

Mechanism of groundwater inrush hazard caused by solution mining in a multilayered rock salt mining area: A case study from Tongbai County, China

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18 **ABSTRACT**

19 The solution mining of salt mineral resources may contaminate groundwater and lead to water
20 inrush out of the ground due to brine leakage. Taking a serious groundwater inrush hazard in a large
21 salt mining area in Tongbai County, China, as an example, this study mainly aims to analyse the
22 source and channel of the inrushing water. The mining area has three different types of ore beds as
23 follows: a) trona (trisodium hydrogencarbonate dihydrate, also sodium sesquicarbonate dihydrate,
24 with the formula $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, is a non-marine evaporite mineral); b) glauber (sodium
25 sulphate is the inorganic compound with the formula Na_2SO_4 as well as several related hydrates) and c)
26 gypsum (a soft sulphate mineral composed of calcium sulphate dihydrate, with the chemical
27 formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Based on the understanding of geological and hydrogeological conditions, the
28 study first obtained hydrochemical data of the groundwater at different points and depths, and then
29 analysed the pollution source and pollutant component from single or mixed brines using both
30 physical-chemical reaction principle analysis and a hydrogeochemical simulation method. Finally
31 possible leakage brine conducting channel to the ground was discussed from both geological and
32 artificial aspects. The results reveal that the brine from the trona mine is the major pollution source;
33 there is a fissure zone in the NW-SE direction controlled by the geological structure that provides the
34 main channels for the leakage brine to flow into the aquifer around the water inrush regions, and a
35 large number of waste gypsum exploration boreholes are the channels that supply the polluted
36 groundwater inrush out of the ground. This research can offer a valuable reference for avoiding and
37 assessing groundwater inrush hazards in similar rock salt mining areas, which is advantageous for
38 both groundwater quality protection and public health.

39 1. **Introduction**

40 Solution mining is commonly used in salt mine exploitation, as salts are soluble in water. In this
41 method, high-pressure and -temperature water with low salinity is injected into a mineral deposit
42 through production wells to dissolve the mineral salts. After being drawn from the wells, the soluble
43 salt is purified and further processed. However, the high-pressure and -temperature water used in this
44 process not only dissolves minerals but can also cause fractures in the strata, which usually results in
45 hazards such as brine leakage or groundwater inrush. In this situation underground drinking water for
46 the public is normally polluted following groundwater inrush, creating a hazard and threatening the
47 health of local residents.

48 Many scholars (Clark and Fritz, 1997; Liu et al., 2015; Wu et al., 2016) have studied groundwater
49 inrush hazards in both coal and metal mines, and some adopted methods are as follows: the use of
50 water level / temperature criterion (Yuan and Gui, 2005; Ma and Qian, 2014), stochastic simulation
51 (Fernandez-Galvez et al., 2007), numerical simulation (Liu et al., 2009; Kang et al., 2012; Shao et al.,
52 2013; Houben, et al., 2017), water chemical analysis (isotope analysis, water quality type correlation
53 analysis) (Robins, 2002; Fernandez et al., 2005; Hu et al., 2010; Cobbina et al., 2015; Lee et al., 2016;
54 LeDoux et al., 2016), multivariate statistics (discriminant analysis, clustering analysis) (Chen and Li,
55 2009; Lu, 2012) , fractional advection dispersion equations (Ramadas et al., 2015) and nonlinear
56 analysis (fuzzy mathematics, grey correlation analysis, etc.) (Hao et al., 2010; Gao, 2012). However,

57 due to the particularity of the solution mining method and the complex chemical-physical reactions
58 during the high-pressure and -temperature mining process, research regarding solution mining was
59 more focused on mining techniques (Jiang and Jiang, 2004; Kotwica, 2008; Namin et al., 2009),
60 mining cavity stability analysis and sinkhole problems (Staudtmeister and Rokahr, 1997; Bonetto et al.,
61 2008; Ezersky et al., 2009; Goldscheider and Bechtel, 2009; Closson and Abou Karaki, 2009; Vigna et
62 al., 2010; Frumkin et al., 2011; Ezersky and Frumkin, 2013; Qiu, 2011; Blachowski et al., 2014), and
63 geohazards particularly in karst areas due to human-induced underground caving (Waltham and
64 Fookes 2003; Parise and Gunn 2007; Zhou and Beck 2011; Parise and Lollino 2011; Lollino et al.,
65 2013; Gutierrez et al., 2014; Parise et al., 2015), but rarely on source and channel analysis of inrush
66 water in a solution mining accident.

67 The studied rock salt mining area is in Tongbai County, Henan Province, China. This mining area
68 has the second largest trona reserves in the world, while its glauber salt reserves reach 45 million tons.
69 Since trona and glauber salt were put into production in 1990 with single- and double-well convection
70 mining as the main producing method, five inrush points appeared in the town of Anpeng, Tongbai
71 County, from June 2011 to May 2013. Among these five inrush points, four (Y1~Y4) were long-term
72 (longer than 2 years) with stable discharge, while one (Y-5) was a sudden inrush point (as shown in Fig.
73 1 and Fig. 2). On 1 February 2013, almost 200 m³ of mud and sediment erupted out of the ground at the
74 Y-5 point. The area of the inrush point was almost 4 m²; the average water inflow was from 20-30 m³/d

75 while the greatest inflow reached 200 m³/d. The water inrush lasted for approximately three months.
76 During the Y-5 inrush accident, according to the field investigation, a trona production well named
77 “S02,” which is 200 m from the inrush point, broke at a depth of 234 m and remained broken for a long
78 period of time. It was repaired on 15 March 2013. During the entire water inrush process, the inrush of
79 groundwater led to a phenomenon of salinization at the base of the houses of many villagers, and made
80 water in many residents’ wells no longer drinkable.

81 Since the groundwater inrush hazard involved a wide geographic area and the inrush source was
82 quite hard to distinguish due to the multi-layer distribution of the different ore bodies and the
83 complexity of the inrush water component. Therefore, in order to put forward a targeted treatment
84 program to stop the water inrush as soon as is possible, and mitigate the groundwater pollution in
85 research region, the source and channel of the inrush water were taken as the research emphasis in this
86 study. Furthermore, this research can provide a valuable reference for avoiding and assessing
87 groundwater inrush hazards in similar rock salt mining areas, which is advantageous for both
88 groundwater quality protection and public health.

89 **2. Geological and hydrogeological setting**

90 ***2.1. Geological conditions***

91 The mining area is located northwestern Tongbai County. The landscape is characterised by
92 hollows and ridges, and has an elevation ranging from 140 to 200 m. The strata, lithology, aquifer, and

93 the position of different ore beds in the research area (Shi et al., 2013) are shown in Fig. 3.

94 According to geologic references and field investigation, in the northeastern mining area, a hidden
95 east-west oriented fault is developed at the bottom of the first segment of the Hetaoyuan Formation,
96 and another four, hidden, south-north oriented faults are developed at the bottom of the second
97 segment of the Hetaoyuan Formation. These five faults are outside the scope of trona mine, so they
98 have had little effect on the ore bed. A few small-scale hidden faults are developed at the bottom of the
99 third segment of the Hetaoyuan Formation, although within the scope of the glauber salt mine, they
100 have had little effect on the glauber salt ore bed which is distributed at the top of the first segment of
101 Hetaoyuan Formation, A hidden east-west oriented fault is developed at the bottom of the Liaozhuang
102 Formation in the range of the glauber salt mine, but it has had little effect on the glauber salt mine
103 because of its small scale.

104 ***2.2. Hydrogeological conditions***

105 The groundwater in the mining area can be divided into pore water in the loose rock mass and
106 bedrock fissure water according to the lithology and hydrogeological features. In the upper part of the
107 Liaozhuang Formation, a mudstone interbedded with gypsum is considered a relative weak permeable
108 stratum especially under the condition of high-pressure and -temperature water injection during the
109 mining period. The shallow aquifer is unconsolidated pore water above this weak permeable stratum,
110 while the deep aquifer is a bedrock fissure beneath this weak permeable stratum.

The flow direction of the shallow groundwater is controlled by the overall terrain. Taking the underground watershed as the boundary, the groundwater on the south side of the watershed is mainly flowing from northeast to southwest with the Yanhong River as the base of the drainage, while the groundwater on the north side of the watershed is mainly flowing from south to north with the Xia River as the base of the drainage. The deep groundwater has relatively closed burial conditions, slow velocity, and nearly the same flowing direction as the shallow groundwater. The water inflow of a single well with poor water content is approximately 100 m³/d, while it can reach from 1000-2000 m³/d if it has rich water content. The annual variation of the groundwater level is from 2-4 m, while the depth is stable at 2.3-4 m. Residents in Anpeng use groundwater as the source of their drinking water, which comes from wells and is from the porous aquifer.

As shown in Fig. 3, gypsum mainly occurs on the top of the Liaozhuang Formation, glauber salt occurs in the third member of the Hetaoyuan Formation, and the trona occurs at the bottom of the second member of the Hetaoyuan Formation as well as on top of the first member of the Hetaoyuan Formation. The surrounding rocks of every mineral layer include mudstone, shale, sandy conglomerate, psammitic rock and dolomite, which have sufficient thickness and good water-resistance. Therefore, the effect of groundwater on the mineral deposit is minimal in the mining area.

128 **2.3 Distribution and characteristics of the ore body**

129 The three ore bodies overlap in plane distribution, as shown in Fig. 4. The vertical distribution of
130 the ore bodies from deep-to-shallow is trona (buried depth: 1560.92-2929.53 m), glauber salt (buried
131 depth: 1003.66-1397.58 m) and gypsum (buried depth: 134-338 m). The trona and glauber salt bodies
132 are at least 250 m apart from each other vertically.

133 The trona has 11 horizontal layers, with an average thickness of 2.11 m. The chemical
134 composition of trona is mainly NaHCO_3 (average of 77.06%) and Na_2CO_3 (average of 16.33%) (Wang,
135 1987). The glauber salt has 4 layers, with an average thickness of 8.93 m. The dip angle of the ore bed
136 layer is less than 10° . The average mineral grade is 60.14%. The main composition of the glauber salt
137 is Na_2SO_4 (>90%) with a small amount of NaCl .

138 **3. Methods**

139 Based on the field investigation results, the chemical characteristic analysis of the inrush water at
140 different sites and time, analysis of the physical and chemical reaction principles for the different
141 brines, and combined with the PHREEQC simulation method the source of the inrush water was
142 determined.

143 **3.1. Sampling and testing**

144 The five groundwater inrush points (Y1~Y5) and some shallow groundwater points (resident
145 wells: SY1~SY6) near the accident site were chosen as groundwater quality sampling points, as

146 shown in Fig. 4. Water from each point was sampled on 9 March 2013.

147 Water samples were filtered using a 0.45 μm millipore filtration membrane in the field, and then
148 filled with a polyethylene bottle which had been soaked in acid and washed with deionised water.
149 Filtered water samples were acidified until the $\text{pH} < 2$ by addition of ultra-pure HNO_3^- for the
150 determination of cations; water samples for the determination of anions were not treated.

151 Elements tested in the laboratory included 26 cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , etc.) and 5
152 anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , NO_2^-). The instrument used for the determination of cations was an
153 inductively coupled plasma atomic emission spectrometer (Agilent ICP-OES 5100), and the minimum
154 detection limit was 0.0001mg/L. The instrument used for the determination of anions was an ion
155 chromatograph (ICS-1100), and the minimum detection limit was 0.001 mg/L. CO_3^{2-} and HCO_3^- were
156 tested according to the “Groundwater quality test method: Determination of carbonate and bicarbonate
157 by hydroxide titration (DZ/T 0064.49-93),” and the minimum detection limit was 0.01 mg/L.

158 In addition, from March to April 2013, at the Y-5 and Y-3 points, three water quality automatic
159 recorders (Levellogger gold, Canada) were arranged for inrush water monitoring. Monitoring
160 indicators were temperature, water level and electrical conductivity. The purpose of the monitoring
161 was to fully understand the inrush water quality during the whole accident, especially in the process of
162 well repair.

3.2. Analysis of the physical and chemical reaction principles in different brine mixing conditions

During the accident, the leakage brine of the trona (2000 m belowground) or glauber salt (1000 m belowground) might flow through the gypsum deposit (200-400 m belowground), which is comprised primarily of CaSO_4 , and cause physical and chemical reactions while it intrudes out of the ground. Thus, the formation of the intruder water chemistry component might be from glauber brine, or trona brine, or a mixture of the two brines, flowing through the gypsum layer with accompanying physical and chemical reactions. To provide the basis for further analysis of the intruder water source, the physical solubility of the gypsum and the reaction when the glauber salt brine, trona brine, or a mixture of trona and glauber salt brine flowing through the gypsum deposits were analysed.

3.2.1. The physical solubility of gypsum (CaSO_4)

Gypsum is slightly soluble; when in water, its acidity is apparent. Eq. (1) provides the dissolution rate equation of gypsum in water:

$$R_{\text{Gypsum}} = k_1 \times \frac{A_g}{V} \left(1 - \left(\frac{IAP}{K} \right)_{\text{Gypsum}} \right) \quad (1)$$

R_{Gypsum} : the dissolution rate of gypsum; k_1 : rate constant; A_g : the surface area of gypsum; V : the liquid volume in contact with the gypsum surface; IAP : the product of ion activity; and K : ion solubility product.

$\left(\frac{IAP}{K} \right)_{\text{Gypsum}}$ is affected by the temperature; thus, it is the same as R_{Gypsum} .

The solubility of gypsum in water reaches a maximum of 0.2097 g/100 g at 40°C. The solubility decreases when the temperature is below or above 40°C. The content of SO_4^{2-} and Ca^{2+} obtained by physical dissolution is very low.

3.2.2. Gypsum (CaSO_4) dissolved by glauber salt brine (Na_2SO_4)

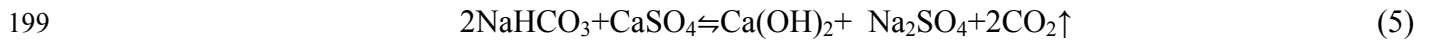
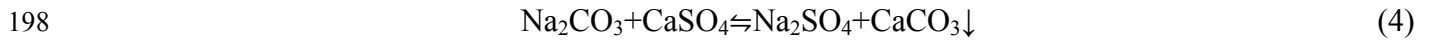
Equations (2) and (3) show the reactions of Na_2SO_4 and CaSO_4 with water.



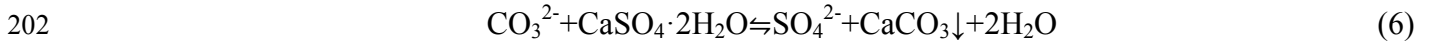
Because of the common-ion effect, the solubility of the electrolyte will decrease when a strong electrolyte with the same ion is placed into an electrolyte-saturated solution. Thus, the solubility of gypsum will be reduced when glauber salt brine flows through and dissolves the gypsum deposits; the gypsum will be even harder to dissolve in this situation. Thus, if the glauber salt brine flows through the gypsum deposits, the brine characteristic would not apparently change.

3.2.3. The reaction of trona brine or a mixture of trona and glauber salt brine with gypsum

The HCO_3^- and CO_3^{2-} contents in trona brine or in mixed brine are very high as is the solution alkalinity and pH. If the reaction kinetics is not taken into account, the pH has little influence on the dissolution of gypsum (Yang, 2003; Xu and Li, 2011). The reaction occurs when the brine with high concentrations of HCO_3^- and CO_3^{2-} flows through the gypsum deposits. The main chemical reactions are as follows:



200 In Eq. (4), CaSO_4 is slightly soluble, while CaCO_3 is insoluble. The reaction easily occurs when
 201 an insoluble substance is produced by a slight soluble substance, and the ionic equation is as follows:



203 The Gibbs Free Energy (ΔG) is -22.7 kJ/mol under the standard state. When ΔG is negative, the
 204 reaction, which is endothermic, occurs freely. The reaction is faster at higher temperatures. Eq. (5)
 205 shows that ΔG is 2102 kJ/mol under the standard state. When ΔG is positive, the reaction will not
 206 freely occur.

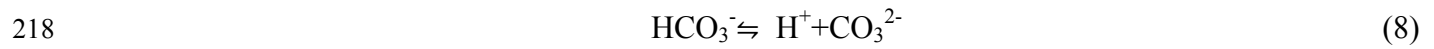
207 Thus, the reaction shown in Eq. (5) will not occur, but the chemical reaction will still proceed as
 208 shown in Eq. (4), when trona brine or mixed brine flow through the gypsum deposits.

209 *3.2.4. The carbonate equilibrium effect during the reaction of different brines*

210 The carbonate equilibrium that exists in the trona brine or mixed brine is affected by pH. The
 211 carbonate in groundwater exists in three forms: free carbonic acid, bicarbonate and carbonic acid.

212 In the trona brine (pH>10), the concentration of HCO_3^- is 5-20 times that of the concentration of
 213 CO_3^{2-} , and CO_3^{2-} in the brine is dominant in this case. When the trona brine flows through the gypsum,
 214 CaSO_4 reacts with CO_3^{2-} and CaCO_3 precipitates. If the concentration of CO_3^{2-} in the brine decreases,
 215 a reversible reaction will take place and drive the equilibrium to the right. Thus, the reverse reaction

will occur when the trona brine flows through the gypsum as follows:



The circular reactions as shown in Eqs. (7) and (8) will occur when mixed brine flows through the gypsum because it has similar properties to the trona brine. Thus, taking the carbonate equilibrium effect into account, the concentrations of HCO_3^- and CO_3^{2-} will decrease, while SO_4^{2-} increases after CaCO_3 precipitates.

3.3. Simulation of groundwater intrush source

For further quantitative analysis of the intrush water source and component, the international hydrological and geochemical simulation software PHREEQC was used to simulate the water-rock interaction. The PHREEQC (D.L. Parkurst and C.A.J. Appelo, 1999) software was developed by the U.S. Geological Survey, and it is able to calculate geochemical action within a temperature range of from 0~300 degrees (Wei, 2010).

Based on the deduction that the main water intrush source around Anpeng was trona leakage brine, the simulation method PHREEQC was used and combined with the possible channel of intrush water to establish a conceptual model and then hydrogeochemical simulation of the water-rock interaction was conducted. Subsequently, the mixed ratio of intrush groundwater and shallow groundwater around Anpeng were quantified, which can better verify the source of the intrush water.

234 3.3.1. *Conceptual model*

235 Around Anpeng, the trona leakage brine flowed through the specified mineral assemblages and
236 mixed with shallow groundwater in different proportions.

237 3.3.2. *Initial data input*

238 The parameters of the trona brine were taken from the enterprise's production testing data; the
239 parameters of the shallow groundwater were taken from the same aquifer but outside the study area,
240 and can basically represent groundwater background values. The specific parameters are shown in
241 Table 1.

242 3.3.3. *Setting of stratum and mineral*

243 The formations from the bottom to the top during the process of the leakage brine flowing into the
244 shallow groundwater and then flowing out of the ground were as follows: the third member of the
245 Hetaoyuan Formation of Paleogene, and the Liaozhuang Formation and Fenghuang Formation of
246 Neogene and Quaternary, respectively. To simplify the mining area, according to the thickness of the
247 rock stratum and the proportion of mineral composition, it can be assumed that the layer through
248 which the trona brine flowed contains Ca-montmorillonite, kaolinite, gypsum, potash feldspar and
249 potash mica.

250 The main ingredients are as follows: Kaolinite: $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$; Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$;
251 Ca-montmorillonite: $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$; Dolomite: CaCO_3 ; Potash feldspar: K

252 [AlSi₃O₈]; Potash mica: aluminium silicate as K, Al, Mg, Fe and Li.

253 **4. Results and Discussion**

254 On 9 March 2013, in Anpeng, water samples from five groundwater inrush points and six
255 surrounding water quality monitoring points (resident well) were tested. The results of water chemical
256 composition are shown in Table 2, and the distribution of the sampling points is shown in Fig. 4.

257 According to the water quality analysis, the inrush brine had a relatively high salinity, with some
258 inrush water samples containing SO₄-Na and some containing HCO₃-Na. The crystals mainly
259 consisted of NaSO₄, Na₂CO₃, and NaHCO₃. The composition of the inrush water and the crystals was
260 the same as that of the high-concentrated ions in the trona brine (Na₂CO₃, NaHCO₃, etc.) and glauber
261 salt brine (Na₂SO₄).

262 **4.1. The source of the inrush water**

263 An automatic water quality recorder was set up at the Y5 inrush point on 4 March 2013. The
264 monitoring lasted from 5 March to 20 March 2013. Thus, the relationship between the inrush points
265 and the S02 well can be assessed according to the correlation of the changes between
266 temperature/electrical conductivity and the concentration of brine during the S02 production well
267 reparation period (5 March to 14 March 2013).

268 The production of glauber ceased during the investigation (2 March to 15 March 2013), so it
269 could be determined how the glauber mining affects the water inrush hazard based on a dynamic water

270 quality situation.

271 *4.1.1. The source of intrush water at the Y-5 point*

272 After successful reparation of the S02 well, the conductivity and temperature of the intrush water
273 decreased significantly. The CO_3^{2-} concentration remained at 0, the concentration of HCO_3^- decreased
274 to 500 meq/L, while the concentration of SO_4^{2-} increased to 600 meq/L. Subsequently, the
275 concentrations of these three ions were in a state of dynamic balance. The analysis shows that the
276 source of the intrush water at the Y-5 point is closely related to the S02 trona well.

277 In order to ensure whether the glauber brine exists at this point as part of an intrush source, further
278 analysis was performed. The depth of the well rupture was 234 m; the gypsum deposit was developed
279 to this depth. While the leakage of the trona brine flowed through the gypsum deposit, reactions would
280 occur as shown in Eqs. (7) and (8).

281 According to the ion milliequivalent concentrations (Ca^{2+} 0.61 meq/L; CO_3^{2-} 905.3 meq/L; HCO_3^-
282 1332.94 meq/L; Cl^- 107.43 meq/L; and SO_4^{2-} 267.89 meq/L) at the Y-5 point, the concentration of
283 Ca^{2+} was negligible compared to the other main ions. Only the reaction between CO_3^{2-} and CaSO_4 had
284 to be taken into account because of the large number of CO_3^{2-} , fast velocity, the short contact time with
285 gypsum, and the high temperature. The reaction of CO_3^{2-} and CaSO_4 would take place at a ratio of 1:1
286 according to Eq. (7), and three types of intrush water sources could be assumed under this precondition
287 as follows:

(1) The inrush water source was only from the trona brine.

The CO_3^{2-} and CaSO_4 in the brine reacted at a ratio of 1:1, and the concentration of SO_4^{2-} was equal to the reacted γCO_3^{2-} content. Thus, the $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$ ratio in the trona brine was equal to the $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ ratio in the inrush water. From this calculation, it could be seen that $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ was equal to 0.88, while $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$ ranged between 0.86 and 1.26. The content of $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ was similar to $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$; therefore, the source of the inrush water was exclusively trona brine.

(2) The inrush water source was only from the glauber brine.

The $\gamma\text{SO}_4^{2-}/\gamma\text{HCO}_3^-$ ratio in the glauber brine was equal to 1237.8, compared to 0.19 in the inrush water. Therefore, this assumption was incorrect because of the widely varying ratios.

(3) The inrush water source was from a mixed brine of glauber and trona,

Assuming that the contribution ratio of the glauber brine was X and that of the trona brine was Y was true, then $1237.8 \times X + (0.86 \sim 1.26) \times Y = 0.88$. This equation showed that when the contribution ratio of the trona brine was equal to 1, the contribution ratio of the glauber brine was equal to 1.6×10^{-5} and was too small to ignore.

Thus, it could be confirmed that the water inrush source at Y-5 was exclusively the leakage of trona brine from the broken S02 well.

305 *4.1.2. The sources of intrush water at the Y-4, Y-3, Y-2, and Y-1 points*

306 The intrush water quantity and the dynamic variation of the concentration of SO_4^{2-} and HCO_3^- at
307 points Y1-Y4 were not obvious when the S02 well was under repair and all the glauber wells were
308 shut down (2-15 March). This result shows that the sources of these water intrush points were not due
309 to the underground mining activities of the glauber brine or the rupture of the S02 well, but because of
310 the brine leakage from other trona wells.

311 *4.1.3. Components and mixed proportions of the intrush water*

312 The PHREEQC simulation conditions were assumed to be as follows: (1) the trona brine did not
313 mix with shallow groundwater after flowing through the mineral layer; or (2) the trona brine mixed
314 with shallow groundwater in a ratio of 1:2, 1:10, 1:100, 1:200, 1:500, 1:1000 and 1:5000 after flowing
315 through the mineral layer. The simulation results are shown in Table 3.

316 Table 3 shows that when the trona brine flowed through the stratum and shallow groundwater, the
317 concentrations of Na^+ , Cl^- and SO_4^{2-} decreased while the concentration of HCO_3^- increased with
318 increasing proportion of the shallow water. The concentration of Ca^{2+} decreased at first and then
319 increased.

320 The ion concentrations at Y-5, except for SO_4^{2-} , were similar to the ion concentrations in the trona
321 brine. However, at the same time, the concentration of HCO_3^- was nearly 0. When the trona brine
322 flowed through the layer, it would react rapidly and pour out of the ground directly because of the fast

323 velocity of the inrush water at Y-5. Meanwhile, the trona brine was not continuously provided in the
324 simulation. Thus, the concentration of HCO_3^- would be near to the concentration of trona brine in
325 reality. Therefore, the trona brine must have a rapid inrush, nearly not mixing with shallow
326 groundwater.

327 The PHREEQC simulation analysis results show that 1) the water inrush source of Y-5 was nearly
328 all of the trona brine from the ruptured S02 well; 2) the water inrush source of Y-3 was a mixture of
329 trona brine and groundwater in a ratio of from 1:10~1:100; and 3) the water inrush sources of Y-4, Y-2
330 and Y-1 were a mixture of trona brine and groundwater under the ratio of 1:200.

331 ***4.2. The channel of the inrush water***

332 *4.2.1. Reason for the brine leakage*

333 Trona is produced by either a single well or double/multiple well convection mining method, a
334 water-soluble mining method (Lin, 1987). The main mining unit consists of a salt cavity and
335 production well. Thus, the instability of the salt cavity and the rupture of the production well are the
336 main possible reasons for brine leakage.

337 (1) Analysis of salt cavity stability

338 The possibility of salt cavity collapse: Trona is distributed at the bottom of the second member of
339 the Hetaoyuan Formation and in the upper part of the first member of the Hetaoyuan Formation, with
340 dolomite strata developed in the roof and floor. The thick and hard surrounding rock structure

determined that the cavity produce by hydrofracture but it is hard to fill with large-scale fractured channels and can remain intact and stable.

The development of a roof fracture: When a mineral is under exploitation, the surrounding rock in the cavity is under pressure from the inner brine. This pressure is equal to the water injection pressure plus the water column pressure in the production well. The water injection pressure of the trona production well is approximately 10-20 MPa, while the 1560.92-2929.53 m (mineral buried depth) water column pressure is approximately 15.3-28.71 MPa. Thus, the greatest water pressure on the surrounding rock in the cavity is 48.71 MPa. The main lithology of the surrounding rock is dolomite which is 500 m in thickness and 142.66 MPa in compressive strength, which is nearly 3 times that of the greatest possible water pressure. Therefore, large-scale fractures in the surrounding rock of the trona mineral would be difficult to develop under the effect of sustained water pressure.

(2) Analysis of production well rupture

The phenomenon of brine leakage caused by the S02 well rupture in Anpeng indicates that production well damage is an important cause of brine leakage. The depth of the S02 well rupture is 234 m underground, i.e. in the gypsum deposit, which is strongly hygroscopic. The pressure caused by the water swelling is approximately 0.15 MPa (Li and Zhou, 1996), which may damage the production well and induce brine leakage. The high concentration of SO_4^{2-} (>250 mg/L) generated by the reaction of leakage brine and gypsum can also corrode the production well and lead to groundwater inrush.

359 4.2.2. Analysis of water-conducting channel

360 According to our analysis, the most probable reason for brine leakage in trona is production well
361 rupture. The leaking brine will flow along the water-conducting channel into the shallow aquifer and
362 even pour out of the ground. However, the geological structure in the mining area shows no
363 water-conducting fault development. Thus, the water-conducting channel, that the leakage brine flows
364 along, is probably a fissure or artificial channel.

365 A structural fissure is the main type of fissure that occurs in groundwater inrush hazards when
366 using the solution mining method. The structural fissure is determined by the maximum horizontal
367 principal stress, which is controlled by the tectonic stress field in the mining area. The connection
368 direction of the S02 well and the other water inrush points is NW-SE, which is the same as that of the
369 structural fissure zone development direction. This indicates that the main water-conducting channel
370 in Anpeng is controlled by the structural fissure zone.

371 The inrush points in Anpeng are all at the abandoned gypsum exploitation wells, which were not
372 closed properly. Thus, high-pressure cavity water or leakage brine can flow along the structural fissure
373 zone, finally connect with these wells, and then pour out of the ground through boreholes. Therefore,
374 the abandoned gypsum exploitation wells are the main channels through which the shallow polluted
375 groundwater flowed out of the ground, as shown in Fig. 5.

376 **5. Conclusions**

377 This study aimed to investigate the source and channel of the inrush water in a multilayer rock
378 salt mining area. To achieve the set objectives, this study combined an analysis of geological and
379 hydrogeological conditions, an analysis of physical and chemical reaction principles of different
380 brines, the PHREEQC simulation method, and an analysis of geological and artificial reasons for the
381 conducting channel where leakage brine flowed from the damage depth out to the ground as the study
382 methodology.

383 Long-term solution mining with high-pressure and -temperature water not only dissolves minerals
384 but also may cause rupture of strata and damage of the production well, which usually results in brine
385 leakage or the inrush of groundwater. Geological and hydrogeological conditions are the basis which
386 determines the total risk of the groundwater inrush hazard. Physical and chemical reaction principle
387 analysis of different brines and hydrogeochemical simulation of water-rock interaction in different
388 assumed conditions using the PHREEQC simulation method can not only determine the exact source
389 of the leakage brine but also identify the mixed proportion of inrush water while the leakage brine
390 flows through the mineral layer in different way. Other than geological reasons, mining techniques
391 such as pressure control of injection water and groundwater quality monitoring of exploitation wells
392 may also determine the risk of a groundwater inrush hazard in a multilayer rock salt mining area.

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396 **Author Contributions**

397 Bin Zeng and Tingting Shi contributed to data analysis and manuscript writing; Zhihua Chen
398 proposed the main structure of this study; Liu Xiang and Muyi Yang designed and performed the
399 experiments; and Shaopeng Xiang performed the PHREEQC simulation. All the authors read and
400 approved the final manuscript.

401 **Conflicts of Interest**

402 The authors declare that they have no conflict of interest.

403

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Figure captions

Fig. 1. One of the long-term (longer than 2 years) groundwater inrush points with stable discharge (Y-3).

Fig. 2. The sudden groundwater inrush point (Y-5). As shown in this figure, the high-temperature inrush groundwater was being pumped after the ground was broken.

Fig. 3. Information about strata, lithology, aquifers, and buried positions of each ore bed in the mining area.

Fig. 4. Sketch map of hydrogeological conditions and the distribution of groundwater inrush points in the mining area.

Fig. 5. Schematic diagram of source and channel analysis of the groundwater inrush hazard in the multilayered rock salt mining area in Tongbai County.



Fig.1



Fig.2

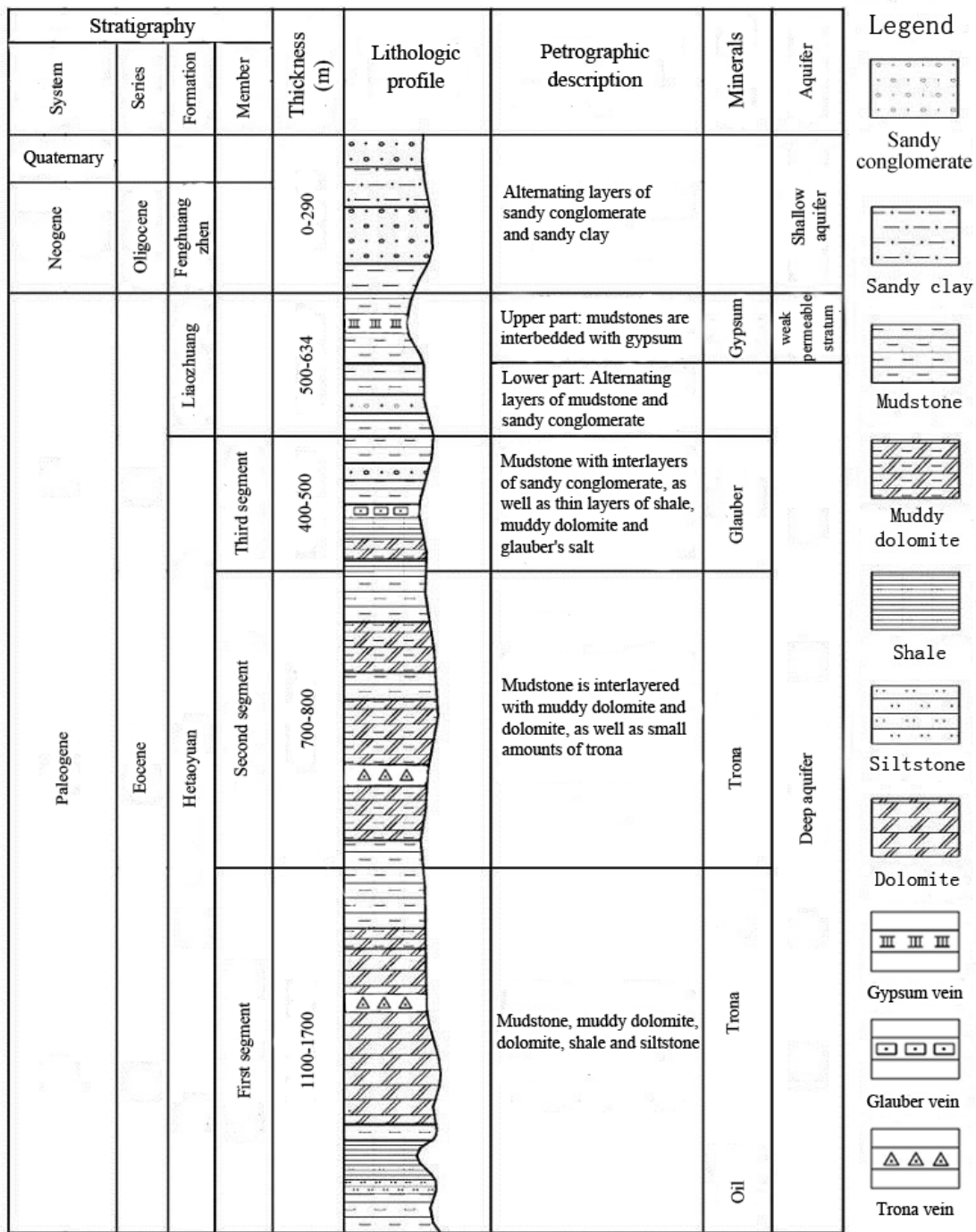
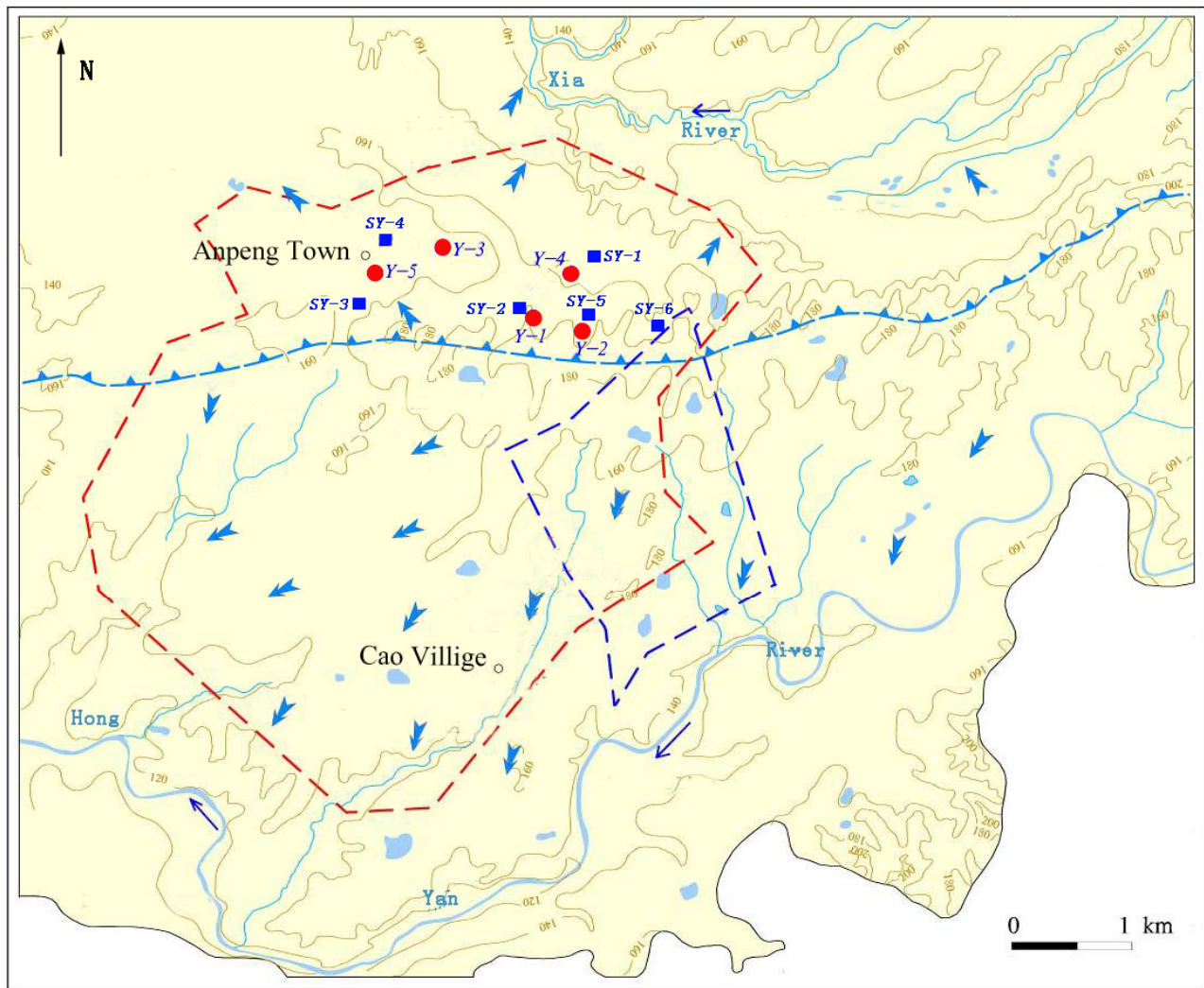


Fig.3



- | | | |
|----------------------------|----------------------------------|-------------------------------|
| Quaternary pore water | The area of trona mine | The area of glauber salt mine |
| Contour and elevation | Drainage divide of groundwater | Rivers and lakes |
| Groundwater flow direction | $Y-I$ Groundwater intrush points | $SY-I$ Resident well points |

Fig.4

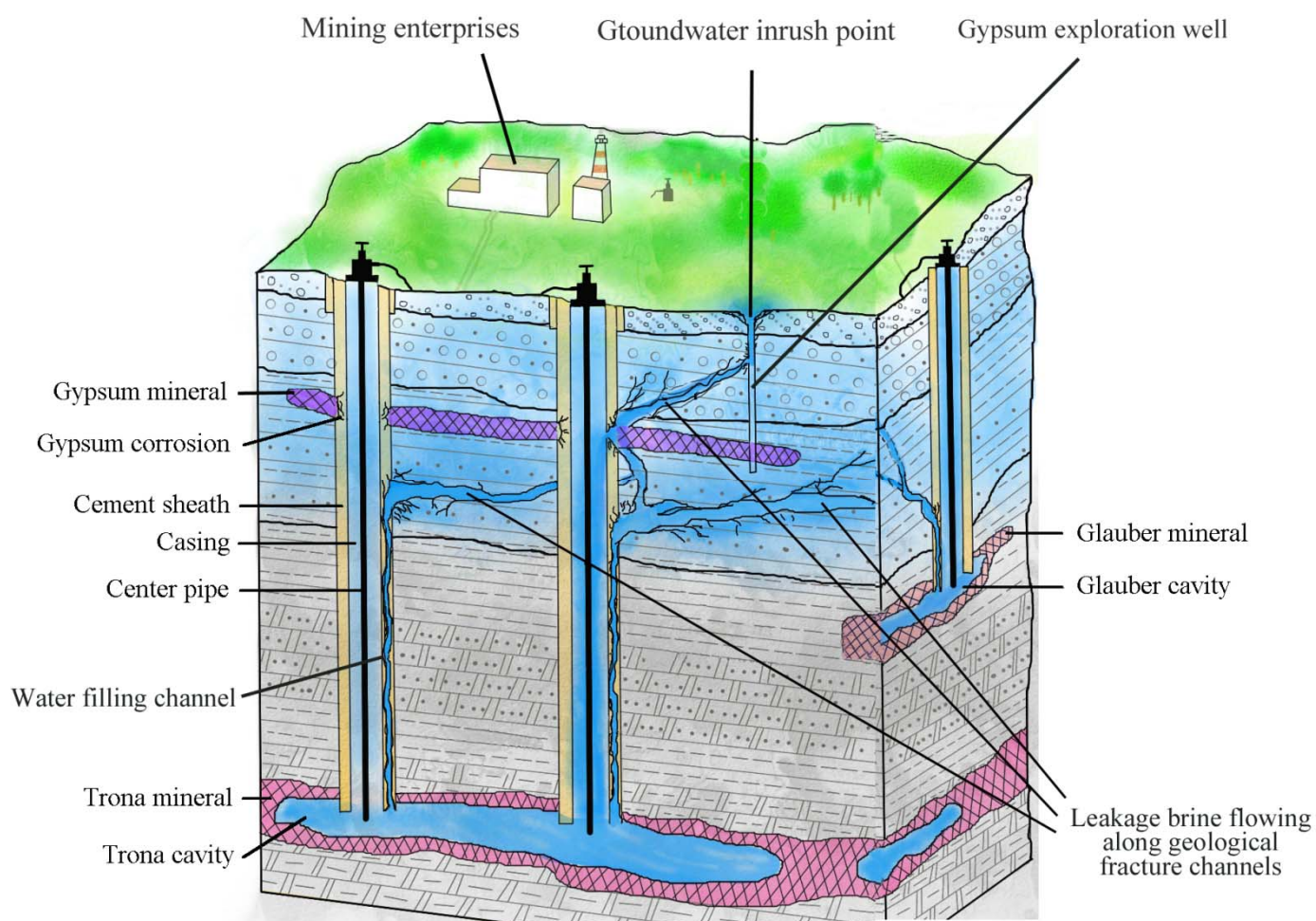


Fig.5

Table 1 Initial data of trona brine and background value of groundwater for the PHREEQC simulation

Type	Temperature (° C)	pH	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
						(mg/L)			
Trona brine	70.0	10.8	85880	5.0	1.0	3819	206.0	104721	4565
Background value of groundwater	14.1	7.5	38.76	67.10	23.88	12.46	39.31	386.87	0.00

Table 2 Chemical composition of groundwater from the inrush hazard points and surrounding resident wells

Source	Point	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	Salinity	Depth
(mg/L)										(m)
Groundwater from inrush hazard points	Y-1	447.30	91.2	74.68	171.18	278.55	1488.89	0.00	1807.35	330.55 ~ 430.2
	Y-2	524.50	89.34	75.32	153.97	298.88	1525.00	0.00	1904.51	
	Y-3	1132.00	146.6	158.30	125.56	4296.44	1012.93	0.00	6365.37	
	Y-4	322.12	98.67	123.88	210.78	346.55	1122.77	0.00	1663.38	
	Y-5	50300.00	12.23	53.21	3813.80	12858.63	81309.15	27159.0	107692.4	
Groundwater from resident wells around the inrush points	SY-1	46.28	76.76	17.29	64.3	14.58	319.03	0.00	378.73	10.00
	SY-2	28.37	98.02	27.46	26.16	10.38	453.84	0.00	417.31	
	SY-3	43.14	46.2	14.42	31.02	117.12	319.03	0.00	316.26	
	SY-4	118.53	278.4	72.3	425.23	175.96	568.52	0.00	1354.68	
	SY-5	31.67	95.51	19.22	53.93	22.59	351.97	0.00	398.9	
	SY-6	36.77	68.82	19.6	18.51	21.55	340.38	0.00	335.43	

Table 3 Simulation results for a mixed proportion of inrush trona brine using the PHREEQC method (mg/L)

Conditions	Mixed proportion with shallow groundwater	Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Trona brine unmixed or mixed with different proportion of shallow groundwater after flowing through the mineral layer (simulation results)	Unmixing	87147.00	301.08	3880.15	68659.20	5.06
	1:1	48093.00	280.00	2145.62	37900.80	9.39
	1:2	33235.00	184.72	1485.68	26188.80	13.97
	1:10	9586.40	148.28	436.30	7561.92	57.95
	1:100	1098.25	90.40	141.63	873.89	306.34
	1:200	571.78	69.60	118.56	459.17	382.17
	1:500	252.77	68.32	104.60	207.84	453.66
Water quality test results in five water inrush hazard points	1:1000	144.81	67.52	99.94	105.12	481.60
	Y-1	447.30	91.20	171.18	276.55	1488.89
	Y-2	524.50	89.34	153.97	298.88	1525.00
	Y-3	1132.00	146.60	125.56	4296.44	1012.93
	Y-4	322.12	98.67	210.78	346.55	1122.77
	Y-5	50300.00	12.23	3813.80	12858.63	81309.15