HEAVY METALS IN STOCKHOLM GROUNDWATER – CONCENTRATIONS AND FLUXES

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Abstract. Sampling of groundwater in the Quaternary deposits was carried out at 70 sites in Stockholm for, among other things, metal analyses. The objectives were to get a notion of the metal content and to get a basis for an estimation of the order of magnitude of the groundwater transported metal contribution to the main surface water bodies in comparison to other routes. Thus, in three watershed areas within the Stockholm Town, groundwater flow and metal concentration propagation were simulated and metal fluxes were calculated. The concentrations of heavy metals were in general found to be very high in comparison with groundwater in forested areas. This was most pronounced for mercury (Hg) and copper (Cu). The most remarkable result was a Hg concentration of 4.57 μg L^{-1} in the vicinity of a closed down hospital. The annual contribution of heavy metals (kg) by groundwater to the main surface water bodies was estimated to: As (2.2), Cd (0.20), Co (4.9), Cr (3.1), Cu (34), Hg (0.06), Ni (28), Pb (2.2) Zn (118). These fluxes are much smaller than those in forest ecosystems, due to lower groundwater recharge in urban areas, where a great part of the runoff is diverted by landsealing, drainage, tunnels etc. The modeling results emphasize the importance of the sorption processes indicating that the modeled areas are in a non-steady state condition. It also shows that the sources generating elevated concentrations of the high adsorptive metals Pb and Hg are likely to be nearby.

Keywords: groundwater, heavy metals

1. Introduction

Groundwater can be considered both as a storage of metals, as the movement in the groundwater zone generally is quite slow, and as a transporting agent for metals. In natural ecosystems it is the only agent for horizontal transport within recharge areas. In urban areas like Stockholm, human impacts have changed the conditions. Infiltration and groundwater recharge are greatly inhibited by land sealing and water is carried away by drainage systems. Tunnels and other subsurface constructions affect groundwater levels and flow directions.

Stockholm has existed as a town for more than 700 years. During that period the soil has become heavily polluted (Linde and Öborn, 1999) by industry, waste deposits, sewage, traffic, constructions, by accidents etc. It has been assumed that the groundwater pollution in the urban area is considerable, but the knowledge has been very poor. A reason why the interest for groundwater quality control has been so weak, is that Stockholm Town relies on surface water for drinking water supply.

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A new borne interest has, however, aroused with the awareness of groundwater quantity and quality being of importance to other parts of the ecosystem as it seeps out into lakes and watercourses. Groundwater discharges to springs and wetlands, which are of importance to vegetation and animal life. Both quantity and quality of groundwater will probably affect biota.

The objectives of the investigation have been:

– to get a notion of the heavy metal concentrations in Stockholm groundwater, and
– to estimate the metal fluxes with groundwater, in order to reveal the importance of this transporting agent compared to other for the input to the Lake Mälaren and The Baltic Sea (Saltsjön).

2. Material and Methods

Hydrogeological mapping based on available information preceded the groundwater quality investigation. Groundwater resources, divides and flow directions are presented in digitally produced hydrogeological and vulnerability maps (Environment and Health Protection Administration in Stockholm (EHPAS), 1997).

There is only one significant groundwater resource in Stockholm, the Stockholm Esker, which transverse the town in a NNV-SSE direction. Parts of the esker, which are uncovered by clay, are important recharge areas, in elevated areas even to adjacent groundwater bodies. Valleys covered by clay and in lowlands by peat otherwise characterize the Stockholm region. The glacial till underlying the clays contains groundwater, often in amounts enough to provide a couple of households with drinking water. These water resources are of insignificant importance for the water supply of Stockholm Town. On the other hand they might be of importance as transporting agents for pollutants towards discharge areas, which finally are the Lake Mälaren and the Baltic Sea (Saltsjön).

2.1. Prerequisite for groundwater sampling in Stockholm

In Stockholm Town, there are about 1200 groundwater level observation tubes. Out of these, 800 are monitored with certain frequencies, foremost for geotechnical reasons, which implies that they are mainly strategically situated in sensitive clay areas. The piezometric head is thus measured in groundwater of layers beneath the clay. Sometimes also in superficial fillings covering the impermeable clays. Observation tubes in the sand and gravel of the esker are unfortunately scarce. A selection of the observation tubes has been used for sampling. They are made of polyethene with a diameter of 9 mm. They are equipped with a ceramic filter with a pore width of 1 to 3 μm. In addition to these existing observation tubes, 19 polyethene tubes, 45 mm in diameter, were installed with filters in the groundwater fluctuation zone. One deep borehole in the bedrock and a newly drilled energy well in the esker were also sampled.

2.2. CRITERIAS FOR SELECTION OF SAMPLING SITES

Areas for groundwater sampling were selected according to special criterias, which include different types of existing or previous polluting activities. Within the chosen areas, existing groundwater level observation tubes were used for sampling. As the sampling was restricted to existing sites (with the exception of the 19 tubes, which were established during the course of the project), the selection could be considered conditionally made at random. Ten areas were selected at random, to get a fairly representative picture of groundwater quality in general. Sampling of heavy metals was carried out at 70 sites (Figure 1).

2.3. CHEMICAL VARIABLES AND ANALYTICAL METHODS

Groundwater sampling was carried out with a suction pump after turn-over of the water included in the observation tubes. The samples for metal analyses were collected in acid cleaned polyethene bottles after filtering through 0.45 μm membrane filter. They were preserved with nitric acid, suprapur. All other analyses were made on unfiltered samples. The water samples for Hg-tot analyses were collected in extensively cleaned teflon bottles. They were not filtered nor preserved. The sampling was conducted according to a clean procedure adopted in the Swedish National Groundwater Monitoring Program (Nordic Council of Ministers, 1988). The base cations [sodium (Na), potassium (K), calcium (Ca), magnesium (Mg)] were analysed with ICP-AES; the other metals [arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn)] with the exception of mercury (Hg) were analysed using ICP-MS, alkalinity with autotitrator and sulphate (SO_4) and chloride (Cl) with IC. These analyses were made by SGAB laboratory, Luleå. Hg was analysed with Au-CVAFS by the Swedish Environmental Research Institute, Gothenburg.

2.4. MODELING APPROACH

The aim of the modeling was to estimate the contribution by groundwater to the leakage of metals into the Lake Mälaren and the Baltic Sea. The calculation was made on yearly basis. Ideally the amount of metals equals the yearly volume of groundwater leaving the catchment at the border-line to surface water (Lake Mälaren or Baltic Sea) multiplied by the concentration at the border-line (or the integrated concentration along the border-line).

The modeling was conducted in two steps, the first step being the modeling of groundwater flow with the 3D finite-difference groundwater flow model MODFLOW (McDonald and Harbaugh, 1988). The second step, transport modeling, aims at getting a better understanding of the metal concentration distribution within the watersheds, time perspective of the transport and a fairly good estimate of the metal concentration in the zone of discharge into the lakes. The transport model

used is referred to as MT3D, which simulates advection, dispersion and chemical reactions of contaminants in groundwater flow systems in either two or three dimensions (Zheng, 1990). The MT3D model is linked to MODFLOW.

The partial differential equation describing three-dimensional transport of contaminants in groundwater can be written as follows (e.g. Javandel *et al.*, 1984):

$$\partial C/\partial t = \partial/\partial x_i(\mathrm{D}_{ij}\partial C/\partial x_j) - \partial/\partial x_i(v_i C) + q_s/\theta C_s + \sum_{k=1}^{N} R_k$$

where the first term on the right side is the expression for dispersion, the second advection, the third sources and sinks and the forth is a chemical reaction term. For many practical problems concerning contaminant transport in groundwater, the advection term dominates. For transport of heavy metals the sorption plays a very important role. The sorption, equilibrium-controlled linear or non-linear, is included in the chemical reaction term. The functional relationship between the dissolved and sorbed concentrations is called the sorption isotherm.

There are three types of isotherms in the model, which are built in to the retardation factor R. One of them, the Freundlich isotherm, is a non-linear isotherm and is expressed as:

$$C_{sb} = K_d C^a,$$

where C_{sb} is the sorbed concentration, K_d is called the distribution coefficient or Freundlich constant $(cm^3/g)^a$, a is the Freundlich exponent (dimensionless). K_d and a are empirical coefficients. When a = 1, the sorbed concentration (C_{sb}) is directly proportional to the dissolved concentration (C), in which case the Freundlich isotherm is an expression for a linear sorption isotherm.

The K_d and a for the different heavy metals are dependent on the soil properties. Buchter et al.(1989) related the retention parameters K_d and Freundlich exponent a of 15 elements by 11 soils from 10 soil orders to basic properties of the soil and elements. They found that pH is the most important soil property that affects K_d and a, that CEC influences K_d for cation species, that the amounts of amorphous iron oxides, aluminum oxides and amorphous material in soils influence both cation and anion retention parameters. They also state that there exist significant relationships between soil properties and retention parameters even in a group of soils with greatly different characteristics. In the absence of experimentally estimated K_d values for the Stockholm soils we have been directed to literature. Bearing in mind that the variations in the saturated zone ought to be of minor importance compared to the unsaturated zone, the results achieved by Buchter *et al.* (1989) have been used. The values have been transformed to fit the assumed prevailing soil properties in Stockholm with regard to pH, amount of amorphous Al_2O_3 and Fe_2O_3 (7.5, 0.5% and 0.25% respectively). The retention parameters used for modeling of heavy metal transport are shown in Table I below.

TABLE I

K_d and of Freundlich exponent a values which were used for the transport model (modified from Buchter *et al.*, 1989)

Element	K_d (cm^3/g)	Freundlich exp. a
Hg	115	1.008
Pb	1096	1.485
Cd	216	0.62
Co	138	0.62
Ni	117	0.62
Cu	1549	0.75
Zn	272	0.62
Cr	6.17	0.79
As	49	0.648

2.5. CHARACTERIZATION OF THE CATCHMENT AREAS WHERE SIMULATIONS WERE CONDUCTED

Simulation of groundwater flow and transport of heavy metals was conducted in three catchment areas in central Stockholm (see Figure 1). Two areas are situated north of Mälaren/Baltic Sea. They are referred to as Northwest and Northeast areas. The area situated to the south of Lake Mälaren is called South area. All areas include parts of the esker. In the northwest area the esker discharges water into Brunnsviken to the north, while it discharges water into the Salt Lake to the south. In the South area the groundwater from the highest altitudes in the eastern part of the area transverses the esker. The esker serves as an important recharge area. In this area the groundwater flows in till and basal part of glacial clay to discharge in a narrow 'strait' of till into the Årsta Bay, a part of Lake Mälaren. The 'strait' is only approx. 200 m wide.

For the modeling, the areas were divided into two layers, layer 1 and layer 2. The depth of layer 1 was approximated to 4 m, which is an average of the available data on depths of the clay covering the coarser material (friction) in the valleys. Layer 2 has no specified bottom, as this layer has hydraulically been characterized by the transmissivity. The different geological elements making up the catchments are presented in Table II.

The morphology of the surface of layer 2 was adjusted according to the digital altitude database. The fillings that cover parts of the primary geological units are not considered in the set-up, but are considered in the calculation of groundwater recharge.

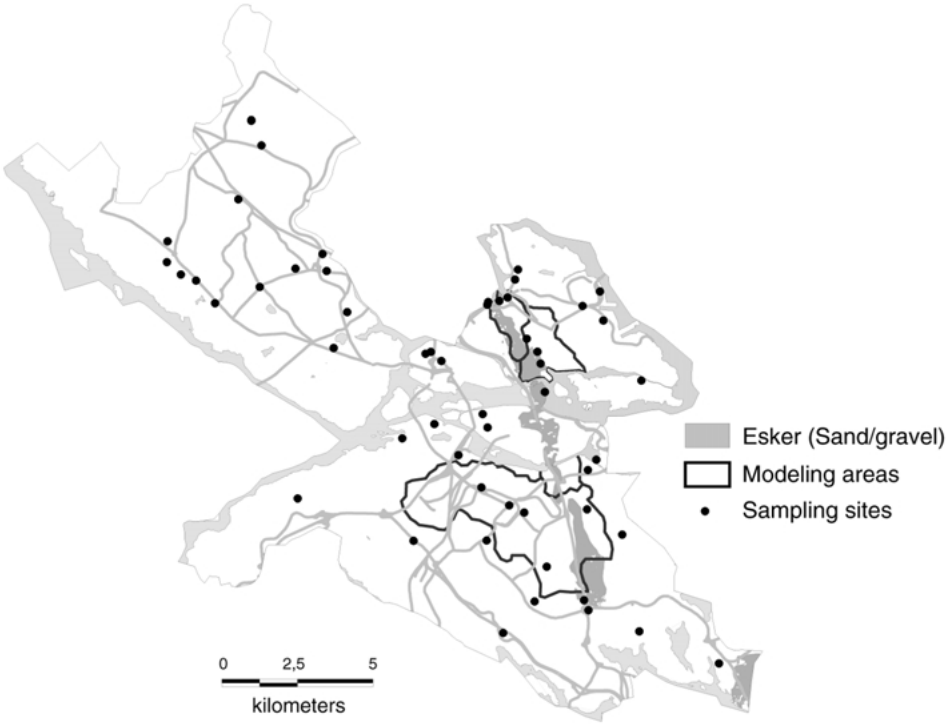

Figure 1. Map over Stockholm Town showing the locations of the modeled catchment areas referred to as Northwest, Northeast and South and the groundwater sampling points. The elongated shaded area is the esker.

TABLE II

Geological elements making up the catchment areas for modeling

Layer	A	B	C	D	E	F
0[a]	–	–	–	–	–	wave washed sand[a]*
1	sand/gravel	clay	clay	till/bedrock	sand/gravel	clay
2	sand/gravel	sand/gravel	friction	Bedrock	bedrock[b]	mixture[c]

[a] Wave washed sand is not included in the modeling set-up.
[b] Is really low permeability material and could also consist of basal till.
[c] Could repeatedly be sand/gravel, till and bedrock in border zones where the knowledge of the extension of the different geological units is poor.

2.5.1. *The Northern Catchment Areas*

The two northern catchments (Figure 1) were treated as one area in the modeling. The Northwest area is 1.76 km^2, while the Northeast is 3.04 km^2. Sources and sinks are bound to layer 1. There is no flow allowed across the boundaries of the modeling area, but across the water divide between the two catchment areas. There

TABLE III
Hydraulic properties of the geological units in the Northern areas

Unit	Layer 1				Layer 2		
	Conductivity m/s	Leakage factor	Porosity total	Porosity effective	Transmissivity m^2/s	Porosity total	Porosity effective
A	5.8×10^{-2}	10000	0.45	0.20	2.3×10^{-2}	0.40	0.20
B	1.2×10^{-5}	100	0.45	0.01	6.9×10^{-3}	0.40	0.20
C	1.2×10^{-5}	100	0.45	0.01	1.2×10^{-3}	0.40	0.20
D	5.8×10^{-5}	0.2	0.05	0.01	5.8×10^{-6}	0.05	0.02
E	9.3×10^{-3}	–	0.20	0.20	5.8×10^{-6}	0.05	0.02
F	1.2×10^{-5}	100	0.45	0.01	5.8×10^{-5}	0.40	0.20
B/C	1.2×10^{-5}	100	0.45	0.01			
A'					1.2×10^{-2}	0.40	0.20
C'					3.5×10^{-3}	0.40	0.20
D'					3.5×10^{-6}	0.05	0.02
D"					3.5×10^{-7}	0.05	0.02

are fixed levels of groundwater in layer 2 on the border to Brunnsviken and Lake Mälaren/Salt Lake (sea level). The sizes of the cells within the grid were 50 m × 50 m. The mean yearly recharge in this modeling area was calculated to 40 mm.

The hydraulic properties of the different geological units outlined in Table II are presented in Table III.

2.5.2. *The South Cathcment Area*

The South catchment area is 15.9 km^2. The esker, which transvers the high altitude eastern part of the catchment constitutes an important recharge area. The groundwater from there mainly flows in the coarser material under the clays in an eastern direction towards the outlet to Lake Mälaren (Årstaviken) The modeling approach is somewhat different from that applied in the northern catchments. The area is drained by artificial drains and by a small stream called Valla å. Drains were included in the modeling set-up with conductances to keep the groundwater head at measured levels. Different groundwater recharge values were set at the different geological units of the first layer. Thus 300 mm were set for the esker (A), 80 mm for the clay (C) and till/bedrock (D) and 150 mm for the recharge area consisting of glacio-fluvial sand/gravel on bedrock (E). The cell sizes within the grid were 167 m × 167 m.

The hydraulic properties of the geological units in the southern catchment areas are presented in Table IV. Two geological units are added, namely wetland with impermeable bottom, denoted G and wetland with minor leakage, denoted G'.

TABLE IV
Hydraulic properties of the geological units in the South area

Unit	Layer 1				Layer 2		
	Conductivity m/s	Leakage factor	Porosity total	Porosity effective	Transmissivity m^2/s	Porosity total	Porosity effective
A	2.3×10^{-1}	10000	0.40	0.20	2.9×10^{-2}	0.40	0.20
B	5.8×10^{-6}	50	0.50	0.01	2.3×10^{-3}	0.40	0.20
C	1.2×10^{-5}	10	0.45	0.01	1.7×10^{-3}	0.40	0.20
D	5.8×10^{-5}	0.2	0.05	0.01	5.8–29 $\times 10^{-6}$	0.05	0.02
E	9.3×10^{-2}	0.01	0.20	0.20			
G	1.2×10^{-5}	1	0.45	0.01			
C'	1.2×10^{-5}	1	0.45	0.01	9.2×10^{-3}	0.40	0.20
E'	5.8	1	0.40	0.20			
G'	5.8×10^{-5}	20	0.05	0.01			
A'					1.2×10^{-2}	0.40	0.20
B'					1.2×10^{-2}	0.40	0.20
C"					1.2×10^{-4}	0.40	0.20

3. Results

3.1. General groundwater quality – conditions for the behavior of heavy metals

The Stockholm groundwater generally has high electrical conductivity (66 mS/m), pH (7.5) and TOC (13.2 mg L^{-1}) compared to median values in Sweden (16 mS/m, 6.4 and 3.4 respectively). Especially calcium (111 mg L^{-1}), alkalinity (360 mg L^{-1} as HCO_3), sodium and chloride (62 mg L^{-1}) concentrations are remarkably high. The concentrations are 6–10 times higher than the country average and about double the concentrations for the region, which, for Swedish standards, has very high total hardness and alkalinity due to high calcareous content in the soils. Low nitrate concentrations in relation to ammonium concentrations indicate low redox potential in the groundwater under the clay.

3.2. Concentrations of heavy metals

The groundwater of practically all (92%) sampling sites had elevated concentrations of at least one of the analyzed metals. Elevated in this context is defined as a concentration, which exceeds the median concentration in groundwater of forested areas more than five times. The concentrations in forest ecosystems are only affected by deposition of long-transported air-borne metals apart from metals

of geological origin. Table V below presents some statistics on the results from the investigation. Comparisons are made with data from the environmental monitoring of groundwater in forested ecosystems.

Cu diverges most from background followed by Hg and Co (Table VI). Then follows a group of metals, As, Cr, Ni and Pb, with median values that are 4.5 to 3.2 times higher than the background medians. The Cd and Zn have the least elevated median concentrations.

The difference in mean values is usually smaller, much smaller for Cu and Co, indicating that the concentration of these metals are more evenly distributed in Stockholm compared to groundwater in the forest ecosystem. It is quite natural as the variation in groundwater chemistry is much greater of the monitoring sites in the forest ecosystem, as it includes all different geochemical settings in Sweden. There is no differences between the S/F mean and the S/F medians for As. This indicates a distribution that is equal to that in the forest ecosystem, parallelly displaced. The Cd is an exception as S/F mean is greater than S/F median. The reason is comparatively high Cd concentrations at a couple of sites in Stockholm groundwater.

The percentage of sampling sites with elevated concentrations (see above) for the different metals is as follows:
Hg: 74% > Cu: 69% > Co: 60% > As: 47% > Pb: 33% > Ni: 27% = Cr: 27% > Cd: 17% = Zn: 17%

3.3. Estimation of the storage of heavy metals in groundwater

A rough estimate of the storage of groundwater can be made by multiplying the median value of the different metals with the estimated volume of groundwater in the Quaternary deposits of Stockholm. The total area of Stockholm Town is 190.0 km^2. The area covered by Quaternary deposits is 139.3 km^2. A 2-m groundwater layer on average is assumed in the unconsolidated aquifers. The assumption is based on available knowledge on depth of the Quaternary deposits and the depth to groundwater surface. This means a groundwater holding volume of 0.279 km^3. The assumption of an average porosity of 30% makes the volume of groundwater 0.0835 km^3, which equals 8.358×10^7 m^3. That gives the storage of metals presented in Table VII.

3.4. Heavy metal fluxes with groundwater

This is an estimation of metal transportation without support by the modeling exercise.

The total land area capturing precipitation is 190 km^2. The mean recharge over this area is estimated to 70 mm. The estimation is based on the areal distribution of geological elements and impediments in Stockholm. The groundwater recharge in forest areas is about half of the precipitation and approximately 300 mm in a corresponding geographical location. Land sealing in great parts and areas of thick

TABLE V

Statistics on metals in Stockholm groundwater with comparison to median and mean concentrations in groundwater of forest ecosystems (within brackets). Metal concentrations are given in μg L^{-1} with the exception for Hg, which are given in ng L^{-1}. TOC is given mg L^{-1} and CV in %. When the minimum values equal or are less than the detection limit, the detection limits are given and are underlined

Variable	min	p10	p25	Median		p75	p90	max	n	mean		CV
As	0.3	0.3	*s*	0.54	(0.12)	1.09	2.48	11.7	59	1.03	(0.23)	163
Cd	0.02	0.02	0.02	0.052	(0.027)	0.107	0.178	1.06	70	0.086	(0.038)	156
Co	0.09	0.47	0.80	1.27	(0.21)	2.26	3.66	59.0	70	2.49	(1.29)	273
Cr	0.2	0.21	0.51	0.79	(0.22)	1.13	1.73	7.83	67	1.06	(0.50)	115
Cu	0.2	1.80	3.81	8.63	(0.84)	15.1	24.3	92.9	70	12.6	(3.79)	122
Hg	0.26	3.65	10.6	15.6	(2.0*)	57.4	146	4566	69	121	(16.5*)	435
Ni	1.05	1.95	3.71	7.03	(2.19)	11.6	17.6	89.6	70	9.59	(6.61)	122
Pb	0.1	0.18	0.26	0.56	(0.18)	1.12	1.74	5.52	70	0.85	(0.36)	109
Zn	1.07	5.44	13.5	30.7	(17.0)	57.7	167	369	70	56.1	(33.4)	125
pH	6.40	7.02	7.40	7.50	(6.40)	7.70	7.90	8.80	53	7.47	(–)	6
TOC	3.50	4.83	7.35	9.75	(3.4)	14.1	23.4	69.2	52	12.8	(–)	87

[a]Based on few analyses (Lindquist *et al.*, 1991)

TABLE VI

Quotas between Stockholm and forest ecosystem medians (S/F median) and means (S/F mean)

Quota	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
S/F median	4.5	1.9	6.1	3.6	10.3	7.8	3.2	3.2	1.8
S/F mean	4.5	2.3	1.9	2.1	3.3	7.4	1.5	2.4	1.6

TABLE VII

A rough estimation of the storage (kg) of metals in Stockholm groundwater

As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
45	4.3	106	67	721	1.3	591	47	2566

clay layers reduces the recharge to approx. 70 mm. Without considerable change of groundwater storage on a yearly basis the same amount of water discharge to the surface water systems including the Lake Mälaren and the Baltic Sea. The discharge of groundwater should thus be $70 \times 190.0 \times 10^3$ m^3 yr^{-1} = 1.33×10^7 m^3 yr^{-1}. This figure can be compared with the estimate of the volume of the groundwater storage, which is 8.358×10^7 m^3, which implies that the groundwater volume on average is being turned over in about 6 years.

If the concentration of the heavy metals equals the median at the points of discharge, the contribution by groundwater to surface water would be in the order of magnitude presented in Table VIII.

From this estimation it also can be concluded that the leakage to groundwater from polluted soils and leaking sewage systems etc. should be in these orders of magnitude, assuming steady-state.

TABLE VIII

Rough estimation of heavy metal fluxes (kg yr^{-1}) with groundwater

As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
7.2	0.68	17	11	115	0.21	94	7.5	409

TABLE IX

The yearly groundwater discharge from the three catchments to Lake Mälaren, Baltic Sea and Brunnsviken Bay (m^3 yr^{-1})

Catchment area	Discharge (m^3 yr^{-1}) Total/Esker	Receiving water body
Northwest	72 708/58 765	Brunnsviken Bay
Northeast	113 880/39054	Lake Mälaren/Baltic Sea
South	318 280 (total)	Lake Mälaren (Årstaviken)

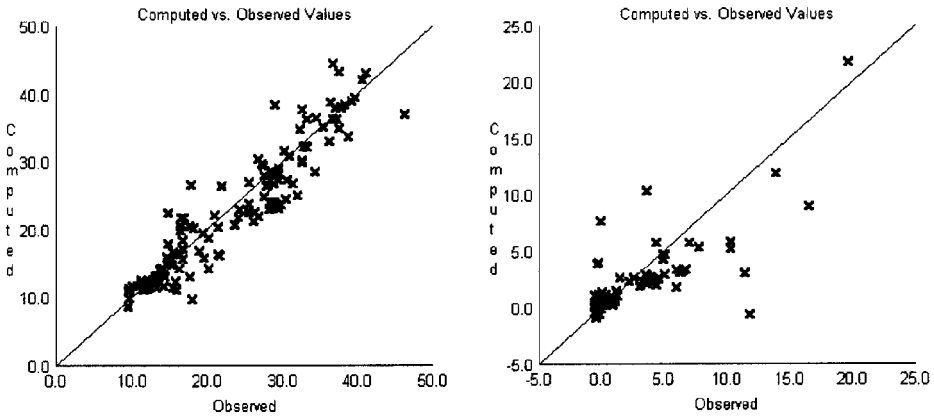

Figure 2. The model is calibrated against observed groundwater levels. Left: South catchment area. Right: Northwest and Northeast catchment areas.

3.5. RESULTS OF MODELING GROUNDWATER FLOW

The simulation with MODFLOW resulted in a more detailed picture of flow directions and figures on the quantity of groundwater leaving the catchments directly to Lake Mälaren, Baltic Sea and Brunnsviken Bay (Table IX).

The model was calibrated against groundwater levels. The calibration results are shown in Figure 2.

The deviations of the simulated groundwater levels was largely attributed to small scale variations in the geology which was not possible to detect with the use of cell sizes. However, the general pattern shows a fairly good agreement with a systematical behavior. In addition, a sensitivity analysis of groundwater recharge in relation to measured groundwater levels indicated that the calibrated groundwater recharge has an accuracy of about 20–30%.

3.6. HANDLING OF METAL CONCENTRATIONS AND TRANSPORT MODELING

The most intriguing issue is to estimate the concentrations of the different heavy metals at the border of discharge to Lake Mälaren, Baltic Sea and Brunnsviken Bay. There are very few sampling sites per area. Few of them are located close to the discharge areas. One station though, in catchment area Northwest is located very close to where the groundwater of the esker discharge to the Brunnsviken Bay and provided reliable metal concentrations for transport calculation at that point. At the other discharge areas of the three catchments, the concentrations predicted by the model simulations have been used. Sampling sites with elevated metal concentrations in groundwater have served as sources, i.e. the initial concentrations of the simulations. Metal concentrations generated by atmospheric deposition have been added to the surface of layer 1. For the calculation of these concentrations, the average of the deposition for the years 1968/69, 75, 80 and 85 has been used. Deposition calculation was based on concentration in mosses in the Stockholm region (Rühling, Å. in Bernes, 1987). The model has been allowed to simulate concentration propagation for different time spans up to 109 years. The concentrations from simulations giving the highest concentrations in the areas of discharge have been used for the transport calculations (Table X). These concentrations are still very low and close to the detection limits and can thus serve as input for calculation of a lower limit of groundwater transported metal contribution. The use of median concentrations (Table V) probably gives a more realistic estimation of the transport. Medians have been used here as the main alternative. To calculate a plausible upper limit of the transport, the 90th percentile values were used (Table V). The extreme outliers of the investigation have thus been excluded. According to the simulation of concentration propagation, these have not had an immediate influence on the concentration in the discharge areas.

The measured and model simulated concentrations (Table X), the 90th percentile and median values (Table V) were multiplied with the yearly discharge (Table IX). These calculations gave a lower and an upper limit and a reasonable magnitude of the yearly contribution of metals by groundwater to the main surface water bodies (Lake Mälaren, Baltic Sea and Brunnsviken Bay). The figures are presented in Table XI.

Most catchment areas in Stockholm have the same geological features as the South catchment area, but without an esker. Small streams also drain them. If thus the area of Stockholm outside the modeled areas is given the same specific groundwater runoff, the contribution from the total area of Stockholm could be estimated, using the median concentrations of the heavy metals. The result of that calculation is presented in table XII.

The rough estimation, which was presented above in Table VIII, gave about 3.4 times higher fluxes. It is not surprising, as only a minor part of the groundwater discharge directly into the main surface water bodies (Lake Mälaren and Baltic

TABLE X

Measured (Northwest A) and model simulated concentrations (μg L^{-1}, Hg in ng L^{-1}) used for transport calculations of heavy metals to Lake Mälaren, Baltic Sea and Brunnsviken Bay. A and C are geological units. A = esker, C = till or sand under clay

Catchment	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Northwest (A)	3.0	0.057	1.17	1.06	10.2	5.69	8.16	0.33	13.2
Northwest (C)	0.01	0.020	0.1	0.50	0.20	2.00	1.00	0.1	3.00
Northeast (A)	2.0	0.020	0.1	1.40	0.40	3.33	0.13	0.1	4.00
Northeast (C)	0.01	0.020	0.15	0.50	0.20	2.0	0.13	0.15	2.50
South (C)	0.15	0.02	0.15	0.70	0.2	5.0	0.25	0.25	3.0

TABLE XI

The annual contribution of heavy metals by groundwater to Lake Mälaren, Baltic Sea and Brunnsviken from the three catchment areas Northwest, Northeast and South in kg

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Lower limit	0.31	0.012	0.13	0.21	0.70	0.0022	0.59	0.12	2.1
Median	0.41	0.026	0.63	0.41	4.5	0.007	3.6	0.27	14
Upper limit	1.28	0.091	1.85	0.87	12.3	0.073	8.9	0.88	84

TABLE XII

The annual contribution of heavy metals by groundwater to Lake Mälaren, Baltic Sea and Brunnsviken from all catchments outside the modeled catchments (Sthlm outside) and the contribution from the modeled catchment areas Northwest, Northeast and South (mod areas) in kg. Calculations based on median concentrations

Catchment	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Sthlm outside	1.8	0.18	4.3	2.7	29	0.053	24	1.9	104
mod areas	0.41	0.026	0.63	0.41	4.5	0.007	3.6	0.27	14
Sthlm total	2.2	0.20	4.9	3.1	34	0.060	28	2.2	118

Sea). The remainder is introduced into streams and small lakes. In urban areas, like Stockholm, it also seeps out into tunnels and other draining constructions.

TABLE XIII

The total flux of the heavy metals investigated, and their direct contribution to Lake Mälaren, Baltic Sea and Brunnsviken Bay (kg yr^{-1})

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Total flux	7.2	0.68	17	11	115	0.21	94	7.5	409
Direct contr.	2.2	0.20	4.9	3.1	34	0.06	28	2.2	118

4. Conclusions and Discussion

The groundwater in Stockholm has elevated concentrations of all heavy metals investigated. Most severe are the extremely high Hg concentrations at one sampling site close to Brunnsviken Bay and the generally high concentrations of Cu. The model simulation shows however that if the source of Hg is close to the sampling site, it has not yet influenced the discharge to Brunnsviken Bay, provided the source has not been there for more than 109 years.

The results on heavy metal concentrations suggest that, apart from point and diffuse polluting sources, the chemical conditions of Stockholm groundwater play a major role for the concentration range. Hence Zn and Cd are the least elevated heavy metals in the groundwater of high pH values. The conditions are more favorable for Hg and Cu, which to a great extent are transported in association with organic matter.

The total storage of heavy metals in groundwater is according to this investigation estimated to be around 4 tons, Zn making up the most of it, approximately 2 tons, while Cu and Ni contribute with more than half a ton each. The storages of the metals of most concern, Pb, Cd and Hg are according to the calculations 47, 4 and 1 kilograms respectively.

The direct contribution of heavy metals to Lake Mälaren, Baltic Sea and the Brunnsviken Bay by groundwater is merely a fraction of the amount totally transported with groundwater. Before it reaches the great bodies of water it flows into streams and small lakes, seeps into tunnels or is drained by the drainage system. The total amount of investigated metals annually transported with groundwater is estimated to about 660 kg, while direct contribution is estimated to 193 kg (estimated lower limit: 18.3 kg; estimated upper limit: 740 kg). The contribution by the different metals is presented in the Table XIII below.

The specific contribution from the catchment areas where the esker has hydraulic connection with the great groundwater bodies are almost two times higher than from the other catchments (1.61/1.86 and 0.99 kg km^{-2} per year).

The transportation of the metals Hg, Cd and Pb with groundwater is much smaller in Stockholm than it is with a shallow groundwater in a forested catchment area

in the middle of Sweden. In the forested catchment area the fluxes of Hg, Cd and Pb were 3.4, 6.3 and 627 g km^{-2}, year (Aastrup *et al.*, 1991 and 1995) compared to the total fluxes in Stockholm, which have been estimated to 1.1, 3.6 and 39.6 g km^{-2}, year respectively. The reason is the small groundwater recharge in the urban area due to land sealing. It implies that the major part of the effective precipitation over the urban area is taking other routes towards Lake Mälaren and the Baltic.

The transport model MT3D is used to simulate transport of pollutants from known sources or rather from the point where the pollution has reached the surface of groundwater. In an urban area like Stockholm, there might be a vast number of sources, point, elongated or diffuse, creating the elevated heavy metal concentrations in groundwater at the scattered sampling sites. The simulation shows how the observed concentrations influence the concentrations down-stream in a time perspective and could have been a good working tool for the estimation of the concentrations at the groundwater outlet to the great water bodies, provided there were no polluting sources downstream the sampling sites. The simulations has, within a 109 years timespan, generated concentrations in the areas of discharge, which are lower, equal to, or very close to the lowest concentrations found in Stockholm. The probability that the concentrations actually would belong to that extreme of the concentration range is very small. The probability is much greater that they will fall within a narrow range around the median. Therefore the median values have been used as the main alternative for the transport calculations. Simulated concentrations of low adsorptive metals like Cr are those coming closest to the median values (compare Tables V and X)

The modeling result has however provided important information. It emphasizes the importance of the sorption processes and indicates thus that the modeled areas are in a non-steady state condition. It also shows that the sources generating elevated concentrations of the high adsorptive metals Pb and Hg are likely to be nearby.

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