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The importance of internal alkalinity generation for an acidified mountain lake as revealed by mass budgets

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Abstract

The dystrophic headwater lake „Huzenbacher See" (A_{Lake}: 19848 m^2, V_{Lake}: 65780 m^3, $Z_{max.}$: 8 m, t_w: 48 days) is situated in the Northern Black Forest in South-West Germany. The watershed (A: 656144 m^2; 740 - 940 m a.s.l.) is formed by a triassic sedimentary sandstone which is very poor in base cations. Podzolic soils dominate the steep char slopes while waterlogged soils like dystric and placic-dystric planosols prevail on the uppermost plain of the watershed. The watershed is almost completely forested with Norway spruce (*Picea abies*) and fir (*Abies alba*) both heavily impacted by „Acid Rain". Lake mass budgets revealed annual retention rates for sulfate, protons, nitrate and „negative" alkalinity with values up to 15%, 43%, 60%, and 48%, respectively. The lake mass budgets are based on well balanced lake water budgets as indicated by a retention rate of 1% for chloride. The lake mass budgets consider the total load from 11 gauged lake tributaries, from groundwater inflow into the lake, and from atmospheric precipitation on the lake surface and on the *Sphagnum* peat mat floating in the lake. The hypolimnion of the lake and its sediments, and the floating *Sphagnum* peat mat belong to the sites where denitrification, nitrate reduction and sulfate reduction can contribute to the retention of imported acidity and the internal generation of alkalinity. In addition assimilatory nitrate uptake by the floating *Sphagnum* peat mat, by the dense littoral stands of the macrophyte *Nuphar lutea*, and by phytoplankton may support the internal alkalinity generation.

Key words: dystrophic lake, mountain lake, mass budget, internal alkalinity generation, acidic rain

Introduction

A key feature of dystrophic lakes is their elevated content of dissolved organic carbon which includes humic substances with their specific physical, chemical and biological properties and ecological impacts (eg. Dickson 1980, Gjessing 1976, Gorham & al. 1985, Kullberg & al. 1993, Perdue & Gjessing 1990). The yet limited knowledge about the manifold functions of dystrophic ecosystems gave rise to a scientific debate on the prevailing origin of acidity in peatlands as well as in adjacent dystrophic surface waters (eg. Brakke & al. 1987, Eshleman & Hemond 1985, Gorham & al. 1984, Gorham & al. 1985, Havas & al. 1984, Hemond 1980, Kortelainen & Mannio 1988, Krug & Frink 1983). Scientific attention was as well drawn to yet another attribute of humic substances, which is their buffering capacity in the range between pH 5 and pH 4 (Cantrell & al. 1990, Dickson 1980, Hedin & al. 1990, Hemond 1980, Johannessen 1980, Kullberg & al. 1993). Proton consumption and alkalinity generation by algal nitrate consumption, by microbial denitrification, nitrate reduction and sulfate reduction (Brewer & Goldmann 1976, Cook & al. 1986, Rudd & al. 1986a, Rudd & al.

1986b, RUDD & al. 1988, SCHAFRAN & DRISCOLL 1987, PSENNER 1988, SCHINDLER 1989) are discussed to enhance the resilience of dystrophic and clear water lake ecosystems with regard to external acidic loadings.

Whereas mass budgets for terrestrial dystrophic ecosystems like bogs are well established (e.g. HEMOND 1980, URBAN & al. 1987), equivalent studies for aquatic ecosystems as dystrophic lakes are rare (cf. ARVOLA & al. 1990, FEGER 1986, PERSSON & BROBERG 1985, WRIGHT 1980). However, the cited study of FEGER (1986) at dystrophic lakes in the Black Forest reveals disputable methods regarding measurements and calculation of water fluxes (eg. no continuous registration for discharge at lake tributaries, no assessment of groundwater inflow into the lake, just bi-weekly instantaneous (!) discharge measurements in lake outflow which were set equal to total lake inflow discharge) or frequency of lake water sampling (just 4 times per year). Another dystrophic lake mass budget study did include epilimnetic but no hypolimnetic water samples (cf. ARVOLA & al. 1990). On the other hand, the comprehensive lake mass budget studies performed by PERSSON & BROBERG (1985) and by WRIGHT (1980) investigated a few parameters only.

The presented study at dystrophic Huzenbacher See intended to assess mass budgets by combining comprehensive hydrological and limnochemical investigations with state-of-the-art techniques (eg. ion chromatography, stream gauges, data loggers).

Material and methods

From November 6, 1988 until October 31, 1990 weekly water samples of lake tributaries, the lake outlet, 1-m-intersected lake vertical profiles and two littoral lake surface sites were analysed for pH, temperature, conductivity, and alkalinity, whereas the lake vertical profile and two littoral sites were additionally analysed for dissolved oxygen and Secchi depth. Regular biweekly water analyses in lake tributaries and lake outlet, and monthly lake water analyses in 2-m-intersected vertical profiles and at two littoral sites included 0.45 µm celluloseester filtered probes for Na, K, Ca, Mg, Al, Fe, Mn, SiO_2, NH_4, Cl, NO_3, NO_2, SO_4, dissolved organic carbon (DOC), dissolved organic nitrogen (DON), ortho-phosphate (o-P), and total dissolved phosphorus (TDP). Particulate phosphorus (PP) was analysed in the residue remaining on top of the filters. Total phosphorus (TP) was calculated as the sum of TDP and PP. Standard analytical procedures were applied with PERKIN ELMER atomic absorption spectroscopy including graphite furnace technique, DIONEX ion chromatography, and spectrophotometry (cf. THIES 1995a). Precision and accuracy of analyses were regularily checked. Ion balance and conductivity calculations were applied for testing analytical plausibility (cf. THIES 1995a). Stage recording in two major lake tributaries and the lake outlet was performed continuously in wooden, rectangular V-notch weirs using dataloggers and strip-chart recorders. The lake water level was recorded similarly close to the lake outlet. Stage-discharge calibrations for weirs and discharge measurements were performed weekly in all eleven gauged lake tributaries and the lake outlet using current meter or vessels. Evapotranspiration from the lake surface and from the floating Sphagnum peat mat in the lake was calculated applying a modified Haude approach (cf. THIES 1995a) using daily weather data of the next weather station of the German Weather Service (15 km south of the lake in Freudenstadt at 797 m a.s.l.). Groundwater inflow into the lake was calculated as the residual term of the total lake water budget calculation procedure. Water seepage through the bedrock of the proper lake basin could be excluded due to the verified absence of bedrock faults in the watershed, lake basin bedrock compactness and due to the extensive sediment formation by fine sand, clay and organic debris since lake genesis about 15000 years ago (HILGERS & al. 1993, THIES 1995a). The applied lake water budget approach thus defines, that water leaves this lake only by evapotranspiration from the lake surface and from the floating Sphagnum peat mat as well as by the single lake outflow. The lake surface area and the lake volume had been determined before this study (THIES 1987, THIES 1995a).

Chemical loads were calculated by linking continuously registrated discharge data of lake tributaries and lake outlet with the respective weekly to biweekly chemical concentration data by the method of the „period-weighted mean“ (LIKENS & al. 1977, DANN & al. 1986). Lake mass contents were calculated by multiplication of discrete partial lake volumes with corresponding monthly lake water concentration applying the model of a „completely mixed reactor“ (FRISK 1989, VOLLENWEIDER 1969). Open bulk precipitation was sampled at biweekly to monthly periods in rain gauges which were positioned on the floating *Sphagnum* peat mat close to the center of the lake. In addition to the regular sampling described above, every major flood event was sampled and analysed for all lake mass budget compartments.

The theoretical lake mass content was calculated as the difference between outlet exports and input loadings [i.e. precipitation, surface inlets, groundwater inflow]. Lake mass budgets were calculated as the difference between theoretical lake mass content and measured lake mass content. A positive number indicates that Huzenbacher See acts as a source while a negative number indicates that the lake is a sink. The lake *response* (i.e. *source* or *sink*) was assessed by expressing the lake mass budget values as percentage values of total input loading (cf. THIES 1997).

In the context of evaluation of lake mass budget results, the Huzenbacher See ecosystem is defined operationally and includes the lake water (epilimnion, hypolimnion, littoral), the lake sediment, the phytoplankton and the macrophyte *Nuphar lutea*, the floating *Sphagnum* peat mat and the microbial communities in prevailing anoxic environments in the sediment, in the hypolimnion and within the floating *Sphagnum* peat mat. Water and mass budgets regarding atmospheric bulk precipitation on the lake surface and the *Sphagnum* peat mat surrounding the lake, all eleven gauged lake tributaries, the lake itself, and the gauged lake outlet were determined during a period of two years (November 1988 until October 1990) with a temporal resolution of one month for all lake mass budget compartments (THIES 1995a). However, as an appropriate lake budget period has to last longer than the mean annual water residence time of the corresponding lake (Huzenbacher See: t_w = 48 days), a full year was choosen as a mass budget period. The criterion of autumnal mixis was used for the separation of annual budgets. The latter implicated that both budget periods differed a little in time from a full year. This difference was balanced to gain full annual budgets by relating the obtained budget results to a period of 365 days. It should be noted, that the second budget year had to be terminated about one week before the autumnal holomixis was entirely completed, which influenced some results in the second budget year. Further details on budget calculation procedures, analytical methods and data are given elsewhere (THIES 1994, THIES 1995a, THIES 1995b, THIES 1997).

Results and discussion

Volume weighted average values of autumnal holomictic overturn (1988 & 1989) characterize Huzenbacher See as a dilute, acidic, mesotrophic, and dystrophic lake (cf. THIES, 1995a, 1995b, 1997 & Table 1).

In both budget years, the annual lake chloride budgets resulted in the same chloride retention rate of only 1% with respect to the total lake chloride loading (i.e. total of open precipitation on the lake and the Sphagnum peat mat surface, of lake tributaries and of groundwater inflow into the lake) (cf. Table 2). As the chloride/sodium ratio of all mass budget compartments closely fetched the corresponding ratio in sea salt, additional atmospheric or geological sources for chloride can be excluded for the watershed of Huzenbacher See (THIES 1995). The calculated annual lake chloride budgets indicate according to HENRIKSEN & WRIGHT (1977) and ESHLEMAN & HEMOND (1988) well-balanced lake water budgets and the validity of the applied approach for the water budget calculation. Moreover a well-balanced lake water budget is a fundamental prerequisite for the determination of a lake mass budget (cf. MOSELLO & DE GIULI 1980, WRIGHT & HENRIKSEN 1980). Response rates of lake mass budgets which differ from the chloride retention value of 1% indicate changes in annual lake mass budgets for Huzenbacher See and should therefore be different from background noise (cf. Table 2). Negative response values in Table 2 indicate a retention within the lake (i.e. the lake acts as a sink), whereas corresponding positive values indicate a generation by the lake (i.e. the lake acts as a source). Due to the relation of positive alkalinity generated in the lake to negative alkalinity imported from the catchment, the corresponding percentage value for alkalinity appears negative: in-lake retention of negative alkalinity = in-lake generation of positive alkalinity!

Regarding these percentage rates of changes in lake mass budgets (cf. Table 2), relevant annual retention rates were determinated for protons, (mostly negative) alkalinity, nitrate, ammonia, sulfate, ortho-phosphate, total dissolved phosphate, aluminum and silica. On the other hand, annual generation rates for dissolved organic nitrogen and most remarkably for particulate (and thus for total phosphorus) could be observed, which is discussed in more detail by THIES (1995a, 1995b, 1997). The base cations calcium and potassium showed only minor retention rates, but are characterized by distinct seasonal retention patterns peaking during the vegetation period (THIES 1995a). This cation retention may be linked to the uptake of base cations by the dense littoral stands of the macrophyte *Nuphar lutea* (THIES 1987) which is indicated by URBAN & al. (1995) for potassium uptake of green plant tissue. A similar pattern was found by KLEM (1992) in mosses of the floating *Sphagnum* peat mat in Huzenbacher See and by HEMOND (1980) at Thoreau's bog. Magnesium and sodium apparently behaved indifferent in the lake, except for sodium in the second year. The majority of investigated parameters demonstrated in both budget years comparable results in a consistent pattern. However, in the second budget year, iron and manganese seemed to show a net generation by the lake instead of a net retention as occured in the first budget year. This variable pattern can be explained with the ultimate sampling at the end of the second budget year, when the autumnal holomictic overturn was not yet complete and redox sensitive compounds as iron and manganese may have been still in a dissolved state which supported an „image" of the lake being a source.

The buffering capacity of Huzenbacher See with respect to the external acidic loading is shown by up to 48% retention for „negative" alkalinity and up to 43% retention for protons (cf. Table 2). The generation of (positive) alkalinity is supported by reductive microbial processes (STUMM & al. 1983), with important contributions of denitrification (RUDD & al. 1986a, 1986b, 1988), nitrate reduction (SCHAFRAN & DRISCOLL 1987, SCHINDLER 1989) and sulfate reduction (COOK & al. 1986, RUDD & al. 1986a, 1986b, SCHAFRAN & DRISCOLL 1987, SCHINDLER 1989). These processes can occur in permanent anoxic sites of the lake sediment and the floating *Sphagnum* peat mat as well as in the anoxic hypolimnion, which covered up to 50% of the total lake volume during summer with high amounts of ammonia and reduced sulfur compounds present (THIES 1994, 1995). According to KLEM (1992) the floating *Sphagnum* peat mat around Huzenbacher See is functionally comparable with an ombrotrophic bog such as Thoreau's bog, for which HEMOND (1980) demonstrated strong nitrate and sulfate retention.

SCHAFRAN & DRISCOLL (1987) and SCHINDLER (1989) pointed out, that due to a higher microbial turnover rate of nitrogen, reduction of nitrate is more important in lakes with shorter

Table 1. – Volume weighted average values of autumnal holomictic overturns (1988 & 1989).

T	O_2	O_2-sat.	pH	Cond.	Alk.	DOC	Na	K	Ca	Mg	Fe	Al	Mn	Si	Cl	NO_3-N	SO_4	NH_4-N	DON	PO_4-P	TDP	PP	TP
°C	mg/L	%		µS/cm	µeq/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
4.3	5.2	43	4.85	26.9	–3	7500	590	950	1400	330	350	430	60	1750	1120	88	4620	140	400	1	4	14	18

O_2-sat.: oxygen saturation, Cond.: conductivity, Alk.: alkalinity, DON: dissolved organic nitrogen (as N), TDP: total dissolved phosphorus (as P), PP: particulate phosphorus (as P), TP: total phosphorus (as P)

Table 2. – Rates of annual generation (+) and retention (-) by Huzenbacher See as percent of total annual loading into the lake.

Response period	H^+	Alk	Na	K	Ca	Mg	Fe	Al	Mn	Si	Cl	NO_3-N	SO_4	DOC	NH_4-N	DON	PO_4-P	TDP	PP	TP
1988–1989	- 43	- 48	- 1	- 3	- 4	- 1	- 5	- 15	- 12	- 25	- 1	- 60	- 12	+ 9	- 53	+ 26	- 68	- 50	+ 126	+ 11
1989–1990	- 40	- 47	+ 7	- 7	- 1	- 1	+ 52	- 13	+ 4	- 18	- 1	- 52	- 15	0	- 88	+ 40	- 82	- 45	+ 237	+ 68

Table 3. – Rates of annual generation (+) and retention (-) by dystrophic lakes as percent of total annual loading into these lakes.

Lake	H^+	Alk	Na	K	Ca	Mg	Fe	Al	Mn	Si	Cl	SO_4	DOC	NO_3-N	NH_4-N	DON	TN	TP
Huzenbacher See[1]	- 43	- 47	+ 3	- 5	- 3	- 1	+ 23	- 14	- 4	- 22	- 1	- 14	+ 5	- 56	- 71	+ 33	- 31	+ 40
Herrenwieser See[2]	+ 4	n.d.	- 6	- 15	- 11	- 9	+ 78	0	- 15	n.d.	- 7	- 2	n.d.	- 44	- 18	n.d.	- 42§	- 58$^{\$}$
Wildsee[2]	0	n.d.	- 5	- 11	- 13	- 10	+ 201	+ 38	- 15	n.d.	+ 1	+ 8	n.d.	- 28	- 67	n.d.	- 32§	- 60$^{\$}$
Nimetön[3]	n.d.	n.d.	- 12	- 2	- 8	- 3	- 53	- 15	n.d.	n.d.	n.d.	+ 20	+ 14$^{\#}$	*	*	*	- 12	- 44
Gardsjön[4]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	- 56	*	*	*	- 38	- 22
Langtjern[5]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	- 6$^{\#}$	*	*	*	+ 2	+ 18

Alk: alkalinity, DOC: dissolved organic carbon, DON: dissolved organic nitrogen, TN: total dissolved nitrogen, $^{\#}$ = TOC: total organic carbon, * = value included in TN, § = value does not include DON, TP: total phosphorus (as P), $^{\$}$ = ortho-phosphate-P only, neg. value = in-lake retention, pos. value = in-lake generation, n.d. = not determined.

[1] Thies 1995, [2] Feger 1986, [3] Arvola & al. 1990, [4] Persson & Broberg 1985, [5] Wright 1980

water residence times (t_w < 1 year) than reduction of sulfate. The mass budget results for Huzenbacher See may support this view as its mean water residence time amounts 48 days and nitrate retention is up to four times higher when compared to sulfate. However, assimilatory nitrate uptake by phytoplankton and the macrophyte *Nuphar lutea* must be taken into account additionally for the observed nitrate retention rate (Brewer & Goldman 1976, Van Miegroet & Johnson 1993). Photolithoautotrophic bacteria in the hypolimnion of Huzenbacher See (e.g. *Chlorobium spec.*) could have had as well reoxidized parts of available hydrogen sulfide by means of anoxic photosynthesis, which counteracts microbial sulfate reduction and feigns a lower sulfate retention rate (Thies 1995).

When comparing mass budget results of Huzenbacher See with cited studies (cf. Table 3) one has to keep in mind the above mentionned limitations of some studies. All cited base cation budgets show low to moderate retention rates (cf. Table 3). Dillon & al. (1988) determined annual lake retention for aluminum with rates ranging between 9% and 86% while the lower values are characteristic for more acidic lakes. This pattern fits to the average annual retention rate for aluminum in Huzenbacher See (14%), which is comparable to the corresponding retention rate for the Finnish Lake Nimetön (15%) (cf. Arvola & al. 1990, cf. Table 3), but is clearly lower than the corresponding retention rate for Woods Lake (43%) (cf. Schofield & al. 1985). Contrawise, Feger (1986) determined an annual generation rate of 38% for aluminum in Herrenwieser See (cf. Table 3). Herrenwieser See is another more acidic dystrophic lake situated nearby Huzenbacher See (cf. Thies 1987). Silica showed distinct retention rates within Huzenbacher See in both budget years (cf. Table 2) while no comparable data exist in the cited lake mass budget studies (cf. Table 3). For DOC no clear pattern was obtainable neither in Huzenbacher See nor in other dystrophic lakes (cf. Table 3). Moderate to strong nitrogen retention was found in most of the cited lakes, whereas for sulfate, both in-lake retention and generation by the lake occured (cf. Table 3). Extensive in-lake buffering of acidity was proved only for Huzenbacher See, which is reflected by the strong retention rates for protons (43%) and „negative“ alkalinity (48%) (cf. Table 3). The areal rates of internal alkalinity generation for Huzenbacher See [0.5 – 0.8 meq m^{-2} yr^{-1}] are higher than those reported for the Austrian mountain lake Piburger See [0.3 – 0.5 meq m^{-2} yr^{-1}] (cf. Thies 1995, 1995b, Psenner 1988). Piburger See is situated in Tyrol (Austria) at an elevation of 913 m a.s.l. within a forested catchment with surrounding steep mountain cliffs of granite and gneiss. This lake is a clear water lake but its tendency to morphogenic meromixis (mostly during spring) is comparable to the one of Huzenbacher See (cf. Psenner 1988, Thies 1994, 1995a). Hence the contribution of microbial reduction of sulfur and nitrogen compounds to internal alkalinity generation should depend in such mountain lakes upon the strength of the negative redox potential which is related to mixing patterns, lake and watershed characteristics (eg. wind shading cliffs, duration of lake ice cover, water residence time, import rates of organic carbon, in-lake oxygen consumption by imported organic matter) and climatic conditions (e.g. wind speed, air temperature, clear sky radiation).

Conclusion

Mass budgets present a combination of hydrological data and chemical analyses which offer valuable conclusions about ecosystem functions (Likens 1984). An acidic, fast flushing, dystrophic headwater lake would generally not have been regarded as a possible mitigator of „Acid Rain“, which has been shown by the applied lake mass budget approach. The study period of two years is common to all cited dystrophic lake budget studies (Arvola & al. 1990, Feger 1986, Persson & Broberg 1985, Thies 1995, Wright 1980), which reflects without doubt the great exigencies to run such an investigation. However, if more sites would be studied appropriately over extended periods, trends in lake ecosystem response with respect to natural variation and anthropogenic impacts (eg. Climatic Change, Acid Rain) could be detected.

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