

Representativeness of Chemical Analysis of Groundwater

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This paper raises the question of the representativeness of a single chemical analysis of groundwater. This is undertaken with the knowledge of the variations in chemical constituents obtained in the groundwater chemistry programme of the Groundwater network of SGU.

The variations in time and space are described for an area of 30 km². The main geological feature of the area is a glaciofluvial esker. The esker is surrounded by littoral sand and till. The measurements show that the pH varies in a similar way in the three types of aquifers, but the variations in alkalinity, calcium content and conductivity are much greater within the till aquifer than in the aquifers consisting of glaciofluvial and littoral material.

An example is also given of the significance of depth and hydrogeological location within a small till aquifer on the level of concentration of some chemical substances in groundwater.

Introduction

This paper gives some examples of the variations in time and space of some groundwater chemical constituents. This knowledge is very important when designing and evaluating groundwater chemistry surveys. In many cases a few chemical analyses are regarded as representing the conditions in large, more or less homogeneous areas. This paper only discusses relatively shallow soil aquifers, which have received special attention in acidification surveys.

The chemical composition of groundwater varies mostly due to the quality of

the aquifer. This is to a great extent determined by the physical and chemical properties of the soil. The chemical composition of groundwater is mostly determined by the:

- reaction velocity between water and minerals
- residence time of water in the aquifer
- contact area between water and minerals

The reaction velocity between water and minerals is determined by the weathering capacity of the rock material contained in the soil. The topography, together with the grain size distribution of the soil, determines the residence time of water in the aquifer, i.e. the time of chemical interaction between water and solid material. The reactive area is reflected by the grain size distribution of the soil.

If the significance of geology, topography and climate are not taken into consideration, there is a great risk of the wrong conclusions being drawn about the cause and effect relationships in chemical surveys. This will naturally also affect the interpretation of the results.

The Observation Area of Tärnsjö

To illustrate some of the natural variations in groundwater chemistry, some examples are shown from the groundwater chemical sampling network at the Geological Survey. The chemical sampling stations are located in the area of Tärnsjö in the province of Västmanland. The bedrock within this area consists mainly of precambrian granite. An esker crosses the moraine landscape in the N-S direction and is split into two branches running parallel towards the north. The surface of the esker has been smoothed by abrasion and is surrounded on each side by redeposited material. Even the top layers of the till deposits have been exposed to wave action. Within the area there are consequently three geologically different types of aquifers, i.e. in glaciofluvial material, littoral sand and in till (Fig. 1).

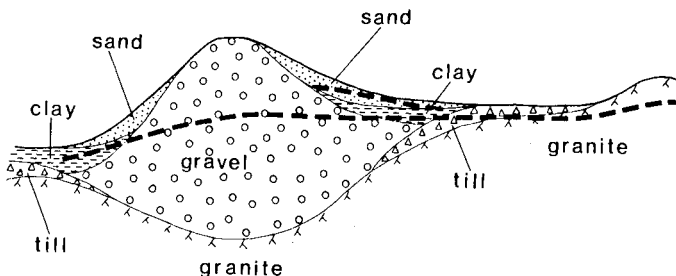


Fig. 1 Schematic picture of different types of soil aquifers within the observation area at Tärnsjö, Västmanland.

Table 1 - Observation stations for groundwater chemistry at Tärnsjö Västmanland.

Geology	Station	Type	Period	Flow (l/s)	Unsaturated zone (m)
Glaciofluvial sand	23 8	Spring	68 - 84	48	15
	23 9	Spring	68 - 84	25	9
	23 15	Spring	71 - 83	4	5
	23 16	Spring	71 - 83	3	8
	23 17	Spring	71 - 83	2	5
Littoral sand	23 11	Spring	70 - 84	0.5	7
	23 14	Spring	71 - 83	4	2
	23 26	Spring	71 - 84	2	1
Till	2 7	Plastic tube	71 - 84		1.5

In these aquifers nine stations with up to 17 years of sampling data have been chosen. The stations in glaciofluvial material and littoral sand are springs with varying discharges (1 l/s up to 50 l/s). In the till aquifer there is only one station consisting of a plastic tube to a depth of about 3 m (Table 1).

For a closer study of the seasonal variations, five stations have been chosen where the measuring frequency is most intense, approximately six times a year (Fig. 3). Stations 23 8 and 23 9 are large springs that discharge from the esker, one from each branch, which consist of glaciofluvial sand. Stations 23 11 and 23 26 are small springs located in littoral sand.

Dependence of Geological Composition on Groundwater Chemistry

The geological composition of a soil aquifer includes both the soil type and its mineral and bedrock composition. Aquifers are not always homogeneous in respect to soil type. The water discharging from some springs has flowed through several soil types, thus causing a very mixed water chemistry.

There is a great difference between the salt content of a pure littoral sand aquifer (Station 23 11, 6.0 mS/m) and a till aquifer (Station 23 7, 28.5 mS/m). The till is an unsorted soil type that contains more fine material than the sorted littoral sand and thus has a larger reactive area. The salt contents of the large springs that discharge from the esker (23 8 and 23 9) are between the extremes of the till and the littoral sand aquifers. (Table 2).

The distributions of pH and alkalinity for different soil types are shown in Fig. 2. In spite of the fact that the till aquifer is represented by only one station its

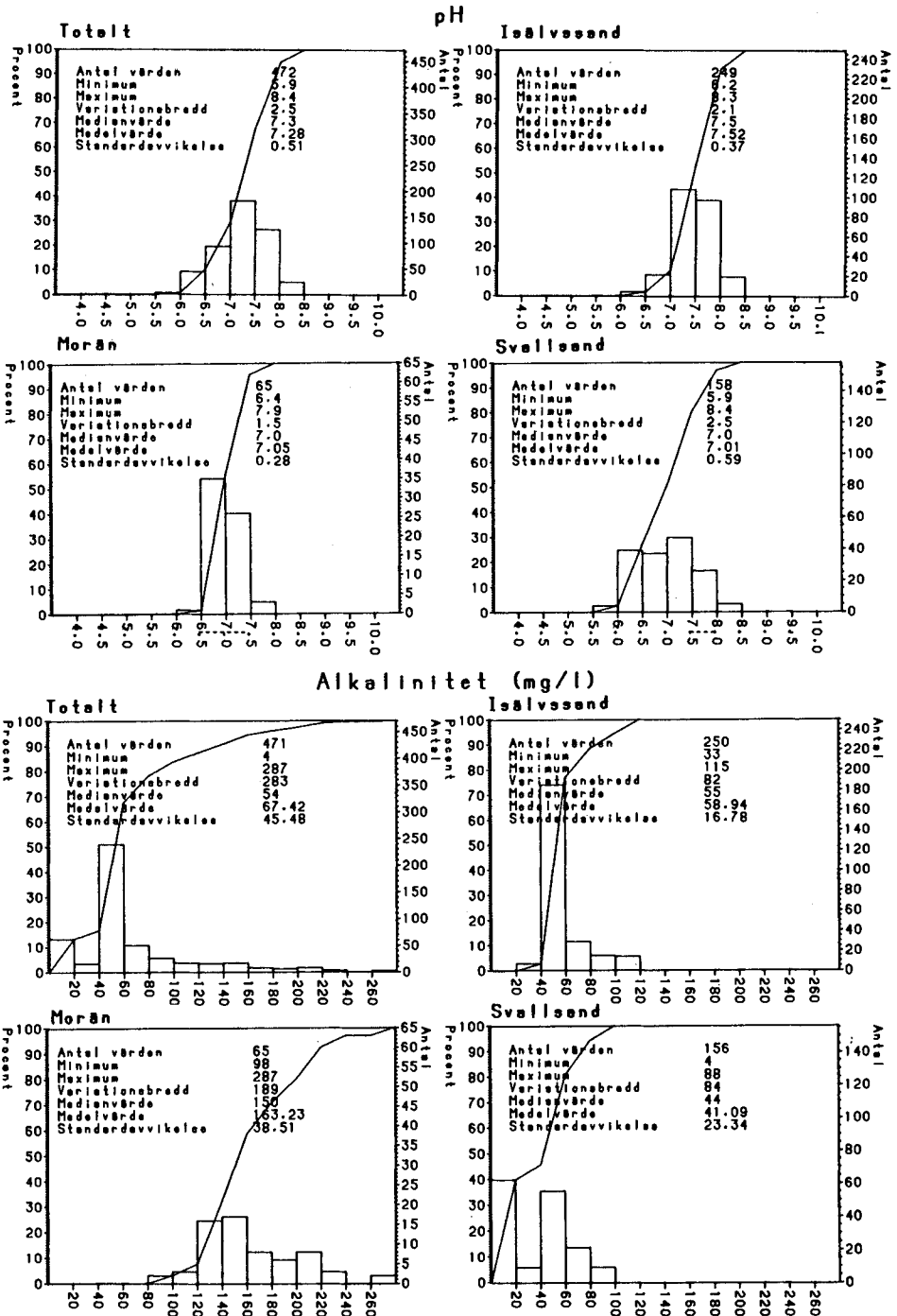


Fig. 2. Distribution of pH and alkalinity of groundwater in different geological settings at Tärnsjö, Västmanland. Isälvsand = glaciofluvial sand, morän = till, svallsand = littoral sand.

Chemical Analysis of Groundwater

Table 2 – Means and standard deviations for specific conductivity, pH, bicarbonate and calcium.

Geology	Station	H ₂₅ (mS/m)		pH		HCO ₃ (mg/l)		Ca(mg/l)	
		Mean	Std	Mean	Std	Mean	Std	Mean	Std
Glacio-fluvial sand	23 8	11.6	1.4	7.4	0.3	51	5	16.8	1.3
	23 9	14.5	2.8	7.8	0.3	60	4	21.6	2.1
	23 15	26.4	3.1	7.6	0.3	101	7	37.5	3.1
	23 16	12.7	2.2	7.3	0.4	48	3	16.9	1.5
	23 17	12.3	1.7	7.3	0.3	47	6	17.0	2.1
Littoral sand	23 11	6.0	2.1	7.1	0.4	17	3	7.0	1.1
	23 14	16.2	2.1	7.8	0.3	80	4	25.6	2.0
	23 26	20.1	4.3	6.6	0.5	50	6	20.7	3.7
Till	23 7	28.7	7.5	7.1	0.3	162	38	36.1	9.1

variation in alkalinity is more than twice that of the glaciofluvial sand (5 stations) and the littoral sand aquifers (3 stations). The variation in pH shows the opposite relationship.

The lowest alkalinity values appear in the littoral sand aquifers. The bimodal distribution reveals the great difference between the separate littoral sand aquifers (Table 2). Springs 23 14 and 23 26 differ markedly from the pure littoral sand aquifer 23 11. This is due to the fact that though the springs are located in sandy aquifers the water discharging has flowed through a clay area and a till aquifer respectively.

The most uniform picture of both pH and alkalinity is shown by the springs in glaciofluvial material. In spite of the great differences both in discharge and thickness of the unsaturated zone.

Springs 23 9 and 23 15 have in general higher values for salt content, pH, alkalinity and calcium. This is due to the location in the eastern branch of the esker, which contains some material of cambrosilurian origin. This fact makes the groundwater in these springs closer to bicarbonate saturation than the water from the springs in the western branch. The bicarbonate concentration varies between 50 and 115 mg/l in the eastern branch but it is only 30 to 60 mg/l in the western one. The pH values are about 0.5 units higher in the eastern branch.

Seasonal Variation of Groundwater Chemistry

The chemical composition of groundwater changes more or less with time. This is true for the relative concentration of the ions as well as for the total salt content.

Reasons for natural variations may include:

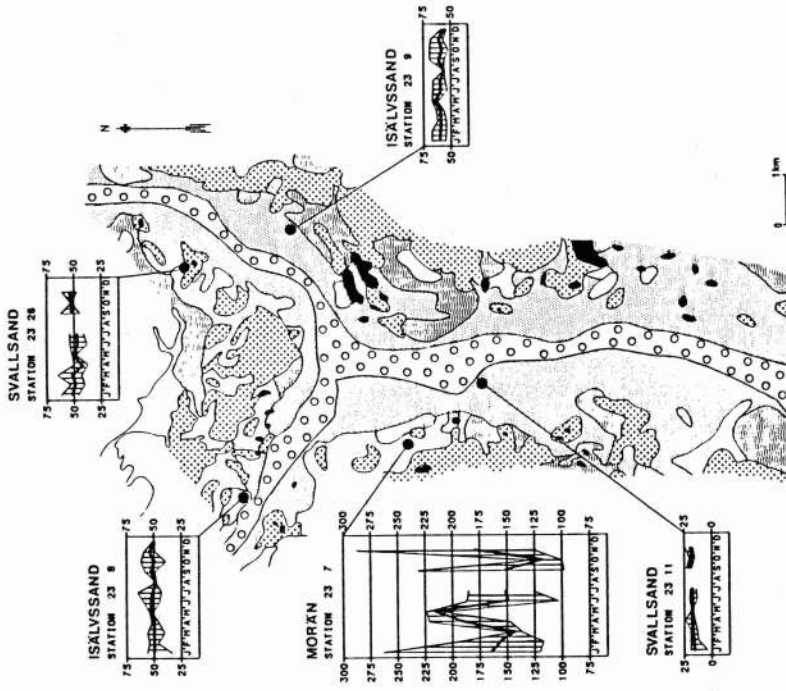


Fig. 4. Seasonal variations of alkalinity (as HCO_3 , mg/l) at Tärnsjö, Västmanland. The coarse lines show the monthly means. The hatched areas show the range of variation.

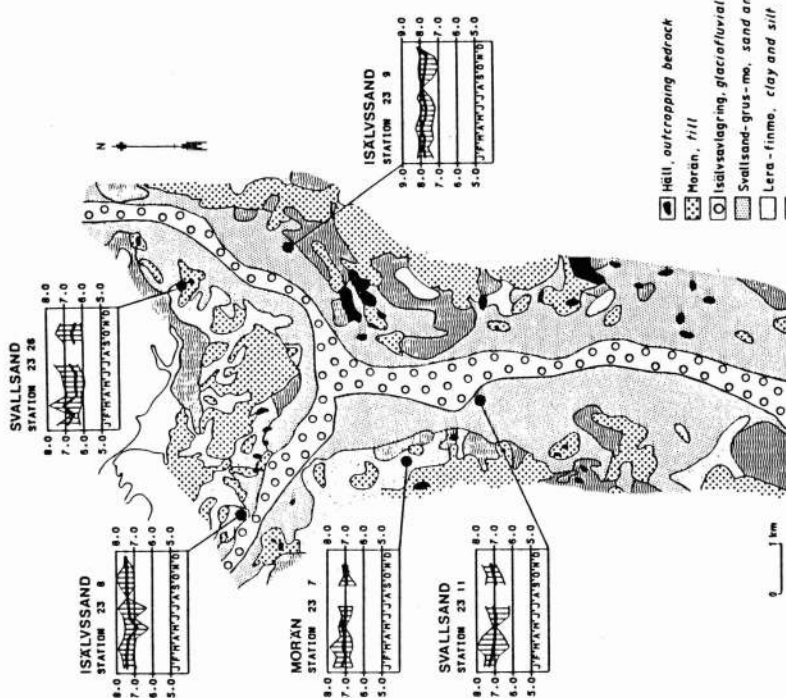


Fig. 3. Seasonal variations of pH at Tärnsjö, Västmanland. The coarse lines show the monthly means. The hatched areas show the range of variation.

- Supply by groundwater from different parts of the aquifer in connection with changes in groundwater level.
- Changes in groundwater level which cause changes of redox situation, effecting ions involved in the redox processes (SO_4 , Fe, Mn).
- Changes in the chemical composition of precipitation.

The graphs in Figs. 3 and 4 show monthly means, monthly minimums and monthly maximums of pH and alkalinity (as HCO_3 , mg/l). Clear seasonal variations of the bicarbonate concentration can only be noticed in the groundwater from the till aquifer. The range is, however, extensive for the single months. The springs discharging from the glaciofluvial and littoral sand aquifers lack regular variation patterns. A minimum may possibly be distinguished in April in the water from the spring in the littoral sand aquifer (23 26). This spring is, however, also receiving water from a till area. Seasonal variations of pH can not be revealed from any of the three types of aquifers.

The reasons why the two stations in glaciofluvial material do not show any seasonal variations, can be explained by the fact that the unsaturated zones are very extensive and the groundwater reservoirs are huge. This causes the differences in the chemistry of the percolating water to be subdued before reaching the springs.

Dependence of Groundwater Level on Groundwater Chemistry

The response of the groundwater level on supplied precipitation depends on the pore volume of the aquifer. The variation of groundwater level is greatest in the till aquifer. The fluctuations in the littoral sand aquifers are significantly smaller and the aquifers in glaciofluvial sand exhibit very subdued oscillation of the groundwater level.

In spite of the greater oscillation of the groundwater level in the littoral sand than in the glaciofluvial sand, the fluctuations of alkalinity in Station 23 11 are significantly smaller than those of the groundwater from the sampling stations in glaciofluvial sand (Fig. 4). When comparing the fluctuations in the chemical composition of groundwater from the sampling station in the till aquifer at Tärnsjö with other stations in till aquifers with large amplitudes in the groundwater level, fluctuations of much smaller magnitudes are obtained. Fluctuations in groundwater level alone are not sufficient explanation for the variation in groundwater chemistry, but may contribute to any or some of the reasons to natural variations mentioned above.

A reasonable explanation for the variations in groundwater chemistry at the sampling station in the till aquifer at Tärnsjö is that the sampling tube is situated just at the outskirts of the till area. The till continues down under a layer of clay. The graph in Fig. 5 shows that the high concentrations of bicarbonate coincides

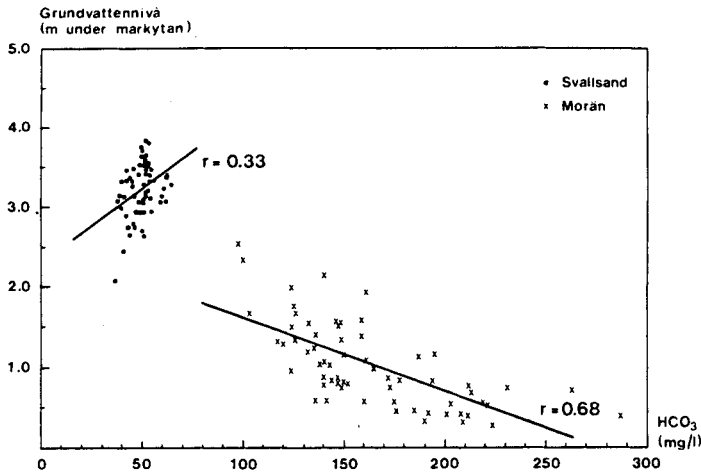


Fig. 5. The relationship between alkalinity (as HCO₃, mg/l) and groundwater level in a till aquifer and a littoral sand aquifer at Tärnsjö, Västmanland. [Grundvattennivå (m under markytan) = groundwater level. (m below ground level)].

with the high groundwater levels. The tube that during periods of low or intermediate groundwater levels receives water from the till, also receives water with higher ion concentrations from the clay area during periods of high groundwater levels. It might also be the explanation for the fact that Station 23 7 has its maximum ion concentration when Station 23 26 has its minimum. At Station 23 26 the reason for the minimum is probably due to the effect of dilution after snow-melt. The correlation between the groundwater level and bicarbonate concentration is very poor in the littoral sand aquifer ($r = 0.33$). There is no correlation between pH and groundwater level in the littoral sand and the till aquifers ($r = 0.08$ and $r = 0.22$).

A study of water from natural springs in a forested area just south of Stockholm shows that pH is poorly correlated with the discharge. The alkalinity of the water from some springs increases with decreasing discharge, while no correlation at all could be found in water from other springs (Samuelsson 1983).

Dependence of Topographic Site on Groundwater Chemistry

The small scale relief of the landscape is of utmost importance for the chemical composition of shallow groundwater. A landscape with strongly broken small scale relief gives repeatedly areas of recharge and discharge and short residence time of the shallow groundwater in the aquifer. This results generally in a groundwater with low salt content and thus a low buffering capacity.

As an example of the variation in groundwater chemistry within an aquifer,

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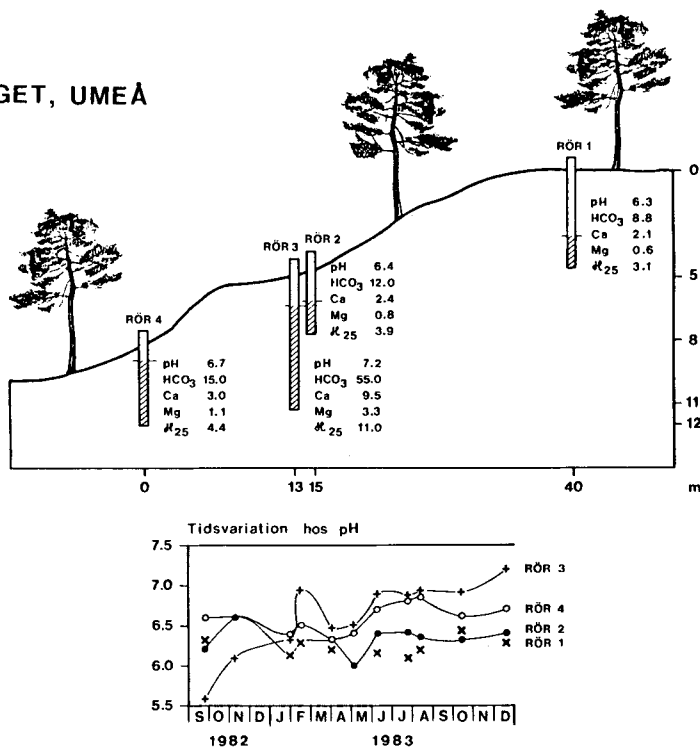


Fig. 6. The chemical composition of groundwater (83-12-14) in a till profile at Svartberget, Västbotten. An illustration of the significance of topography and depth on the chemical composition of groundwater. [Rör = tube].

depending on the hydrogeological site and depth, a profile from an observation area (Svartberget) in the county of Västerbotten is shown in Fig. 6. Four observation tubes were established in a small slope from the water divide down the slope almost to the recharge area. The soil cover consists of till. The distance between tube 1 and tube 4 is only 40 m. Between these two tubes another two were drilled close to each other to depths of 3 and 6 m. The lowest metre of each tube is screened. It is evident (Fig. 6) that the ion content of the groundwater increases steadily from the recharge area down the slope. The concentration of bicarbonate doubles while the concentration of hydrogen decreases, that is, the pH increases. A comparison between the chemistry of the groundwater at different depths in the tubes 2 and 3 shows that both the calcium and the bicarbonate concentrations are four times as high at six m depth as they are at three m depth. Even the pH is almost one unit higher at the deeper level. The change in pH from September 1982 to December 1983 is also shown in Fig. 6.

Similar results were obtained in a study of a till covered area at Kloten (Lundin 1982).

Conclusions

The geological composition of the soil aquifers is of vital importance to the chemistry of the groundwater. The soil texture as well as the geochemical composition of the soil gives the groundwater its chemical status.

The evaluation of the groundwater chemical data from the Tärnsjö area in the county of Västmanland shows that no regular seasonal variations in pH can be found. The range of pH seems to be independent of the geological composition of the aquifer (Fig. 3). Distinct seasonal variations of alkalinity of the water from the glaciofluvial and littoral sand aquifers do not exist, and the range within the months is small. On the other hand there is a distinct seasonal variation of alkalinity in the till aquifer.

There is no correlation between groundwater level and pH and alkalinity. Factors determining how the groundwater chemistry is affected by the groundwater level are:

- activation of different parts of the aquifer
- dilution conditions
- redox processes (oxidation at low groundwater level)

An example of the significance of the topography to groundwater chemistry is shown in Fig. 6. It is found that the sampling depth is of the utmost importance. There is a fourfold increase in the alkalinity and calcium concentrations and an increase of one pH-unit from the sampling depth of 3 m to that of 6 m. This gives an indication of the natural variations which can occur within a small till area.

The most representative chemical analysis in both time and space will be obtained by sampling in the huge soil aquifers that have considerable turnover.

References

- Lundin, L. (1982) Soil moisture and groundwater in till soil and the significance of soil type for runoff. UNGI Report No. 56, Uppsala, Sweden.
- Samuelsson, M. (1983) Shallow groundwater chemistry and turnover. Trita-Kut 3023, KTH, Stockholm, Sweden. (In Swedish)

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