998).

7.   AECI

This large chemical factory houses a plant that produces an effluent containing nitrate and organic solvents both in the gram per litre range. Isotope analysis of the wastewater showed that the ^{15}N value of the nitrate is close to that of atmospheric nitrogen.

Sample E1141; $\delta^{15}N(NO_3)=+1.2$ ‰AIR.

This waste water reflects the mean ^{15}N content of the product and is close to that of the ultimate source, atmospheric nitrogen.

In 1983 Heaton (pers. comm.) established that the input and output of the ammonia plant at AECI are both within –4 and –6 ‰AIR. The difference from AIR is attributable to the fractionation during nitrogen separation from atmospheric air.

The near-atmospheric ^{15}N content of these samples can be expected from industrially produced nitrogen since the high temperature of the Haber-Bosch ammonia production process precludes any significant fractionation from air nitrogen. At higher temperatures the fractionation between components in a chemical reaction tends to decrease. It also appears that little, or no, fractionation occurred during subsequent processing of the waste water. Work in the plant does not involve gaseous nitrogen compounds and nitrogen isotope fractionation will therefore be small in most processes.

This site did not yield data that are of use for this study.

8. CONCLUSIONS

- Large isotope fractionation of $^{15}N/^{14}N$ of ammonia or ammonium can occur during a phase change between the gaseous and dissolved states. In an industrial process involving phase changes the first fraction of a product, or the residual after most of the reaction has been completed can therefore have very different $\delta^{15}N$ from the original nitrogen source.

- Examples of isotope fractionation during phase changes in industrial systems were found during ammonia removal from a coke oven gas stream with water, during steam induced ammonia gas transfer from ammonia liquor to an acid bath and during ammonia removal from water by air blowing off an alkaline solution.

- Isotope analyses from industrial plants are difficult to interpret quantitatively in terms standard Rayleigh fractionation concepts. The systems frequently work on a batch basis and do not represent the isotopic stationary state that Rayleigh theory would predict for continuously flowing processes. Operating conditions in the industrial plants that were sampled are not always stationary and the inertia in the processes not always known.

- The ^{18}O values of nitrate produced in these industrial processes appear to be higher than can be explained by the usual sources of atmospheric oxygen and oxygen from water that are known in natural surface and ground water.

- The anomalously high ^{15}N values in waste water will persist in waste ponds and during underground flow.

- Ammonia rapidly oxidizes to nitrate in South African groundwater, during which relatively little isotope fractionation occurs. This enables the use of the anomalous ratio as water tracer.

- Vegetation will reflect the ^{15}N content of the ammonia or nitrate that supports the plant. The root system and the longevity of the plant will determine the isotope composition of the plant.

- Long term monitoring of the nitrogen isotope composition seems feasible with the use of suitable plants.

Nolte of Iscor for this work at times when he had many other matters on his mind. We hope that this study can be a contribution towards solving the problems that environmental managers have to contend with in the situations that they have inherited. We thank Dr Tim Heaton for constructive comments and for the use of some of his earlier data. Financial support from the CSIR and the IAEA is acknowledged.

REFERENCES

[1] BUTLER, M. and VERHAGEN, B.T., 1997. Environmental isotopic tracing of water in the urban environment of Pretoria, South Africa. In: *Groundwater in the Urban Environment: Problems, Processes and Management*, edited by Chilton, P.J. Balkema, Rotterdam, p. 101–106.

[2] HANDLEY, L. L. and RAVEN, J. A. 1992. The use of natural abundance of nitrogen in plant physiology and ecology. *Plant, Cell & Environm.* 15:965–985.

[3] HEATON, T.H.E., TALMA, A.S., and VOGEL, J.C., 1983. Origin and History of Nitrate in confined groundwater in the Western Kalahari. *J Hydrol* 62:243–262.

[4] HEATON, T.H.E., 1984. Sources of the nitrate in phreatic groundwater in the western Kalahari. *J Hydrol* 67:249–259.

[5] HEATON, T.H.E. and COLLET, G.M., 1985. The analysis of $^{15}N/^{14}N$ ratios in natural samples, with emphasis on nitrate and ammonium in precipitation. CSIR report no 624, Pretoria.

[6] HEATON, T.H.E. 1985. Isotopic and chemical aspects of nitrate in the groundwater of the Springbok Flats. *Water SA* 11:199–208.

[7] HEATON, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem Geol* 59:87–102.

[8] HEATON, T.H.E., 1987a. $^{15}N/^{14}N$ ratios of nitrate and ammonium in rain at Pretoria, South Africa. *Atmos Envir* 21(4):843–852.

[9] HEATON, T.H.E., 1987b. The $^{15}N/^{14}N$ ratios of plants in South Africa and Namibia: relationship to climate and coastal/saline environments. *Oecologia* 74:236–246.

[10] HEATON, T.H.E., SPIRO, B. and ROBERTSON, S.M.C., 1997. Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition. *Oecologia* 109:600–607.

[11] IAEA 1992. Statistical Treatment of Data on Environmental Isotopes in Precipitation. Technical Reports Series. International Atomic Energy Agency, Vienna. 781p.

[12] KENDALL, C. 1998. Tracing nitrate sources and cycles in catchments. In: *Isotope Tracers in Catchment Hydrology*, edited by Kendall, C. and McDonnel, J. Elsevier, Amsterdam, p. 519–576.

[13] KIRSHENBAUM, I., SMITH, J.S., CROWELL, T., GRAFF, J. and MCKEE, R. 1947. Separation of the nitrogen isotopes by the exchanges reaction between ammonia and solutions of ammonium nitrate. *J Chem Phys* 15:440–446.

[14] KREITLER, C.W. 1975. Determining the source of nitrate to groundwater. Univ Texas Bur Econ Geol Inv Rep No 83, 57pp.

[15] ROBINSON, D., HANDLEY, L.L. and SCRIMGEOUR, C.M., 1998. A theory for $^{15}N/^{14}N$ fractionation in nitrate-grown vascular plants. *Planta* 205:397–406.

[16] Tredoux, G. 1993. A preliminary investigation of the nitrate content of groundwater and limitation of the nitrate input. Water Research Commission, Report 368/1/93, Pretoria, 76pp.

The influence of artificial recharge for controlling land subsidence on groundwater quality in Shanghai area

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Abstract

Shanghai City is supplied mainly by river water, therefore, quality of tap water is not good enough. In this connection it has been decided to exploit high quality groundwater from deep confined aquifer. This drinking water will be supplied separately form the normal tap water. Groundwater in Quaternary aquifers in Shanghai area up to date was exploited mainly for industrial use. Since 1965, the artificial recharge of aquifers using tap water has been carried out in order to control land subsidence. The influence of artificial recharge on groundwater quality thus should be assessed if groundwater will be used as drinking water. For this purpose, isotope techniques, especially tritium measurement, were used in combination with ICP-MS trace element analyses, and GC/MSD analyses for natural organic tracers. 36 samples from production and injection wells, 2 tap water samples, 3 samples from Huangpu River and Yangtze River were taken in 1998 and 1999. Results obtained show, that tritium content is sensitive to presence of artificially recharged water. Some major chemical constituents, such as sulphate and bicarbonate, some volatile organic compounds, such as chloroform, bromo-dichloro-methane and 1,2-dichloro-ethane, are also good for tracing recharge water. Some trace elements in water samples, such as Li, Cr, which may derived from the base rock, show relatively high content in deep groundwater. While some other trace elements, such as Pb, Mn and Ni, are obviously from the wastewater. They are characteristic for surface water. Based on results obtained for these available indicators, it was concluded, that a few production wells of the IV layer, which is the major layer for drinking water exploitation, are in the sphere of influence of injection wells.

1. INTRODUCTION

Shanghai is the industrial, financial, trade center and the largest city of China with an area of 6,186 km^2 and a population of 14 million. It is situated on the coast of the East China Sea, at the mouth of the Yangzte River. It is developing along the last tributary of the Yangtze River, the Huangpu River, which serves as raw water source for a substantial part of water supply to the City (Fig. 1).

Groundwater of Quaternary aquifers up to date was exploited in Shanghai mainly for industrial use. Since the beginning of the 1960's, the artificial recharge of aquifers through wells using tap water has been carried out in order to control land subsidence. The rapid industrial development and low treatment level of wastewater have led to serious deterioration of water quality of the Huangpu River. In this connection it has been launched a vast scheme for wastewater treatment. At the same time it has been decided to exploit high quality groundwater from deep confined aquifers as drinking water, which will be supplied separately from the normal tap water. If groundwater will be used as drinking water, the influence on groundwater quality during more than 30 years of artificial recharge must be assessed.

In this research project, isotope techniques, especially tritium measurement, are used in combination with ICP-MS trace element analyses and GC/MSD analyses for organic tracers to identify the existence of the water artificially recharged in the aquifers, and to evaluate the groundwater quality in the near future.

Main attention of the work plan was paid to find out some available natural tracers, which could be used for recognizing the artificially recharged Huangpu River water in confined aquifers. This is a final report, in which main hydrogeological conditions of the Shanghai City are introduced, and the main results obtained are presented.
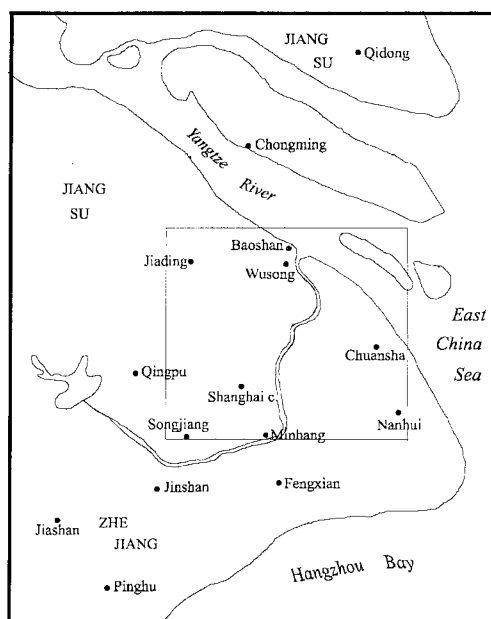
Fig. 1   Sketch map of the investigated area.

2. HYDROGEOLOGICAL CONDITIONS

Shanghai City is located in the front of the Yangtze River delta, where thick Quaternary loose deposits are widespread. Groundwater is exploited from Quaternary aquifers mainly for industrial use. There are five confined aquifers [1,2].

Above 60-70 meters deposits consist of silt clay of littoral - river mouth facies. It is the first confined aquifer, which is shallow, relatively thin and has limited productivity and low water quality.

The second and the third confined aquifers are at the depth of 60-100 meters and 100-150 meters, respectively. Lithologically, they are deposits of littoral - river mouth facies. Generally speaking, fresh water could only be found in northern part of the Shanghai City. In the rest part groundwater from these two aquifers is brackish or salt. The close hydraulic relationship between these two aquifers is observed. At the first stage of exploitation of groundwater, the second and the third aquifers were main layers exploited intensively for industry use. Since 1965 they are main layers being artificially recharged through drill holes.

Underlying the fourth and the fifth confined aquifers of fluvial deposits are at the depth of 150-250 meters and below 250 meters, respectively. Distribution of the fifth confined aquifer is mainly controlled by the geomorphology of the base rock. Groundwater of these two aquifers is fresh, except some limited areas, where brackish or salt water could be found.

3. LAND SUBSIDENCE IN SHANGHAI

Land subsidence is mainly caused by exploitation of groundwater in loose deposits. At the beginning of 1960's Shanghai and Tianjin were only known in China as cities with remarkable land subsidence [3].

Shanghai City is built on loose Quaternary deposits, thickness of which is up to 300 meters. Shanghai began to exploit groundwater in 1860 and the first drill hole for groundwater exploitation was made in 1910 [4]. Since then, rapidly developing industry took more and more groundwater. Subsidence of benchmarks in the urban district was observed in 1936. Therefore, 101 observation points were arranged in 1938 and a mean value of subsidence of 2.57 cm in urban district was observed [3]. In 1950 the annual exploitation of groundwater was 90 millions m^3. In 1963, it was 200 millions m^3. There was a marked drop in groundwater level. The annual value of land subsidence increased in this period from 3.5 cm to 10.5 cm. A maximum accumulated subsidence of 263 cm for the benchmarks was observed in the center of the Shanghai City in 1965 [3].

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The harmfulness of land subsidence is obvious.

In order to control land subsidence, a series of measures were adopted since the beginning of the 1960's. These measures included:

- Reducing the groundwater exploitation;

- Adjusting layers of exploitation;

- Artificial recharge of groundwater aquifers.

Since 1965, on the one hand the main exploitation layers were readjusted, the IV and V confined aquifers became major exploitation layers. On the other hand an intensive artificial recharge of the II and III confined aquifers was carried out. At the same time the amount of groundwater exploitation decreased 50%. In the urban district it was allowed to take groundwater of only 10% of the previous amount. For the time being annual amount of artificial recharge is about 20 millions m³. The mean value of subsidence was 10.5 cm per year in 1959, and it decreased to 2.2 cm in 1965, and then to 1 cm per year. Since 1966 through 1990, mean accumulated value of subsidence was 5.7 cm [3]. Subsidence of two benchmarks in the period of 1921 - 1990 is shown in Fig. 2 [3,4]. Benchmark No. 0-264 is located in the center of the urban district, and No. 0-301 is in its west part. It can be seen clearly that the measures adopted are effective and at the end of 1960's the land subsidence in Shanghai was brought under control.
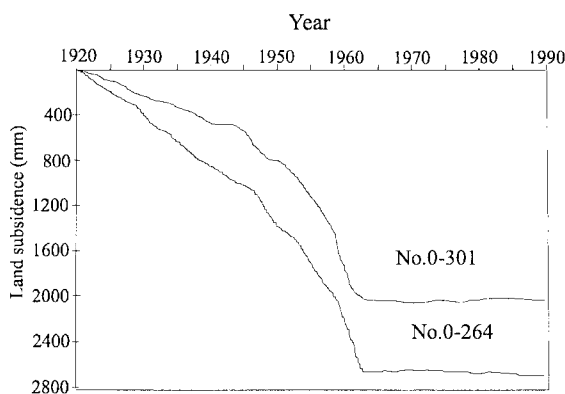

Fig. 2   Land subsidence of benchmarks in urban district
in the period of 1921-1990   (After Yan, L. 1980 and 1992).

In the course of intensive artificial recharge of aquifers through drill holes, groundwater quality has been changed because of mixing of groundwater with admitted water. In the case of Shanghai City recharge water is tap water, which is pumped from the Huangpu River. Chemical constituents of the Huangpu River water are different from normal groundwater. In comparison with normal groundwater, Huangpu River water has lower Cl^- content and low degree of mineralization, but higher content of some contaminants. Besides, the isotope composition of groundwater, especially tritium content of groundwater, must be changed during more than 30 years of artificial recharge.

4. ISOTOPE COMPOSITION OF GROUNDWATER

Systematic studies of the isotope composition of groundwater were carried out in 1980's by the Institute of Geochemistry in cooperation with the Geological Survey of the Shanghai City [5]. Main results are as follows.

- Mean tritium content of rainwater in the period of 1979-1980 was 30 TU. The tritium content of the Yangtze River water was 40 TU in 1980 - 1981, while that of the Huangpu River was 27 TU, which was close to the level of local precipitation. Besides, the surface seawater at the station N28°, E127° was 7.7 TU in May 1978.

- The tritium content of water from shallow wells (several meters depth) was very close to that of local rainwater, implies that the unconfined aquifer is recharged directly by rain water.

Groundwater from the first confined aquifer was less than 2 TU (the detect limit). It infers a slow infiltration and long turnover time for water in this aquifer. Groundwater from the II and III confined aquifers had also very low tritium content. The only exception was water from some drill holes in Gaoqiao near the Yangtze River, where groundwater from the III confined aquifer contained 6-8 TU in 1980. It might be caused by an intensive exploitation of water from the III aquifer in this area. According to statistical data the amount of water exploited from the II aquifer in the period of 1963-1981 in Gaoqiao was 0.12 million tons, while that from the III aquifer was 120 million tons. The chemistry of groundwater of the III aquifer has also been changed due to intensive pumping of groundwater. The hydrochemical type of HCO_3 - Ca-Na or HCO_3-Cl - Ca-Na was replaced gradually by a relatively low Cl⁻ content type of HCO_3-Ca·Mg in Gaoqiao area. Groundwater from the IV and V confined aquifers is generally tritium free.

- The equation of local meteoric water line obtained in the year of 1979 - 1980 is $\delta^2H = 8.2 \, \delta^{18}O + 15.8$. The mean δ^2H value of the Huangpu River was -32.5, while that of the Yangtze River water was -61.8 ($\delta^{18}O = -8.8$) because of the "continental effect".

- Groundwater samples from the II confined aquifer lay on a straight line through the origin on the $\delta^2H - \delta^{18}O$ plot (Fig. 3). Its equation was $\delta^2H = 6.9 \, \delta^{18}O + 0.6$, which is quite different from the local meteoric water line, but was identical with the Yangtze River - seawater mixing line: $\delta^2H = 6.8 \, \delta^{18}O$. This is a clear message of mixing of the Yangtze River water with seawater.
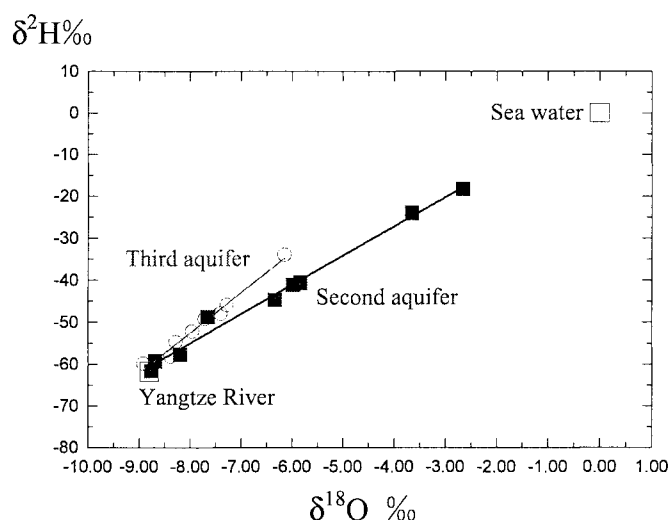
Fig. 3 $\delta^2H - \delta^{18}O$ plot of groundwater of the II and III aquifers.

Groundwater in coastal plains contains more heavy isotopes because of mixing with seawater. Fig. 4 is a sketch map of isolines for δ values in groundwater of the II confined aquifer, which is recharged by the Yangtze River in the north and mixed with seawater from the south. Water sample from a drilling hole located very close to the Yangtze River had $\delta^2H = -59.3$, $\delta^{18}O = -8.69$, which are actually the mean values of water in the Yangtze River. The δ values of groundwater decrease northward. The same distribution should be observed in mineralization and chemical types of groundwater.

The isolines for groundwater in the III confined aquifer have a similar pattern as for those in the II aquifer, but δ values for groundwater samples from the south-western part are lower than those from the south-eastern part. It seems that for the III confined aquifer there is another fresh water source from the southwest of the Shanghai City.

- The δ values for groundwater in the IV aquifer are more or less identical, but there is still a little difference between samples from the old stream channel of the Yangtze River in the north and those of the Qiantangjiang water system in the south.

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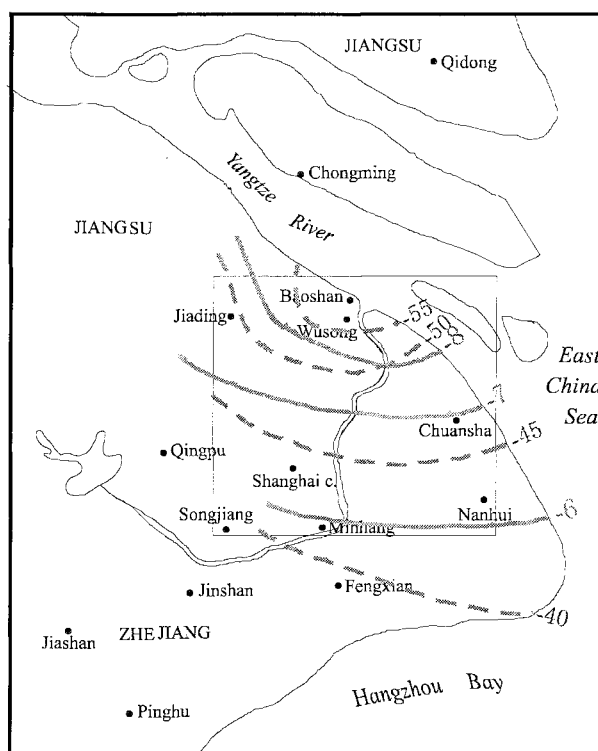
Fig. 4 δ value isolines of groundwater from the II aquifer
(lines of deshes are δ^2H isolines, others are $\delta^{18}O$ isolines).

5. SAMPLING IN 1998 AND 1999

Groundwater and river water samples were collected in 1998 and 1999. Main attention was paid to find out some available natural tracers, which could be used for recognizing artificially recharged Huangpu River water in confined aquifers. As the IV confined aquifer was fixed in advance as the major layer for drinking water exploitation, it will be a focal point of this research. All samples are listed in Table 1 and sampling sites are illustrated in an attached sketch map.

TABLE 1. WATER SAMPLES COLLECTED IN 1998 AND 1999 IN SHANGHAI CITY

Number	Type	Layer	Function	Water Temperature
SH/-5	Groundwater	IV	Injection well	14°C
SH/-7	Groundwater	IV	Injection well	13°C
SH/-15	Groundwater	III	Injection well	14°C
SH/-17	Groundwater	II	Injection well	13°C
SH/-19	Groundwater	IV	Injection well	21°C
SH/-20	Groundwater	II	Injection well	14°C
SH/-21	Groundwater	III	Injection well	10°C
SH/-41	Groundwater	II	Injection well	9°C
SH/-42	Groundwater	III	Injection well	14°C
SH/-43	Groundwater	II	Injection well	13.5°C
SH/-44	Groundwater	IV	Injection well	13°C
SH/-1	Huangpu River water			
SH/-2	Huangpu River water			
SH/-3	City tap water			
SH/-4	Yangtze River water			
SH/-52	City tap water			

SH/-6	Groundwater	IV	Production well	19°C
SH/-8	Groundwater	IV	Production well	22°C
SH/-9	Groundwater	IV	Production well	24°C
SH/-10	Groundwater	IV	Production well	24°C
SH/-11	Groundwater	IV	Production well	24°C
SH/-12	Groundwater	IV	Production well	21°C
SH/-13	Groundwater	IV	Production well	24°C
SH/-16	Groundwater	IV	Production well	24°C
SH/-22	Groundwater	IV	Production well	21°C
SH/-27	Groundwater	IV	Production well	24°C
SH/-28	Groundwater	IV	Production well	24°C
SH/-31	Groundwater	IV	Production well	25°C
SH/-32	Groundwater	IV	Production well	24°C
SH/-33	Groundwater	III	Production well	23°C
SH/-35	Groundwater	IV	Production well	24°C
SH/-36	Groundwater	IV	Production well	23°C
SH/-38	Groundwater	III	Production well	22°C
SH/-39	Groundwater	V	Production well	25°C
SH/-40	Groundwater	V	Production well	25°C
SH/-45	Groundwater	II	Production well	19°C
SH/-46	Groundwater	III	Production well	23°C
SH/-47	Groundwater	III	Production well	25°C
SH/-48	Groundwater	II	Production well	20°C
SH/-49	Groundwater	IV	Production well	24°C
SH/-50	Groundwater	III	Production well	19°C

Together with groundwater samples from different aquifers two Huangpu River water samples and one sample from the Yangtze River were collected for reference of recharged water, even though the chemistry and the isotope composition of river water could be changed during these decades. As the city water supply is organized mainly on pumping water from the Huangpu River, tap water sample SH/-3 and SH/-52 were actually the Huangpu River water after treatment.

6. MAJOR CHEMICAL CONSTITUENS OF WATER SAMPLES

The chemical constituents of recharge water may differ sufficiently from original groundwater. Therefore, the major ions could first be indicators of existence of recharge water in groundwater aquifers. The major chemical constituents of water samples collected in 1998 and 1999 are listed in Table 2.

TABLE 2. MAJOR CHEMICAL CONSTITUENTS AND TRITIUM IN WATER SAMPLES

No	Na^+	K^+	Ca^{+2}	Mg^{+2}	Cl^-	SO_4^{-2}	HCO_3^{-2}	pH	$^3H(TU)$
SH/-5	13	8.6	57.4	19.8	52.5	86.7	137	7.6	7.3
SH/-7	9	6.6	37.4	15.3	45.5	63.3	88.9	6.8	6.1
SH/-15	57	5.8	34.7	13.1	45.5	64.5	73.8	7.2	7.7
SH/-17	13	8.2	56.4	28.6	70.0	77.5	185	7.0	6.1
SH/-19	22	7.5	48.0	19.9	66.5	74.6	149	6.7	9.3
SH/-20	9	6.1	34.5	13.4	46.2	69.8	73.8	6.9	9.4
SH/-21	11	10	64.8	22.0	50.8	113	181	6.8	7.8
SH/-41	9.0	8.6	53.0	20.4	50.8	94.8	130	6.90	6.9
SH/-42	26	11	53.5	19.4	82.3	74.6	116	6.65	7.8
SH/-43	76.4	8.3	71.0	20.3	254	83.9	176	6.65	8.5
SH/-44	36.0	5.8	64.5	11.6	120	90.1	110	6.25	9.6

SH/-1	34	11	47.1	14.8	63.0	72.6	148	6.5	7.0
SH/-2	32	12	58.1	12.8	68.3	72.6	164	7.4	7.8
SH/-3	11	8.0	40.4	14.1	43.8	81.9	61.5	6.7	5.4
SH/-4	20	3.4	31.1	10.2	8.75	27.0	92.3	7.4	8.9
SH/-52	8.5	4.8	37.9	18.3	59.9	28.0	88.1	6.65	9.4
SH/-6	50	2.6	50.8	25.5	35.0	28.2	388	7.6	5.2
SH/-8	57	3.0	53.9	28.8	31.5	23.8	472	7.5	1.5
SH/-9	104	2.2	53.9	26.0	228	72.6	417	7.6	0.1
SH/-10	82	1.8	40.4	21.1	128	14.1	431	7.3	1.1
SH/-11	79	2.0	42.9	20.9	98.0	16.1	441	7.7	1.0
SH/-12	46	3.0	64.3	37.0	68.3	6.05	444	7.6	1.4
SH/-13	8	5.9	34.2	14.8	46.2	74.6	78.6	7.5	7.8
SH/-16	57	2.3	46.3	24.8	20.0	8.07	468	7.7	0.7
SH/-22	68	2.3	37.9	17.2	42.0	11.3	435	7.3	1.0
SH/-27	8.0	7.6	71.5	19.8	21.7	28.7	335	6.87	2.8
SH/-28	53	1.9	37.0	14.8	9.46	19.6	383	7.20	1.1
SH/-31	9.2	5.4	62.3	24.5	241	37.3	383	7.66	2.0
SH/-32	92	2.8	44.3	15.3	151	22.0	465	7.36	0.5
SH/-33	3.7	6.9	68.2	19.4	45.5	22.2	383	7.22	1.2
SH/-35	58	3.6	58.9	28.1	40.3	16.1	462	7.30	2.2
SH/-36	4.4	5.1	68.3	24.2	7.0	10.9	458	7.48	1.3
SH/-38	103	7.5	198	56.2	677	9.32	417	7.62	3.7
SH/-39	103	4.4	130	7.15	357	139	465	7.31	3.0
SH/-40	86	3.6	42.9	17.4	91.1	24.2	465	7.30	2.0
SH/-45	65.0	7.8	44.7	19.8	67.3	24.8	428	7.20	2.0
SH/-46	29.5	5.4	54.0	17.1	41.1	3.11	343	6.65	1.5
SH/-47	104	10	49.6	18.3	164	122	482	7.25	2.5
SH/-48	78	8.9	68.4	24.8	180	16.8	387	7.20	1.1
SH/-49	27.9	5.7	67.1	18.2	54.2	28.0	389	7.00	0.9
SH/-50	86.1	9.9	112	22.8	276	21.7	441	7.30	0.9

The chloride ion usually serves as major tracer for recognizing the origin of water bodies. Li Qinfen et al (1992) has noticed the desalinating process of chloride content in confined aquifers in Shanghai area due to artificial recharge [6]. We found that although chloride content in deep confined aquifers is higher than that in surface water, but the difference in chloride content between water samples from production wells and injection wells is not so obvious. As it can be seen from data in Table 3, that the ion Na^+ is not sensitive, but HCO_3^{-2} and SO_4^{-2} are indicative for water from deep confined aquifers. Besides, the pH value of water samples from production wells is higher than that from injection wells.

TABLE 3. MAJOR CHEMICAL CONSTITUENTS IN GROUNDWATER SAMPLES (MG/L)

Type of water	Na^+	K^+	Ca^{+2}	Mg^{+2}	Cl^-	SO_4^{-2}	HCO_3^{-2}	pH
Overall injection wells (11 samples)	25.6	7.86	52.3	18.5	80.5	81.2	129	6.9
Overall production wells (25 samples)	33.3	4.86	64.1	22.5	125	32.0	410	7.3

All water samples are illustrated in Fig.1, in which bicarbonate content is plotted vs. sulphate content. As it can be seen from Fig.1, dots of injection wells are concentrated in an area of high sulphate–low bicarbonate content, while those from productive wells are distributed in an area of low sulphate–high bicarbonate content. Therefore, some major chemical constituents, such as sulphate

and bicarbonate, are indicative for the presence of water artificially injected into aquifers. Groundwater of deep layers has sulphate content less than 40 mg / L, and bicarbonate content more than 330 mg / L. The injected river water has sulphate content more than 60 mg / L, and bicarbonate content less than 180 mg / L. Exceptions are water samples SH/-47 and SH/-39 which were collected from two pharmaceutical factories. They show high bicarbonate content, and high sulphate content instead of low sulphate content for normal production wells. Perhaps it may be caused by pollution in limited area. Water sample SH/13 is also from a productive well, but it has low content of bicarbonate and high content of sulphate that is typical for injection wells. It is obvious that the groundwater of the IV layer near the sampling site SH/13 is influenced by artificially recharged water. We will discuss this problem in detail later.
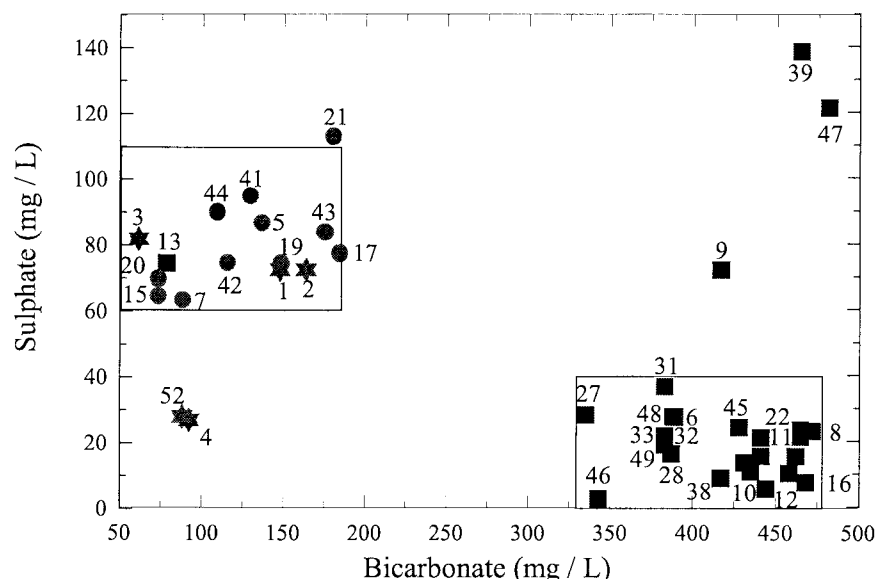

Fig.5. Bicarbonate vs. sulphate plot for all water samples collected in 1998 and 1999. Squares are water samples from production wells. Circles are those from injection wells. Hexagons are surface water samples.

7. VOLATILE ORGANIC COMPOUNDS (VOC) IN WATER SAMPLES

Some organic compounds may serve as indicator of presence of recharge water in groundwater aquifers. Benzene, toluene, ethylene, xylene (BTEX) and other volatile organic compounds (VOC) in river water are mainly derived from industry wastewater. This kind of organic contaminants should be free in original groundwater.

Water samples were collected without stirring and bubbling, in separated plastic bottles of 100 ml volume. Laboratory analysis was conducted by Tekmar 3000 Purge & Trap Concentrator interfaced with HP-5972 GC-MSD in State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The results obtained are listed in Table 4.

There are 6 items presented in Table 4, but not all of them can be practically used as indicators of presence of recharge water in groundwater aquifers. First of all, chloroform, which is produced mainly in the course of chlorination, is an useful indicator. Chloroform in Huangpu River water has a concentration of several µg /L, while it is almost free in original groundwater. The content of chloroform in water samples of injection wells are 1-3 µg /L. Some other VOC, such as bromodichloro-methane and 1,2-dichloro-ethane, are also good for tracing recharge water.

The chloroform concentration of all water samples was plotted vs bicarbonate content in Fig. 6, in which all symbols are the same as in Fig.5. It can be seen from this figure, that all water samples from injection wells have rather high chloroform concentration, which is undoubtedly admitted together with recharge water. The highest values of chloroform concentration, 23 µg/L and 18 µg/L are in water samples, taken from injection wells of the III and IV confined aquifers (SH/15 and SH/7) in the same cotton mill.

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TABLE 4. VOC CONCENTRATION IN GROUNDWATER SAMPLES (μ G /L)

No	Chloroform	Bromo-dichloro-methane	1,2-dichloro-ethane	Hexane	Benzene	Toluene
SH/-5	2.62	0.64	0.29	nd*	nd	0.05
SH/-7	18.7	6.56	0.30	nd	nd	nd
SH/-15	23.2	6.41	0.13	nd	nd	0.03
SH/-17	9.42	0.94	1.01	nd	nd	nd
SH/-19	7.53	1.97	0.69	nd	nd	nd
SH/-20	15.7	4.14	0.12	nd	nd	nd
SH/-21	2.45	0.27	1.23	nd	nd	0.02
SH/-41	1.19	0.27	0.16	nd	nd	0.02
SH/-42	3.02	0.08	5.31	nd	nd	0.03
SH/-43	1.82	1.82	0.53	nd	nd	nd
SH/-44	1.21	0.61	0.53	nd	nd	nd
SH/-1	1.51	nd	0.27	0.25	0.24	0.05
SH/-2	1.81	nd	5.23	0.27	0.56	0.08
SH/-3	4.78	nd	0.72	nd	0.06	0.08
SH/-4	0.32	nd	0.35	nd	nd	nd
SH/-52	1.51	1.21	0.53	nd	nd	nd
SH/-6	0.08	nd	nd	nd	nd	nd
SH/-8	0.31	0.20	nd	nd	nd	nd
SH/-9	nd	nd	nd	nd	nd	nd
SH/-10	nd	nd	nd	nd	nd	0.02
SH/-11	nd	nd	nd	nd	nd	0.02
SH/-12	nd	nd	nd	nd	nd	nd
SH/-13	1.55	0.53	0.22	nd	nd	0.03
SH/-16	0.49	0.24	nd	nd	nd	nd
SH/-22	0.06	nd	010	nd	nd	nd
SH/-27	nd	nd	nd	nd	nd	nd
SH/-28	nd	nd	nd	nd	0.04	0.02
SH/-31	0.02	nd	nd	nd	0.03	nd
SH/-32	nd	nd	nd	nd	0.02	nd
SH/-33	nd	nd	nd	nd	nd	0.04
SH/-35	nd	nd	nd	nd	0.02	nd
SH/-36	nd	nd	nd	nd	0.02	nd
SH/-38	nd	nd	nd	0.26	0.25	nd
SH/-39	nd	nd	nd	nd	nd	nd
SH/-40	nd	nd	nd	nd	nd	nd
SH/-45	nd	nd	nd	nd	nd	nd
SH/-46	nd	nd	nd	0.69	1.50	0.70
SH/-47	0.45	nd	nd	nd	0.50	0.35
SH/-48	nd	nd	nd	nd	nd	nd
SH/-49	nd	nd	nd	0.13	nd	nd
SH/-50	nd	nd	nd	0.52	nd	nd

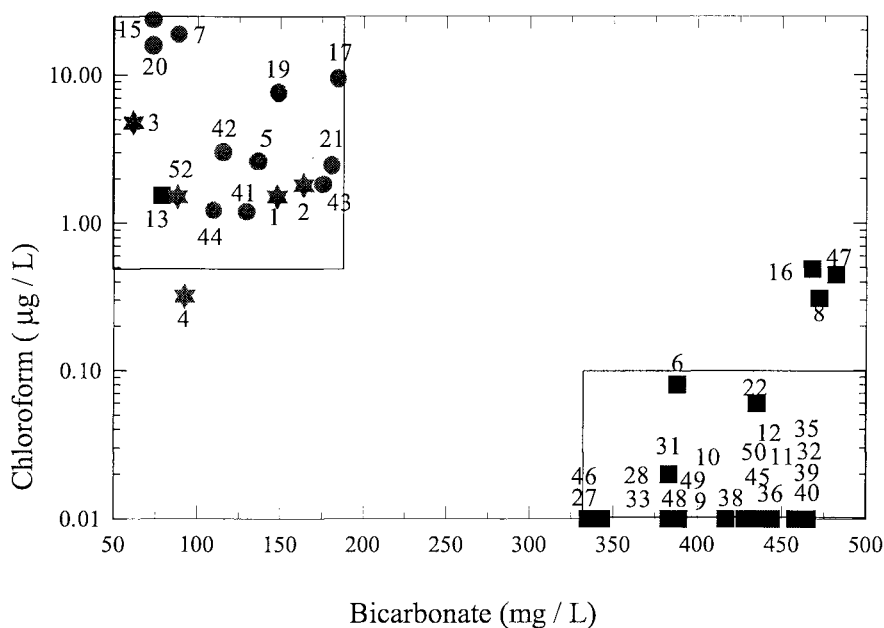* nd – content is below the detection limit.

Fig.6. Chloroform concentration plotted vs. bicarbonate content Squares are
water samples from production wells. Circles are water samples from injection
wells. Hexagons are surface water samples.

It is noticed above, that groundwater samples from injection wells are similar to Huangpu river water in major chemical constituents. As concerning organic contaminants, the chloroform content of the Yangtze river water is low. Huangpu river water has higher chloroform content, but it is still lower than most of water samples from injection wells. Perhaps, Huangpu river water now has lower concentration of VOC than before, because much improvement has been made in the wastewater treatment in this decade in Shanghai City.

Concentration of VOC in production wells should be very low. However a few productive wells have chloroform content from 0.1 µg /L to 1.0 µg /L. Only exception is SH/-13, chloroform content of which is 1.55 µg /L. Its bicarbonate content is 78.6 mg/L, which is typical for injection wells. Perhaps this production well is under a strong influence of the artificial recharge.

8. TRITIUM CONTENT IN RECHARGE WATER AND GROOUNDWATER

Tritium content is measured by low-background scintillation counting in combination with electrolytic concentration. The initial volume of water samples was 500 ml or 250 ml, whereas the final volume was about 8 ml. The tritium content of Huangpu river water is 7-8 TU in 1998, much less than it was (27 TU) in 1979-1980. The tritium content of Yangtze River water is 8.9 TU in 1998, a bit higher than that of Huangpu river water.

Tritium data obtained in 1998 and 1999 are listed in the last column of Table 2. Samples from injection wells have tritium content of 6 - 10 TU, while those from production wells are lower than 2 - 3 TU.

Tritium content of all water samples is plotted vs. chloroform concentration in Fig.7. In this diagram all symbols are the same as in Fig.5. As it can be seen from this figure that most water samples from production wells are concentrated in a limited low chloroform - low tritium area. Samples from injection wells and river water and tap water samples are scattered in the rest part of the diagram. The only exception is SH/-13 from a production well. Not only its tritium content and chloroform concentration, but also some major chemical constituents, are very close to those of water samples from injection wells. It seems that this production well is under strong influence of artificial recharge.
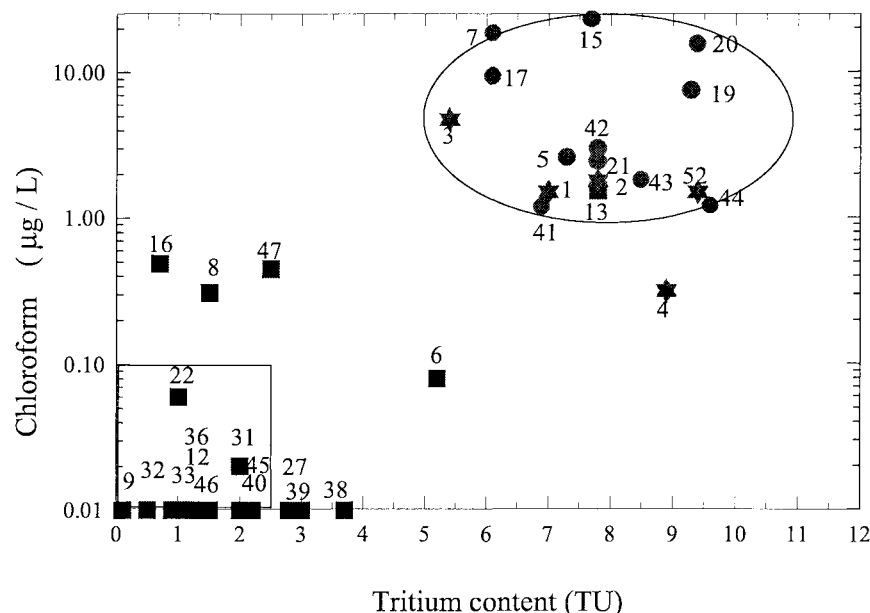
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Fig.7. Tritium content plotted vs. chloroform concentration for all water samples. Squares are water samples from production wells. Circles are water samples from injection wells. Hexagons are surface water samples.

The tritium content of the Huangpu river water is lower than that of some groundwater samples from injection wells, because it has been decreased during recent decade. Besides, although water samples SH/98-13 and SH/98-6 were taken from production wells, but they are not pure original groundwater in light of rather high tritium content and relatively low sodium concentration. It can be attributed to the influence of intensive recharge through drill holes in adjacent area.

9. TRACE ELEMENTS IN RECHARGE WTER AND GROUNDWATER

Trace elements in water samples were measured using ICP Mass-spectrometer, model PE ELAN 6000. Altogether contents of 45 elements in water samples are obtained, only 16 or 14 of them are listed in Table 5.

Some trace elements in water samples listed in Table 5, such as Li, Cr, show relatively high contents in deep groundwater of confined aquifers. These metal elements are mainly derived from the base rock. Fig. 4 shows lithium vs. tritium plot. As it can be seen from this diagram, that water samples from injection wells are concentrated in a limited area with Li content lower than 10 μ g/L and tritium content higher than 6 TU. While samples from production wells have higher Li content up to 32 μ g/L. At the same time, some of them have Li content lower than 10 μ g/L. Therefore, high Li content indicates, that these water samples may be derived from deep confined aquifer. As concerning the trace element chromium, it's content of lower than 3 μ g/L may indicate the presence of recharge water in confined groundwater aquifer.

Some other elements, such as Pb, Mn and Ni, are obviously from wastewater and they are characteristic for surface water. Contents of these elements in groundwater of deep confined aquifer should be very low. Therefore, these elements may be also indicative for the presence of recharge water. Fig. 6 shows Lead content vs. tritium plot. Water samples from production wells have lead content lower than 3 μ g/L. The same value is for the most of water samples from injection wells. Only a few water samples from injection wells show lead content higher than 10 μ g/L. These samples are definitely related to surface water bodies. The highest lead content of 52 μ g/L is observed in a sample from an injection well SH/21, located in a cotton mill. Water sample SH/13 from a production well shows lead content of 27 μ g/L, implying groundwater pollution due to intensive artificial recharge in surrounding area.

TABLE 5-1. SOME TRACE ELEMENTS IN WATER SAMPLES (Mg/l)

No	Li	Cr	Mn	Ni	Cu	Rb
SH/-5	4.09	2.37	0.78	3.10	7.51	8.59
SH/-7	4.87	1.340	22.6	2.28	7.64	8.40
SH/-15	5.09	1.47	22.3	3.81	14.5	10.1
SH/-17	2.03	3.29	8.36	2.50	11.9	9.64
SH/-19	4.71	2.85	0.76	2.41	12.9	9.02
SH/-20	4.94	1.75	49.1	4.45	9.42	9.20
SH/-21	5.23	2.86	11.3	3.39	20.9	10.7
SH/-41	4.41	4.05	1.18	3.59	2.99	5.47
SH/-42	3.47	1.69	4.80	2.47	4.88	10.5
SH/-43	7.92	2.50	1.33	2.75	5.24	7.75
SH/-44	10.7	2.01	19.3	5.45	5.78	11.2
SH/-1	6.31	2.50	0.00	6.29	28.9	14.2
SH/-2	7.21	2.14	142	9.92	9.93	15.0
SH/-3	14.0	1.40	58.0	3.60	14.5	9.38
SH/-4	3.23	2.18	0.54	2.57	8.47	9.38
SH/-52	9.10	1.98	3.02	3.41	4.48	6.65
SH/-6	13.0	3.72	0.39	1.05	3.43	7.22
SH/-8	16.0	4.38	0.00	0.79	1.90	8.55
SH/-9	19.1	6.53	121	1.03	8.69	5.69
SH/-10	18.7	4.67	0.29	0.69	2.33	4.94
SH/-11	18.5	4.59	0.35	0.63	2.21	6.08
SH/-12	13.4	4.34	0.42	1.20	1.27	10.3
SH/-13	3.18	1.58	14.2	2.70	12.2	8.28
SH/-16	18.3	5.28	0.27	0.64	1.52	7.19
SH/-22	15.3	6.30	0.00	0.75	2.81	4.71
SH/-27	3.14	5.52	4.17	1.60	0.60	1.08
SH/-28	8.41	5.52	0.62	1.07	0.94	0.74
SH/-31	31.8	5.56	0.33	0.77	2.32	3.41
SH/-32	14.4	6.92	1.04	1.12	2.58	3.03
SH/-33	3.30	5.92	0.34	2.49	1.63	1.08
SH/-35	15.9	5.84	0.23	0.86	0.83	1.71
SH/-36	12.9	6.24	1.84	1.04	4.59	1.46
SH/-38	9.76	4.76	2.58	2.28	2.50	2.87
SH/-39	32.4	4.56	0.27	0.91	2.15	2.86
SH/-40	23.6	5.84	0.14	0.67	1.26	2.36
SH/-45	18.0	3.75	0.18	0.67	1.48	3.01
SH/-46	6.20	3.46	0.20	1.65	3.06	4.14
SH/-47	23.6	4.24	0.16	0.83	2.57	3.96
SH/-48	7.33	3.18	0.14	1.22	2.26	2.78
SH/-49	4.52	3.14	1.13	1.28	2.79	2.60
SH/-50	8.19	2.40	0.27	0.61	1.70	4.53

TABLE 5-2.   SOME TRACE ELEMENTS IN WATER SAMPLES (Mg/l)

| No	Sr	Zr	Mo	REE	Tl	Pb	Bi
SH/-5	209	0.11	2.29	0.129	0.012	4.15	0.004
SH/-7	164	0.10	1.94	0.374	0.009	25.0	0.022
SH/-15	191	0.08	2.81	0.272	0.015	7.64	0.006
SH/-17	289	0.47	1.74	0.243	0.026	0.00	0.022
SH/-19	249	0.21	3.54	0.177	0.014	0.00	0.011
SH/-20	186	0.06	2.09	0.430	0.012	20.2	0.034
SH/-21	269	0.62	4.06	0.662	0.016	52.5	0.071
SH/-41	209	0.069	3.24	0.238	0.031	1.44	0.004
SH/-42	212	0.043	2.84	0.692	0.109	0.97	0.011
SH/-43	274	0.149	10.7	0.041	0.034	3.67	0.002
SH/-44	258	0.090	13.1	0.044	0.036	3.39	0.001
SH/-1	238	0.16	4.79	0.074	0.013	0.00	0.003
SH/-2	249	0.16	5.18	0.068	0.010	0.00	0.002
SH/-3	197	0.20	2.95	1.002	0.016	14.9	0.049
SH/-4	188	0.12	2.08	0.188	0.016	7.00	0.008
SH/-52	176	0.099	9.02	0.050	0.021	3.66	0.002
SH/-6	281	0.11	2.07	0.029	0.008	0.00	0.003
SH/-8	307	0.11	1.94	0.022	0.006	0.00	0.002
SH/-9	360	0.49	5.59	0.077	0.006	3.63	0.000
SH/-10	275	0.12	4.35	0.036	0.005	0.00	0.003
SH/-11	256	0.14	3.81	0.030	0.003	0.00	0.003
SH/-12	355	0.09	1.80	0.012	0.005	0.00	0.002
SH/-13	170	0.27	2.88	0.778	0.014	27.6	0.052
SH/-16	270	0.14	2.01	0.028	0.003	0.00	0.003
SH/-22	272	0.15	3.18	0.797	0.008	0.00	0.006
SH/-27	312	0.008	2.75	0.052	0.004	0.47	0.005
SH/-28	245	0.006	6.18	0.039	0.003	0.64	0.002
SH/-31	461	0.002	35.4	0.063	0.004	0.57	0.001
SH/-32	287	0.006	18.9	0.048	0.003	0.28	0.001
SH/-33	271	0.004	1.11	0.031	0.002	0.19	0.003
SH/-35	386	0.003	3.13	0.042	0.001	0.14	0.001
SH/-36	278	0.002	2.14	0.047	0.002	0.14	0.000
SH/-38	576	0.002	0.45	0.075	0.003	0.06	0.000
SH/-39	479	0.005	24.3	0.024	0.003	0.14	0.000
SH/-40	316	0.002	38.9	0.066	0.004	0.63	0.000
SH/-45	238	0.046	6.78	0.046	0.018	1.65	0.001
SH/-46	222	0.051	3.19	0.038	0.041	3.95	0.004
SH/-47	107	0.063	24.9	0.020	0.026	3.02	0.004
SH/-48	289	0.064	5.95	0.055	0.025	2.24	0.005
SH/-49	207	0.027	1.29	0.028	0.026	1.22	0.002
SH/-50	265	0.025	1.27	0.041	0.030	0.72	0.001
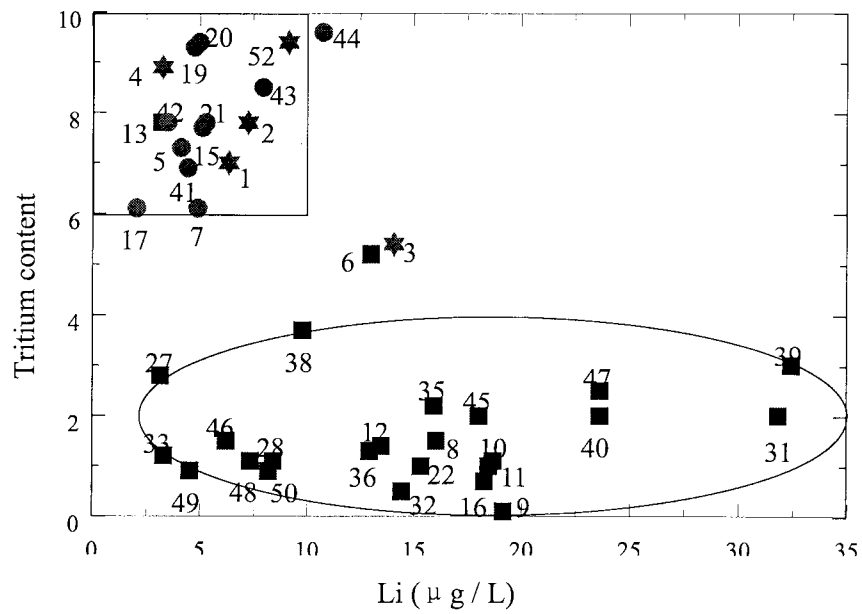
Fig.8. Lithium vs. Tritium content plot for all water samples collected in 1998 and 1999. Squares are water samples from production wells. Circles are water samples from injection wells. Hexagons are surface water samples.
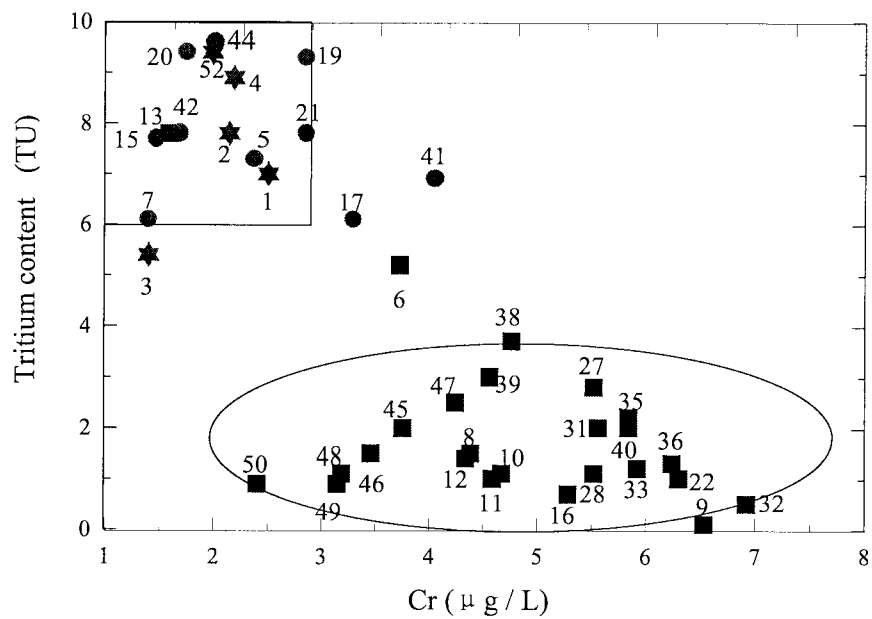

Fig.9. Chromium vs. Tritium content plot for all water samples collected in 1999 and 1999-8. Squares are water samples from production wells. Circles are water samples from injection wells. Hexagons are surface water samples.
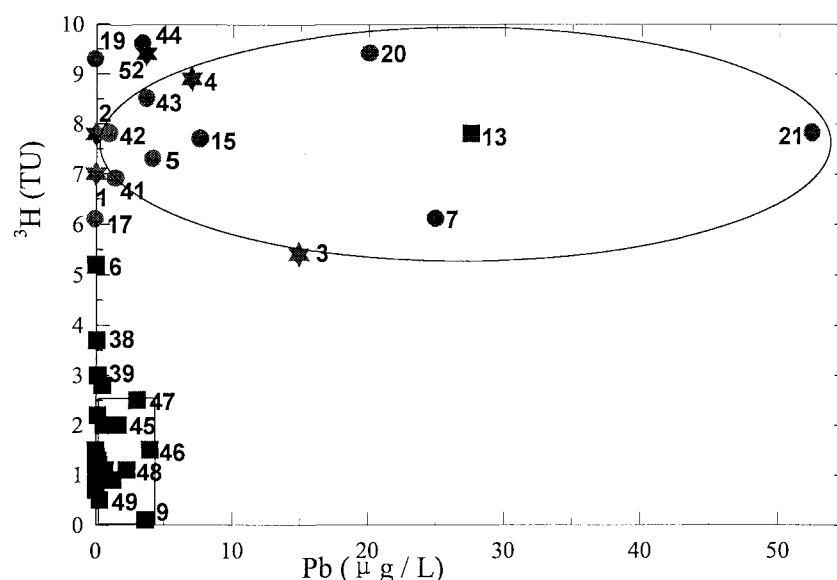
Fig.10. Lead vs. Tritium content plot for all water samples collected in 1999 and 1998. Squares are water samples from production wells. Circles are water samples from injection wells. Hexagons are surface water samples.

10. THE INFLUENCE OF ARTIFICIAL RECHARGE ON GROUNDWATER QUALITY

In this research project, tritium was used in combination with other tracers to identify the existence of surface water artificially recharged during the period of intensive injection. The characteristics of water from production wells and injection wells based on results of present work are summarized in Table 6.

TABLE 6. GEOCHEMICAL CHARACTERISTICS OF WATER FROM PRODUCTION AND INJECTION WELLS

Geochemical characteristics	Water from production wells	Water from injection wells
Tritium content (TU)	< 2.5 TU	2.5 - 10 TU
Bicarbonate (mg/L)	> 330 mg/L	< 180 mg/L
Sulphate (mg/L)	< 40 mg/L	60 - 120 mg/L
Chloroform (μ g/L)	< 0.1 μ g/L	> 1.0 μ g/L
Lithium (μ g/L)	5 - 30 μ g/L	2 - 10 μ g/L
Chromium (μ g/L)	3 - 7 μ g/L	< 3 μ g/L
Lead (μ g/L)	0 - 4 μ g/L	0 - 50 μ g/L

All above listed indicators could be used for assessment of the impact of artificial recharge on groundwater quality. However, collecting water samples now becomes more difficult in urban district. As mentioned above, maximum accumulated land subsidence was observed in the center of the Shanghai city in 1965. Since then, in order to control land subsidence a series of measures were adopted, including artificial recharge of groundwater aquifers. Artificial recharge was mainly carried out in the urban district, where production and injection wells were concentrated mainly in factories. During recent 10 years in the process of reconstruction of the city these factories were removed from

the urban district one after another. Therefore, it is difficult now to collect water samples from production wells in the urban district. Besides, artificial recharge into the IV layer was stopped because the problem of groundwater pollution is now under consideration. Nevertheless, there is an area shown in the sketch map (Fig. 7), where 9 wells are concentrated. SH/5 and SH/7 in the center of this area are injection wells of the IV layer. SH/41 and SH/15 are injection wells of the II and III layers, respectively. All other wells, SH/13, SH/6, SH/8, SH/12 and SH/35, are production wells of the IV layer. Values of 7 available indicators obtained for all water samples from these wells are listed in Table 7.
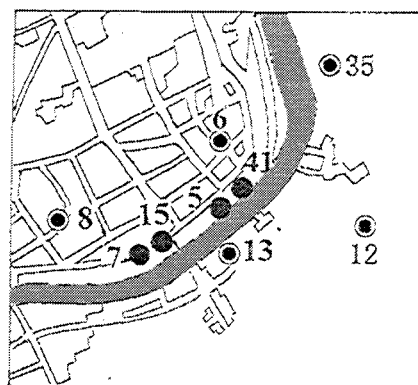

Fig.7 Sketch map showing the sampling sites on both banks of the Huangpu River around the well SH/5.

TABLE 7. GEOCHEMICAL CHARACTERISTICS OF WATER SAMPLES AROUND THE WELL SH/5.

| Number	Function	Tritium (TU)	Bicarbonate (mg/L)	Sulphate (mg/L)	Chloroform (μg/L)	Lithium (μg/L)	Chromium (μg/L)	Lead (μg/L)
SH/5	Injection well (IV)	7.3	137	86.7	2.62	4.09	2.37	4.15
SH/7	Injection well (IV)	6.1	88.9	63.3	18.7	4.87	1.40	25.0
SH/15	Injection well (III)	7.7	73.8	64.5	23.2	5.09	1.47	7.64
SH/41	Injection well (II)	6.9	130	94.8	1.19	4.41	4.05	1.44
SH/12	Production well (IV)	1.4	444	6.05	0.00	13.4	4.34	0.00
SH/35	Production well (IV)	2.2	462	16.1	0.00	15.9	5.84	0.14
SH/8	Production well (IV)	1.5	472	23.8	0.31	16.0	4.38	0.00
SH/6	Production well (IV)	5.2	388	28.2	0.08	13.0	3.72	0.00
SH/13	Production well (IV)	7.8	78.6	74.6	1.55	3.18	1.58	27.6

As it can be seen from Table 7, water sample from production well SH/13 shows typical characteristics of injection well. Values of 7 indicators in Table 7 for the sample SH/6 are evidently shifted to those of injection well. The distance between injection well No.5 and production well No.13 is about 1 km, while that between No.5 and No.6 is about 1.4 km (Fig.7). It seems that these two wells are located in the sphere of influence of the injection well No5. Deep confined aquifers are recharged by the Yangtze river in the north, thus the groundwater flow is from the north to the south. Therefore, the well No.13 is located in downstream side. So it shows greater impact of artificial recharge than upstream well SH/6.

Characteristics of water samples from two pairs of wells in Wusong area are listed in Table 8. SH/44 and SH/27 are located 1.8 km from each other. SH/44 is an injection well of IV layer, while

SH/27 is a production well. Another pair is SH/43 and SH/45 of the II layer. Distance from each other is 1.0 km. There is no evidence of any groundwater pollution due to artificial recharge. Therefore, it can be concluded that if there is an injection well nearby at a distance less than 1 km, the production well may be influenced by artificial recharge. Of course, distance is not the only factor. Perhaps the intensity and duration of the recharge may also be important in assessment of the impact.

TABLE 8. GEOCHEMICAL CHARACTERISTICS OF WATER SAMPLES IN WUSONG

Number	Function	Tritium (TU)	Bicarbonate (mg/L)	Sulphate (mg/L)	Chloroform (μ g/L)	Lithium (μ g/L)	Chromium (μ g/L)	Lead (μ g/L)
SH/44	Injection well (IV)	9.6	110	90.1	1.21	10.7	2.01	3.39
SH/27	production well (IV)	2.8	335	28.7	0.01	3.14	5.52	0.47
SH/43	Injection well (II)	8.5	176	83.9	1.82	7.92	2.50	3.67
SH/45	production well (II)	2.0	428	24.8	0.01	18.0	3.75	1.65
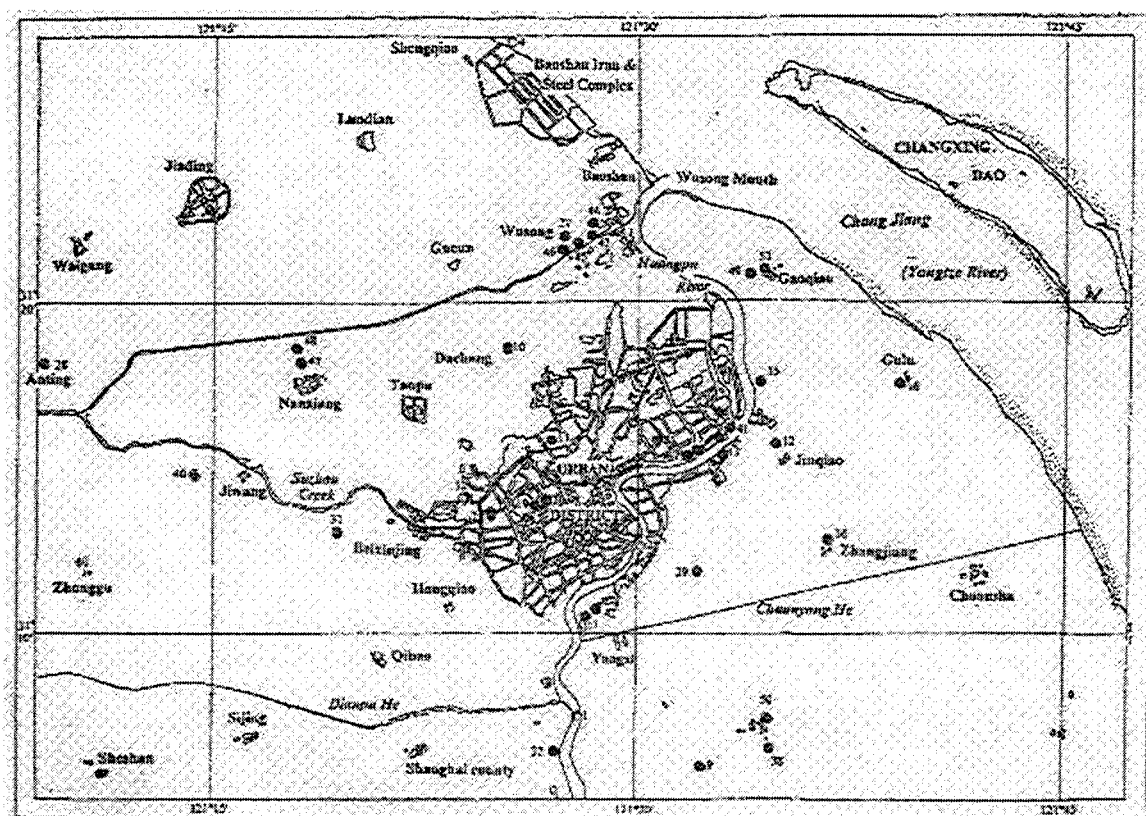
11. CONCLUSIONS

- In the period of 1998-1999, 41 water samples were collected from production wells of the II, III, IV and V confined aquifers, and also from injection wells of the II, III and IV confined aquifers. Obtained results show, that tritium content is sensitive to presence of artificial recharged water. The tritium content of Huangpu River water was around 7 - 8 TU in 1998. Most of the water samples from production wells have tritium content less than 2.5 TU. So tritium content higher than 2.5 TU may be regarded as some contribution of recent surface water in confined aquifer.

- Besides some major chemical constituents, such as sulphate and bicarbonate, some VOC compounds and trace elements are also good for tracing the recharge water. Therefore isotope techniques in combination with ICP-MS trace element analyses and GC/MSD analyses for organic tracers could be used to identify the existence and distribution of water artificially recharged in aquifers.

- In some limited areas water samples from the IV confined aquifer show typical characteristics of water from injection wells. It can be concluded from obtained results that if there is an injection well nearby at a distance less than 1 km, the production well of the same layer may be influenced by artificial recharge. Therefore, an assessment of the influence of artificial recharge on groundwater quality could be carried out on the basis of results obtained in this research project.

REFERENCES

[1] YUAN, Z., The origin of hydrochemical types of Quaternary confined aquifers in Shanghai area, Shanghai Geology, No.2(1981), 8-13.
[2] LU, Z., The distribution of the confined fresh-water aquifer in Shanghai and its extension to the sea, Shanghai Geology, No.1(1994) 1-12.
[3] YAN L., Survey of the city land subsidence in China, Shanghai Geology, No.1(1992) 40-48.
[4] YAN L., The land subsidence in Shanghai: My opinion concerning the groundwater exploitation as motivation of the land subsidence, Shanghai Geology, No.1(1980) 40-48.
[5] WEI, K., LIN, R., WANG, Z. et al., Isotopic study of ground waters in Shanghai area, Annual Reports, Institute of Geochemistry, Academia Sinica, (1982-1983) 48-50.
[6] LI, Q., XIU, W., SUN, Y., Artificial recharge and desalinating process of Cl- content in confined aquifer, Shanghai Geology, No.4(1992) 40-46.
[7] BAO, M., The effects of artificial recharge of groundwater to control the land subsidence of Shanghai and its influence on groundwater quality, Shanghai Geology, No.1(1988), 43-44.

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