Quantification of Acidity Deposition in the Sediment of a former lignite mining lake in the Wackersdorf Mining District (Eastern Bavaria)

Wolfgang Schäfer[1], Matthias Alte[2], Martin Bauer[2], Thomas Söll[3], Stefan Peiffer[4]

[1]Steinbeis Transfer Center for Groundwater Modeling, Wiesloch, Germany,
Wolfgang.Schaefer@schaefer-gwm.de
[2]Base Technologies München, Germany, matthias.alte@base-technologies.com
[3]Büro für geohydraulische Modellrechnungen, Schwäbisch Gmünd, Germany, soell.hgsg@t-online.de
[4]Chair of Hydrology, University of Bayreuth, Germany, s.peiffer@uni-bayreuth.de

Abstract

From 1982 to 2001 acidic conditions prevailed at former lignite mining Lake Knappensee. Since 2001 the acidity of the lake water continuously decreased reaching circum-neutral pH conditions in 2010.

Based on acidity time series of the lake water in combination with water budgets derived from a regional groundwater model the cumulative acidity loss in the lake for the time span from 2001 to 2015 can be estimated to be 8400 kmol.

Internal neutralization by biogenic sulfate reduction with consecutive deposition of reduced sulfur in the lake sediment was supposed to be the crucial process leading to the observed decrease in lake water acidity. In order to test this hypothesis elaborate quantitative field and laboratory investigations were launched in December 2014.

15 sediment cores distributed over the lake`s area were sampled and analyzed for reduced sulfur species at the hydrological laboratory of the University of Bayreuth. The measured sulfur contents were converted into deposited proton equivalents and finally the results were extrapolated for the total lake sediment.

The amount of at least 6400 kmol of acidity deposited and fixed in the lake sediments estimated with this procedure compares well to the acidity-loss of 8400 kmol which was calculated for the lake water as mentioned above.

Measurements and data evaluation allowed for identification of naturally occurring internal neutralization to be the major process for the observed acidity decrease in the lake water. The internal neutralization processes are not only beneficial to the lake water quality, but are also of great practical importance for the assessment of the hydrochemical state of the lake.

The methodology applied to Lake Knappensee consisting of field scale sediment investigations combined with water budgets gained from regional groundwater modeling could also be used for the assessment of the hydrochemical state of other mining lakes.

Key words: Lignite mining lakes, internal neutralization, field scale studies, sulfur deposition

Introduction

Lake Knappensee is located in the former lignite mining area of Wackersdorf, Eastern Bavaria (Germany). The lake has an extension of 52 ha and is embedded in the regional ground and surface water flow regime.

Until the year 2001 the acidity in the lake`s water body amounted to more than 0.5 mmol/l. Lake Knappensee was therefore clearly affected by acidification processes as a result of former lignite mining. As of 2001 lake water acidity continuously decreased reaching acidity values of about zero mmol/l in 2010. Since then the lake water is practically acidity-free (fig. 1). The decrease in acidity also appears in a drop of lake water pH. After remaining at values of about pH=3.5 for many years, it increased to meanwhile neutral values around pH=7 since 2001.

Based on the acidity time series in combination with water budgets derived from a regional groundwater model for the site the cumulative acidity loss in the lake water for the time span from 2001 to 2015 can be estimated to be 8,400 kmol. Constant acidity load from the inflowing groundwater into the lake was assumed for this period.

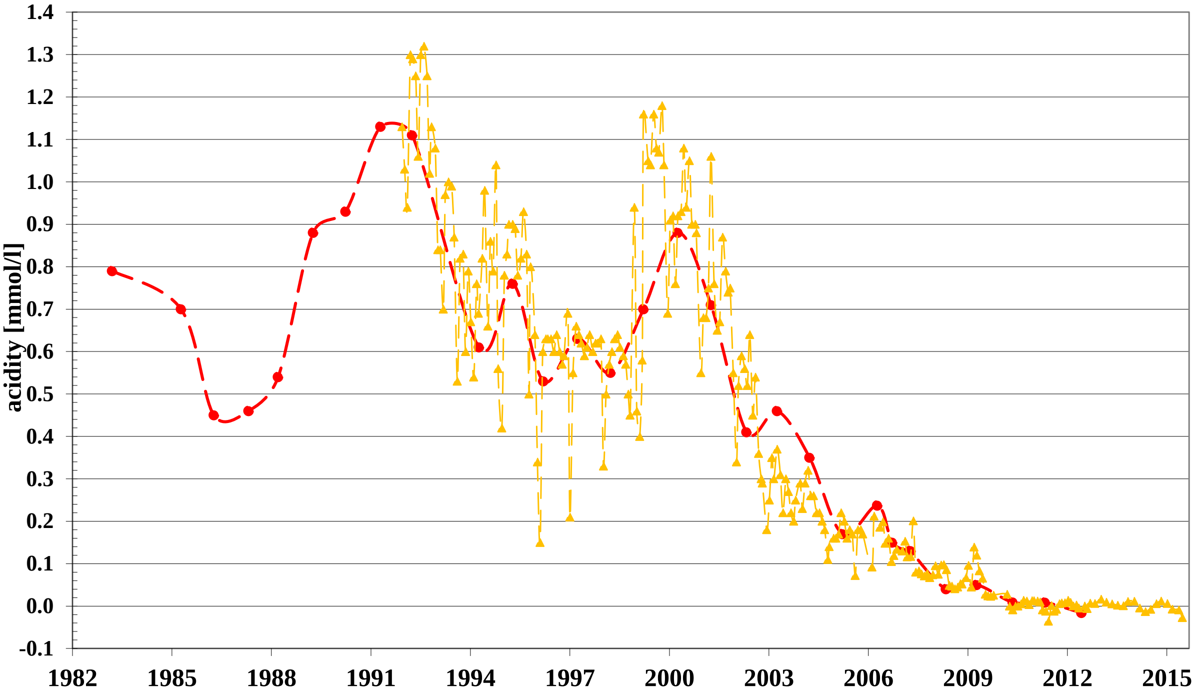

Figure 1 *Time series of acidity values in Lake Knappensee from 1982 to 2015. Red dots show acidities based on measurements from Landesgewerbeanstalt Bayern,yellow triangles are based on measurements from E.ON Kraftwerke*

Processes

Basically several processes could have led to the observed decrease in acidity. In the following these processes are assessed concerning their possible significance for the de-acidification.

First, the assumption of continuous acidity inflow from the surrounding aquifer could be wrong, i.e. the decrease could be caused by decreasing acidity of the inflowing groundwater (flushing of the mining dumps). However, this process is not likely to be the cause of the acidity decrease, as the time scale of the typical residence time of groundwater in the dumps is much larger (> 20 years) than the time scale of the decrease in the lake water (10 years). Furthermore the acidity in the surrounding groundwater entering the lake does not show any decrease since 2001 but is continuously high (> 6 mmol/l). Therefore internal neutralization processes remained as the most likely explanation for the acidity decrease in the lake water.

Transport simulations with a regional scale numerical groundwater/lake model corroborated this assumption. Taking a groundwater inflow showing the acidity observed in the surrounding sampling wells acidity in the lake should remain in the order of 1 mmol/l instead of being neutral. The only way to reproduce the observed acidity decrease in the model was to assume a sink term in the lake itself.

This sink term could be accomplished in principle by alkaline fluids leaking from red mud depositions below the lake bottom. The red mud originated from a nearby aluminum plant and was dumped in the former open pit from December 1965 to April 1973. Later on the red mud depositions were covered by ash layers of up to 20 m thickness. However, the red mud fluids show extremely high pH-values of up to pH=14, while the pH-increase in the lake stopped at circum-neutral pH-values. Thus, it is not very likely that leakage from red mud depositions are the reason for the neutral pH-conditions in the lake. Moreover, red mud influenced fluids should contain high amounts of sodium, but a sodium increase along with the pH increase was not observed in the lake. Finally, the hydraulic situation in the groundwater surrounding the lake with downward hydraulic gradients in the area of the red mud depositions would not allow for flux from red mud into the lake water.

In the end, biogenic neutralization remains the only probable mechanism that could act as an acidity consuming sink term. The northern half of the lake is characterized by low water depth (mostly < 2 m) and an extensive growth of partially submersed bulbous rush (*Juncus bulbosus*). Therefore a large amount of organic matter is produced and organic debris can accumulate at the lake`s bottom. The decomposition of this organic litter will lead to chemically reducing conditions including sulfate reduction. The sulfate reduction together with sulfur and sulfide mineral precipitation is in turn linked to proton consumption and thus to an increase in pH. The conditions for sulfate reduction und sulfide precipitation are especially favorable in the Lake Knappensee as the water shows elevated sulfate levels of about 700 mg/l and also elevated ferrous iron contents (e.g. from former pyrite oxidation).

The transformations can be described by the following net reaction equations:

Formation of elementary sulfur S^0

$$3CH_2O + 4H^+ + 2SO_4^{2-} \rightarrow 2S^0 + 3CO_2 + 5H_2O$$

Formation of iron monosulfide FeS

$$9CH_2O + 8H^+ + 4SO_4^{2-} + 4FeOOH \rightarrow 4FeS + 9CO_2 + 15H_2O$$

Formation of iron disulfide FeS_2

$$15CH_2O + 16H^+ + 8SO_4^{2-} + 4FeOOH \rightarrow 4FeS_2 + 15CO_2 + 25H_2O$$

CH_2O stands for organic material in the sediment; FeOOH denotes three-valent iron minerals.

As can be seen from the stoichiometric expressions shown above 2 moles of protons are neutralized per one mole of reduced sulfur produced from sulfate. Essential for a long-lasting de-acidification by this mechanism is that the reduced sulfur species are buried in the sediment, preventing them from being re-oxidized.

Methods

Exploratory investigation in 2011 revealed that layers with sulfide minerals covered by a thin oxic layer can be found in the sediment of the Lake Knappensee. The sulfide minerals were identified qualitatively by release of hydrogen sulfide after treatment with 0.1 molar hydrochloric acid.

In order to test the hypothesis of sulfate reduction and reduced sulfur deposition being the key process promoting in-lake neutralization, elaborate quantitative field and laboratory investigations were launched in December 2014.

15 sediment cores were sampled by lowering plexiglass liners of 6 cm diameter and 1 m length into the lake bottom. The locations of the sampling points are displayed in fig. 2.

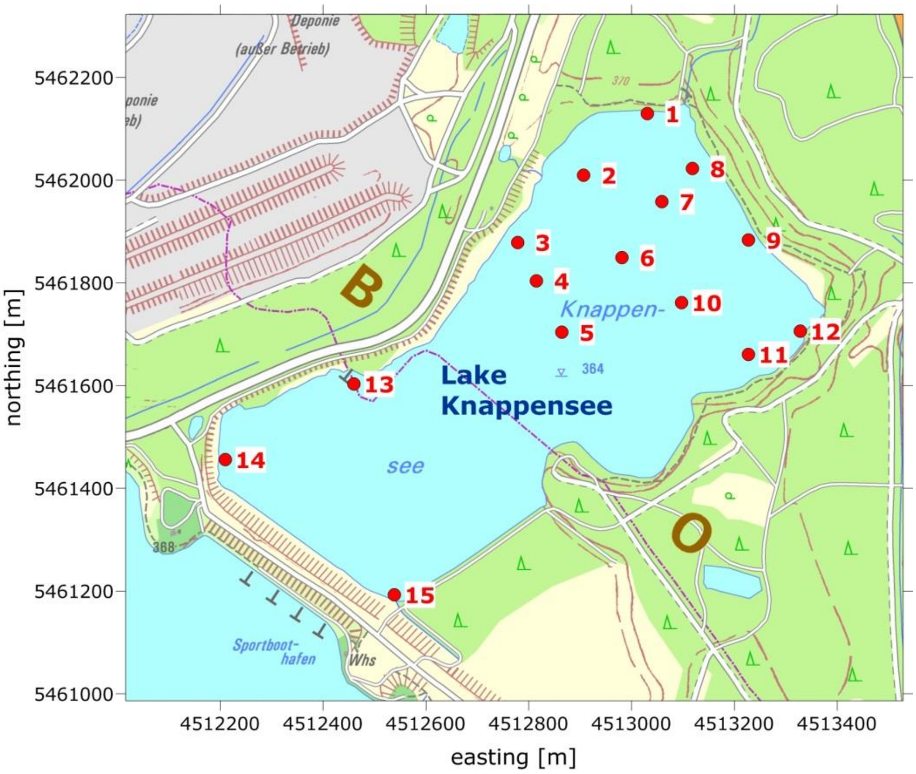

Figure 2 *Location of the sediment cores gathered from Lake Knappensee (map from Bayerische Vermessungsverwaltung).*

The sampling tubes were driven manually into the lake sediment until the compact underlying ash layer was reached. The tubes were then sealed with rubber plugs. The thickness of the black-colored organic-rich surface layers varied between < 1 cm and 29 cm, the total thickness of the cores (surface layer + ash) varied between 25 cm and 61 cm.

The cores were immediately delivered to the hydrological laboratory of the University of Bayreuth maintaining strictly anaerobic conditions during transport and storage. In the glovebox of the lab several samples were taken from the organic-rich surface layer of each core and analyzed for their content of elementary sulfur (S^0), acid volatile sulfide AVS, and chrome-reducible sulfur (CRS).

AVS is mainly made up of iron monosulfide, while elementary sulfur and disulfide sulfur are captured by the CRS method. The disulfide content of the sample can be calculated as the difference between CRS and S^0.

Besides sulfur species the dry matter content of the original sediment and the thickness of the organic surface layer were determined.

An overview on the mean observed sulfur contents of the individual cores expressed in mmol sulfur per kg dry matter is given in fig. 3. Obviously, appreciable amounts of reduced sulfur species were found in most of the samples. The relatively high content of AVS is a hint at recent sulfate reduction and sulfur deposition occurring in the lake and the sediment.

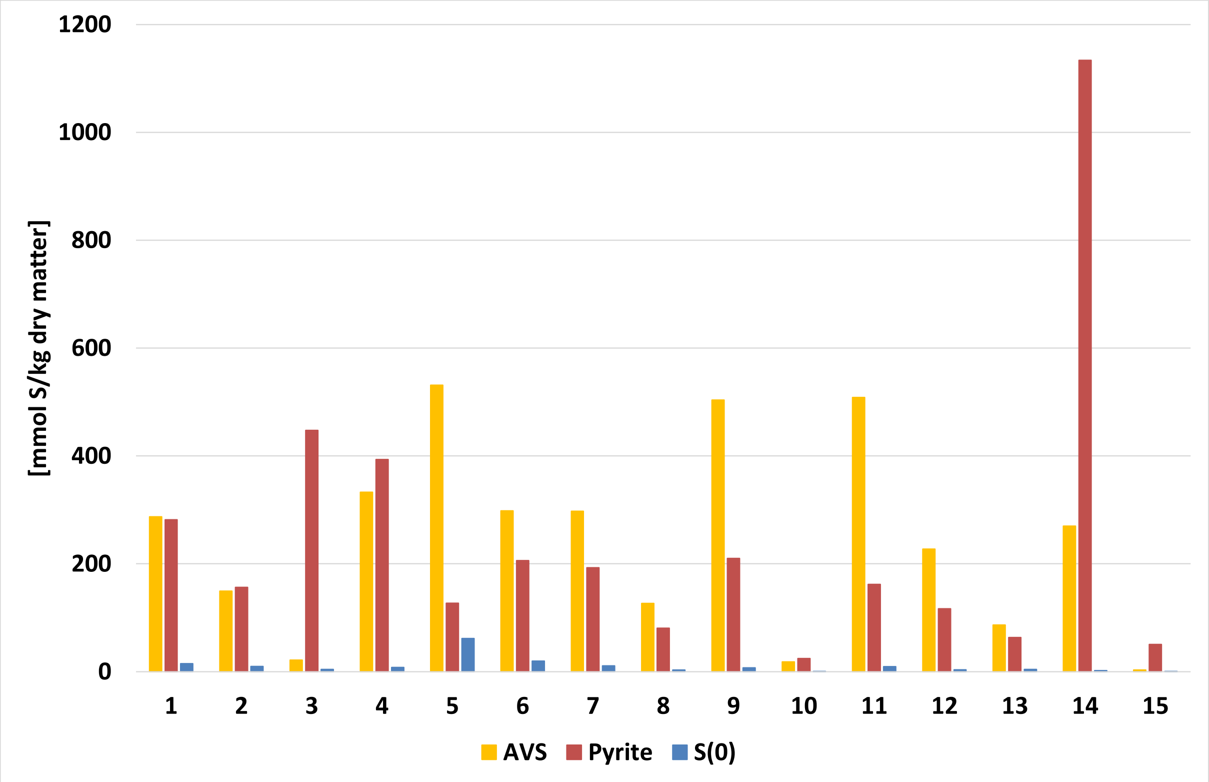

Figure 3 *Mean sulfur species contents at the 15 sediment sampling locations. Sulfur values are based on dry matter mass of the surface layer.*

Results

The first step in evaluating the field data consisted in calculation of proton (acidity) equivalents from the measured sulfur species content according to the stoichiometric relations given in the equations shown above. Sediment cores 3, 10 and 15 were not considered for proton equivalent calculations, as no clear organic surface layer could be identified for the three cores. The results of the calculations are displayed in tab. 1.

Table 1 *Proton equivalents calculated from measured sulfur species.*

mean sulfure species contents [mmol/kg]				calculated proton equivalents [mmol/kg] from…			
core no.	S(0)	AVS	disulfide-S	...S(0)	….AVS	….disulfide S	sum
1	14.9	287.3	282.0	29.8	574.6	563.9	1168.4
2	9.6	149.5	156.4	19.2	299.0	312.9	631.1
4	7.9	332.8	393.6	15.8	665.5	787.1	1468.4
5	61.5	531.3	126.9	122.9	1,062.5	253.7	1439.2
6	19.6	298.3	206.0	39.2	596.7	412.0	1047.9
7	10.7	297.6	192.7	21.4	595.3	385.3	1002.0
8	3.3	126.6	80.8	6.7	253.1	161.5	421.3
9	7.3	503.9	210.2	14.6	1,007.8	420.5	1442.9
11	9.4	508.5	161.8	18.7	1,017.0	323.6	1359.3
12	3.6	227.3	116.6	7.2	454.7	233.2	695.1
13	4.3	86.5	63.4	8.5	173.0	126.9	308.4
14	2.0	270.0	1134.0	3.9	539.9	2,268.0	2811.9

With the help of the calculation steps shown below the proton equivalents determined for the individual sampling locations were extrapolated for total proton equivalent mass in the lake sediment.

At first specific dry matter mass per unit surface area was calculated from dry matter content of the sample and the thickness of the organic surface layer.

Multiplying proton equivalents of dry matter with the specific dry matter mass per unit surface area yields the specific proton equivalents per unit surface area of the sediment.

Finally the specific proton equivalents have to be multiplied with the surface area attributed to the respective sampling location. The attribution of a surface area was performed graphically with the help of polygons surrounding the sampling locations (fig. 4).

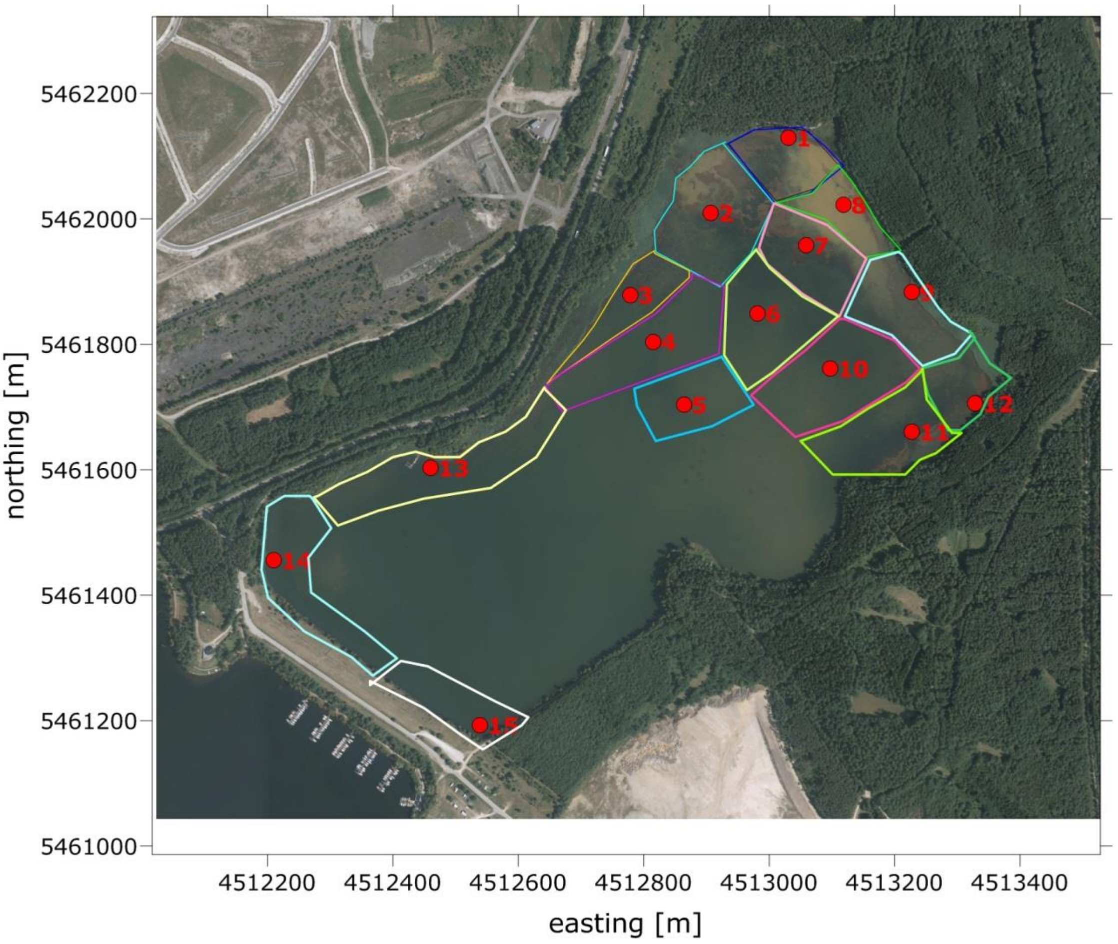

Figure 4 *Polygons attributing surface areas to the individual sampling location (aerial photograph from Bayerische Vermessungsverwaltung).*

The transformation of the proton equivalents derived from measured reduced sulfur contents to specific proton equivalent masses and their extrapolation to total proton equivalent masses is shown in tab. 2 and exemplified in the following for sediment core no. 1.

The samples from the organic-rich surface layer of core no. 1 yielded a mean dry matter content of 10.9 % (column 2 in tab. 2) and a corresponding water content of 89.1 %. The density of the dry matter was estimated to be 1.5 kg/l assuming dry matter being a mixture of organic and mineral compounds.

The bulk density of the surface layer (dry matter + water) is then 0.109 x 1.5 kg/l + 0.891 x 1 kg/l = 1.05 kg/l = 1050 kg/m^3 (1 kg/l being the density of water).

The thickness of the organic surface layer in sediment core no. 1 was 130 mm = 0.13 m. The specific mass of the surface layer per unit sediment area is then 1050 kg/m^3 x 0.13 m = 137 kg/m^2. Multiplying the specific surface layer mass with the measured dry matter content of 10.9 % (0.109) yields a specific dry matter content of 15 kg/m^2.

***Table 2** Extrapolation from specific to total proton equivalents*

sediment core no.	dry matter content [%]	densitiy of the surface layer [kg/l]	thickness of the surface layer [mm]	specific dry matter mass [kg/m^2]	proton equivalent based on dry matter mass [mol/kg]	specific proton equivalent [mol/m^2]	attributed area [m^2]	total proton equivalents [kmol]
1	10.9	1.05	130	15.00	1.17	17.53	13015	228
2	17.7	1.09	180	34.59	0.63	21.83	27095	591
4	10.3	1.05	290	31.50	1.47	46.25	27348	1265
5	13.0	1.07	170	23.59	1.44	33.95	15265	518
6	15.7	1.08	125	21.14	1.05	22.15	22193	492
7	14.8	1.07	150	23.77	1.00	23.82	17879	426
8	23.7	1.12	175	46.47	0.42	19.58	11166	219
9	11.5	1.06	120	14.65	1.44	21.14	19390	410
11	14.2	1.07	210	32.05	1.36	43.56	21635	942
12	19.9	1.10	200	43.70	0.70	30.38	11905	362
13	29.8	1.15	70	23.98	0.31	7.40	25698	190
14	12.6	1.06	85	11.40	2.81	32.07	22643	726
sum								**6369**

The proton equivalent of dry matter of core no. 1 calculated from measured reduced sulfur was 1.17 mol/kg (cf. last column in tab. 1). Multiplying the dry matter proton equivalent with the specific dry matter content of core 1 of 15 kg/m^2 leads to a specific proton equivalent mass per unit area of 1.17 mol/kg x 15 kg/m^2 = 17.5 mol/m^2.

A sediment surface area of 13015 m^2 was attributed to core no. 1 (see also fig. 4). Multiplication of the specific proton equivalent mass per unit surface area of 17.5 mol/m^2 with the attributed area of 13015 m^2 provides a total proton equivalent mass of 17.5 mol/m^2 x 13015 m^2 = 228 kmol (last column of tab. 2) for the area represented by core no. 1.

The calculating steps exemplified for core no. 1 were performed for all other cores except for cores no. 3, no. 10 and no. 15. As mentioned above, those cores were not considered for total proton equivalent calculations as no clear organic surface layer could be identified.

Highest amounts of proton equivalents were found for sediment core no. 4, mainly owing to the thick organic surface layer observed for this core.

The 12 polygons considered for proton equivalent calculation cover a surface area of 235232 m^2. This area makes up about 45 % of the total surface area of the lake. It was assumed that the remaining sediment area of the lake does not provide significant additional amount of proton equivalents. This is a conservative estimate with regard to the total acidity equivalents buried in the lake`s sediment.

The total proton equivalent mass buried in the sediments of Lake Knappensee was estimated to amount to 6369 kmol (cf. tab. 2). This value fairly matches the acidity loss of 8390 kmol which was calculated based on the acidity evolution in the lake since 2001 and water budgets derived from the regional groundwater model (see above).

Discussion

Estimations for total masses or charges for large natural objects like Lake Knappensee are always afflicted with various uncertainties. They may arise from spatial and temporal variations in the underlying processes and parameters, which often are only roughly encompassed.

Considering the acidity losses calculated for the lake water it is mainly the acidity of the inflowing groundwater which gives rise to uncertainty. Here we assumed the hypothetical acidity resulting from pure mixing of acidic groundwater entering the lake with neutral surface waters discharging into the lake to be 0.8 mmol/l (cf. fig. 1). If the hypothetical acidity of the lake water without internal neutralization processes was higher or lower, higher or lower acidity losses were estimated respectively.

Furthermore, the onset date of de-acidification processes is not precisely known. In our case, we assumed the processes to start in the year 2001, but neutralization process might as well have started a few years earlier.

While the proton equivalents calculated from sulfur measurements constitute relatively hard data, it is mainly the spatial heterogeneity of the parameter distribution providing a source of uncertainty for estimation of the total masses. Despite the relatively high number of 15 sediment cores and the appreciable effort which was taken for data analysis only a coarse picture of the real spatial distribution pattern of lake sediment parameters could be gained.

The estimated total proton equivalent of 6369 kmol buried in the lake sediment most probably provides a lower limit for the internal neutralization capacity of the lake, as only roughly half of the sediment area was considered for the calculations. Assuming that the proton equivalent mass in the order of the mean value of 30 mol/m^2 (cf. tab. 2) prevails in the remaining sediment area (about 200000 m^2), an additional amount of 30 mol/m^2 x 200000 m^2 = 6000 kmol of proton equivalents could be expected. The total amount of proton equivalents in the lake sediment would then increase to about 12000 kmol.

Conclusions

In spite of the uncertainties concerning detailed parameter distribution, results from the sediment studies prove that appreciable amounts of reduced sulfur compounds are buried in the Lake Knappensee sediments.

An important finding is that the acidity loss that is linked to the reduced sulfur fixation in the sediment is in the order of magnitude of the acidity loss derived from a mass balance approach in the lake water.

That means that the acidity stored in the sediment is sufficient to explain the de-acidification observed in the lake water since 2001. Naturally occurring internal neutralization could therefore be identified to be the key process leading to neutral pH-conditions in the formerly acidic lake.

The storage of large quantities of acidity equivalents in the sediment reveals to be the process underlying the sink term used in the transport model. This sink term was necessary to reproduce the observed neutral pH-conditions in the lake which is continuously fed by strongly acidic ground water to the day.

The internal neutralization processes in Lake Knappensee are not only beneficial to the lake water quality, but are also of great practical importance for the assessment of the hydrochemical state of the lake. One of the consequences for future management strategies of the lake should be that water level changes should be strictly avoided, as e.g. water level decreases would trigger re-oxidation of sediment areas exposed to the atmosphere and therefore initiate acidity pushes in the lake water. Overall the results suggest that Lake Knappensee contributes decisively to the partial neutralization of the acid mine drainage of the Wackersdorf lignite district.

The methodology consisting of field scale sediment investigations combined with water budgets gained from regional groundwater modeling applied to Lake Knappensee could also be used for the assessment of the hydrochemical state of other mining lakes.

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