Institut für Hydrologie Albert-Ludwigs Universität Freiburg i. Br.

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Interactions of stream flow dynamics and mercury variations in a small mountainous catchment in the Adirondack Mountains, NY State - Process understanding and modeling.



Diplomarbeit unter der Leitung von Prof. Markus Weiler

> Freiburg im Breisgau, Oktober 2008

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List of Symbols

Symbol	Explanation	Unit
a.s.l.	Above sea level	[m]
A_{254}	UV Absorbance at 254 nm	$[m^{-1}]$
α	Fractionation factor	[-]
Ce	Event water concentration	[mg/L]
Cf	Refreezing factor	$[mm/^{\circ}C \cdot d]$
Ci	Concentration of i	[mg/L] or $[ng/L]$
Cp	Pre-event water concentration	[mg/L]
D	Soil deficit	[mm]
D_s	Maximum clear sky duration of sunshine	[h]
\overline{D}	Average soil deficit	[mm]
$\delta^{18}O$	¹⁸ O with respect to a standard	[%0]
d_m	Melting rate	[mm] or [in]
d_{max}	Maximum stream length	[km]
DOC	Dissolved organic carbon	[mg/L]
E(i)	Event water amount	[mm/d]
f	Remaining fraction	[%]
FHg	Filtered total mercury	[ng/L]
FMeHg	Filtered methyl mercury	[ng/L]
f_p	Fraction of pre-event water	[%]
h	Elevation	[m]
HC	Holding capacity	[%]
$\mathrm{Hg}(\mathrm{II})$	Divalent mercury	[ng/L]
Hg^{0}	Elemental mercury	[ng/L]
Ι	Topographic index	$[\ln(m)]$
K	Saturated lateral hydraulic conductivity	[mm/h]
λ	Average topographic index	$\left \ln(m) \right $
m LF	Loss factor	[-]

М	Melting factor	$[\mathrm{mm}/^{\circ}\mathrm{C} \cdot d]$
m	Scaling parameter	[mm]
M(i)	Melt water amount	[mm]
Mi	Melting factor	$[\mathrm{in}/^{\circ}\mathrm{f}\cdot d]$
μ	Micro, SI prefix: 10^{-6}	[-]
n	Nano, SI prefix: 10^{-9}	[-]
n_{drain}	Drainable porosity	[%]
N_{eff}	Nash-Sutcliffe efficiency	[-]
P_{net}	Net precipitation	[mm]
Р	Precipitation	[mm]
PET	Evapotranspiration	[mm]
pН	Negative logarithm of the hydrogen ions	[-]
PHg	Particulate total mercury	[m ng/L]
PMeHg	Particulate methyl mercury	[m ng/L]
Q	Water volume or flux	$[m^3]$ or $[m^3/s]$
R	Relation of 18 O to 16 O	[-]
RF	Amount of refreeze water	[mm]
ρ	Absolute humidity	$[\mathrm{g/m^3}]$
RLWC	Retained liquid water capacity	[%]
RSME	Root mean squared error	[-]
SUVA	UV Absorbance divided by DOC concentration	$[L/mgC \cdot m]$
SWE	Snow water equivalent	[mm]
t	Timesteps	[d]
T_0	Lateral transmissivity	$[\mathrm{m^2/h}]$
T_a	Air temperature	$[^{\circ}C]$ or $[^{\circ}f]$
Θfc	Field capacity	[%]
T_m	Melting temperature	$[^{\circ}C]$ or $[^{\circ}f]$
TOC	Total organic carbon	[mg/L]
u	Relative atomic weight	[-]
UHg	Unfiltered total mercury	[ng/L]
UMeHg	Unfiltered total methyl mercury	[m ng/L]
V_{rout}	Routing velocity	$[\rm km/d]$
z	Soil depth	[m]

Abbreviation	Explanation
CMW	Current melt water approach
dFCL	Normalized difference between UFCL and LFCL
GLUE	Generalized Likelihood Uncertainty Estimation
IHS	Isotope hydrograph separation
ISM	Isotope Snowmelt Model
LFCL	Lower confidence limit
MCAT	Uncertainty calculation tool
ROS	Rain on snow event
runCe	Interative calculation of Ce
UFCL	Upper confidence limit
V-SMOW	Vienna Standard Mean Ocean Water
VWA	Volume weighted average approach
	·

Summary

Mercury (Hg) is an environmental pollutant and high amounts of stored Hg in soils are a threat for many remote catchments. The mobilization of terrestrial Hg is not well understood - but the transport to surface waters seems to be strongly influenced by hydrological controls, especially by the state of saturation in catchment soils and by the hydrologic connectivity of uplands to riparian areas.

The aim of this thesis was to investigate the role of these hydrological controls on the mobilization during the melting period in a forested, mountainous catchment in the northeastern US. The Fishing Brook Catchment is a 65 km² headwater tributary with abundant riparian wetlands in the Hudson River basin of the Adirondack Mountains, New York.

In the first part of the project the hydrological and chemical response of the Fishing Brook catchment was examined: For the 2008 snowmelt concentrations for unfiltered total Hg (UHg) ranged from 1.8 to 3.1 ng/L, peaking with high flow conditions. In contrast, unfiltered methyl Hg (UMeHg) concentrations decreased indicating supplylimited flushing during early spring. Dissolved organic carbon (DOC) which is often referred to have a similar flushing behavior to Hg was just weak related to Hg concentrations during the melt, showing a counterclockwise hysteresis to discharge.

In the second part of the study a distributed model for the δ^{18} O signature of the snowpack and the water released from the snowpack to the soil was developed. This model, called the 'Isotope Snowmelt Model' allowed to simulate a detailed hydrograph separation for meltwater when it was conducted to a model which approximates the retention of event water within the catchment (runCe model). The results of this combined approach indicated that the hydrograph of the 2008 snowmelt was dominated by a pre-event water contribution of 58%. The role of event water contribution on the mobilization of DOC and SUVA₂₄₅ was tested, but no direct relation was found.

In the third part of the thesis the hydrological model TOPMODEL was applied to investigate if the topographic index based calculation of soil saturation can explain the mobilization behavior of mercury and DOC. UHg concentrations were strongly related to the simulated average soil saturated deficit as well as to the percentage of saturated area in the catchment. Different relations were found for periods with and without a snowpack showing that mobilization and runoff generation follow different patterns under snow/no snow conditions.

These results indicate that as the water table rises to the surface during snowmelt, Hg is flushed to surface waters, whereas a supply limitation of MeHg results in diminishing concentrations as the snowmelt proceeds. Thus snowmelt can be assumed as a main process to form sufficient supply of inorganic Hg and DOC to 'hot spots' of methylation.

Keywords: mercury, methylmercury, dissolved organic carbon, flushing, hydrograph separation, saturated area, TOPMODEL, wetland, adirondacks

Zusammenfassung

Quecksilber (Hg) ist ein Schadstoff von welchem große Mengen in den Böden vieler abgelegener Gebiete gespeichert sind. Diese stellen eine Bedrohung dar, wenn sie mobilisiert werden. Diese Mobilisierung ist bisher nicht sehr gut untersucht - jedoch scheint sie stark von hydrologischen Prozesse abzuhängen, insbesondere vom Grad der Sättigung der Böden eines Gebietes, als auch von der hydrologischen Verbindung der Hangbereiche zu den Feuchtgebieten um die Gewässer.

Das Ziel dieser Arbeit war die Rolle dieser hydrologischen Steuergrößen auf die Mobilisierung während der Schneeschmelze in einem bewaldeten Mittelgebirgseinzugsgebiet im Nord-Osten der Vereinigten Staaten zu untersuchen. Das "Fishing Brook Cachtment" ist ein 65 km² großes Einzugsgebiet welches von Feuchtflächen geprägt ist. Das Gebiet zählt zum Neubildungsgebiet des Hudson-River, welcher in den Adirondacks im Bundesstaat New York entspringt.

Im ersten Teil dieser Arbeit wurde die hydrologische- und chemische Reaktion des Untersuchungsgebietes auf die Schneeschmelze 2008 genauer untersucht. Die ungefilterten Quecksilber Konzentrationen aller chemischer Spezies (UHg) lagen dabei im Bereich von 1.8 bis 3.1 ng/L. Die höchsten Konzentrationen wurden während hoher Fließbedingungen verzeichnet. Im Gegenteil dazu nahmen die die Konzentrationen des ungefilterten, methylierten Quecksilbers (UMeHg) ab, was auf einen limitierten Speicher an mobilem methyliertem Quecksilber hindeutet. Die Konzentrationen an gelöster organische Substanz (DOC), von welcher oft angenommen wird, dass es sich ähnlich wie Quecksilber verhalte war nur gering zu Quecksilber korreliert und zeigte eine linksdrehende Hysterese zum Abfluss.

Im zweiten Teil der Diplomarbeit wurde ein flächendetailliertes Model zur Simulation der δ^{18} O Signaturen der Schneedecke sowie des Schmelzwassers, welches das Schneepaket verlässt entwickelt. Das 'Isotope Snowmelt Model' erlaubt eine Isotopen basierte Ganglinienseparation, wenn es mit dem runCe Model, welches die Retention von Schmelzwasser im Einzugsgebiet berechnet kombiniert wird. Die Ergebnisse dieser Separation zeigen, dass der Anteil an Vorereignisswasser während der Schneeschmelze 2008 bei 58% lag. Zudem wurde der Einfluss von Ereigniswassermengen auf DOC und SUVA₂₄₅ untersucht. Beide zeigten jedoch keine direkte Relation.

Im dritten Teil dieser Arbeit wurde das hydrologische Model TOPMODEL auf das Untersuchungsgebiet angewendet, um zu untersuchen, ob die auf topographischen Indices beruhende bodenfeuchte Simulation das Verhalten der Mobilisierung von Quecksilber und DOC erklären kann. Die UHg Konzentrationen waren stark zum mittleren Sättigungsdefizit des Bodens und zum prozentualen Anteil simulierten Sättigungsflächen korreliert. Für Phasen mit und ohne Schneedecke wurden verschieden Zusammenhänge identifiziert, was die Abhängigkeit der Mobilisierung und der Abflussbildungsprozesse von der Schneebedeckung zeigt.

Die gefundenen Ergebnisse zeigen, dass der steigende Bodenwassergehalt während der Schneeschmelze den Transport von Quecksilber zu Oberflächengewässern begünstigt, wohingegen die abnehmenden MeHg Konzentrationen durch die limitierte Verfügbarkeit geprägt sind. Daher kann die Schneeschmelze als einer der Hauptprozesse für den Transport von Quecksilber und DOC zu den so genannten 'Hot Spots', in welchen organische Quecksilberverbindungen entstehen angesehen werden.

Stichworte: Quecksilber, methyliertes Quecksilber, gelöste organische Substanz, Mobilisierung, Ganglinienseparation, Sättigungsflächen, TOPMODEL, Feuchtflächen, Adirondacks

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1. Introduction

1.1. Mercury

Mercury (Hg), a chemical element, is known for his special properties. Beside the facts that it has a high atomic weight of 200.59u (APPELO and POSTMA, 2005) and a high density, which classifies mercury as a heavy metal, it is also the only metal which is liquid at normal earth surface temperatures, which always led to high curiosity of scientists.

This interest became even higher, when mercury was identified as a toxic substance. Mercury became recognized as an environmental pollutant in aquatic environments in the 1960's and 1970's (HEM, 1985). The long term input of atmospheric Hg to remote locations in the temperatured and arctic climate, became another field of interest in the 1990's. A high number of studies focused on the mercury cycle by looking at input and output fluxes of the different Hg species (ST.LOUIS ET AL., 1995; BISHOP ET AL., 1995, e.g.). In the early 2000's the main processes of transformation of inorganic mercury to methylmercury were explored (BENOIT ET AL., 2003, e.g.). Current research is trying to get further insight into transport processes and the mobilization of stored mercury in ecosystems in the northern climates (SCHUSTER ET AL., 2008; SELVENDIRAN ET AL., 2008, e.g.).

1.2. Aim of this study

The purpose of this study is to get better insight into the mobilization of Hg during high flow conditions in the catchment scale. This mobilization is assumed to be a major relationship between the aquatic and the terrestrial part of the mercury cycle. The objective of this study is to refine the knowledge of hydrological controls on mobilization and transport of Hg in an forested watershed in northern New York. Thus the general research hypothesis can be formulated in the following way: "The main variation of mercury and other biochemical parameters (e.g. DOC) can be explained by runoff dynamics. The runoff generation processes can be used to predict biochemical parameters. Chemical reactions are less important at a given temporal and spatial scale."

This hypothesis assumes that the major controls for the chemical parameters are hydrological processes, especially the processes of runoff generation during the snowmelt. Beneath the general hypothesis, a number of questions can be addressed to the study:

- Which are the major hydrological controls on Hg flushing during the snowmelt?
- How are chemical constituents and Hg species related during the springflood?
- Can different sources of Hg and other constituents be identified?
- Is there a direct influence of snowmelt water on wash-out effects?
- How can models improve the estimation of meltwater fractions during the melt?
- How can simple hydrological modeling approaches be applied as tools to identify the major controls affecting the Hg mobilization?

As a part of the study a broad field survey was initiated during the high flow period of the snowmelt 2008 in the Fishing Brook Catchment, northern New York. A broad sampling of Hg-species, water chemistry and Oxygen-18 was performed before, during and after the snowmelt. Samples were analyzed at different laboratories in the U.S. and Germany.

This diplom-thesis is structured the following way: After this introduction a site description of the Fishing Brook Catchment, NY will be given. After that a general description of the current state of research regarding to the Hg cycle will follow. In the following chapter the methods and results from the field survey will be pointed out. The fourth chapter will present the use of oxygen-18 for an advanced isotope hydrograph separation. In the last part, the application of the hydrological model TOPMODEL will be shown. In the final chapter the conclusions and an outlook of this work will be given.

The Fishing Brook Catchment -Site description

In this chapter the research site - the 'Fishing Brook Catchment' in the northern NY-State - will be described. The focus will be on the geography, geology, pedology, climate and the general hydrological conditions. This will give an introduction to fundamentals relevant to the research conducted to this site.

2.1. Geography

The Fishing Brook Catchment is located in the central part of the Adirondack State Park in northern New York (43°58'31.5"N, 74°20'04.3" W). The catchment is situated between the town of Newcomb and the town of Long Lake and has an extent of about 10.4 km in northern-southern direction and about 9.4 km in east-western direction. The drainage area of the Fishing Brook Catchment is about 65 km² (unpublished Data, USGS 2008). An overview of the catchment is given in the map (figure:2.1.1).

The Fishing Brook Catchment is part of the Upper Hudson River Basin, the Hudson River Headwaters. These headwaters are all located in the south and southeast of the High Peaks, the highest mountains in the Adirondack Park. The High Peaks divide drainage area to the south/north. The Hudson River drains to the southern part and flows into the Atlantic Ocean about 450 km south of the research site.

2.1.1. Morphology

The morphology of the Fishing Brook Catchment is mainly characterized by the strong influence of the glacial epochs. The valleys are not very steep, most with large wetland areas at the valley bottoms. The lowest elevation of Fishing Brook is 501.5 m a.s.l. at the outlet. To the north and the south the catchment is limited by higher elevations over 1000 m a.s.l.. The highest elevation is found in the southeast (1082.4 m a.s.l.) at the border of the catchment (unpublished Data, USGS 2008). The terrain level



Figure 2.1.1.: The Fishing Brook Catchment in northern NY State. The watershed boundaries are marked (red line). The outlet with the the gauging station is also marked (red dot).



Figure 2.1.2.: The distribution of terrain levels of the Fishing Brook Catchment. Less than half of the area has an elevation above 600m a.s.l.

distribution of the catchment is shown in figure 2.1.2.

2.1.2. Landscape Units

The landscape of the Fishing Brook Catchment can be divided into three major units: (1) upland areas, (2) wetlands and (3) areas with open water (i.e. lakes, rivers and ponds). The proportion of the upland unit is about 89%, the weltand part accounts for 8% and the open water areas for the remaining 3% of the catchment area (RIVA-MURRAY, 2008).

There are also additional landscape units which can be assumed to be less important due to their small areal extent: The logging areas (most 75-100% cutting) account for less than 0.5% of the catchment area. Also less important is the amount of imprevious areas (there is one major Road, the 28N). The percentage of this impervious area is also less than 0.5%.

2.1.3. Vegetation

In general the vegetation of the Fishing Brook Catchment can be summarized as mixed northern hardwoods. During numerous field investigations different species were observed:

(1) The upland areas are dominated by american beech tree (*fagus grandifolia*), sugar maple (*Acer sachharum*) and red spruce (*pinus rubens*).

(2) The wetland area vegetation is characterized by speckeld alder (*alnus incana*) some red spruce trees (*pinus rubens*) and balsam fir (*abies balsamea*).

Similar species were observed by MCHALE ET AL. (2004) in the nearby Archer Creek Watershed.

2.2. Pedology

The mineral soils in the Fishing brook catchment are typically less than one meter thick. They can be divided into upland soils and wetland soils in the valley bottoms. The following soil characterization is given by MCHALE ET AL. (2002) for the Archer Creek Watershed. Similar soil characteristics were observed during field investigations in summer 2007.

The upland mineral soils are coarse, loamy, mixed frigid and can be classified as podzols (haplothords in the Becket-Mundell association). These podzols have a Oi horizon which is mostly about 5 cm thick. The following A horizon is most between 0-5 cm thick and has several roots and macropores. A strongly leached E horizon is also present at many locations. This horizon is between 0 and 2 cm thick. The B horizon is between 25-30 cm thick. It contains clay and coarse fragments. The following C horizon is underlain by bedrock or glacial till (described in section 2.3). In general the upland soils have high amounts of stored carbon, as shown by MITCHELL ET AL. (1992). The wetland areas also have high amounts of organic substances: They are accumulated in peat layers (Greenwood mucky peats) with a varying thickness of 1 up to 5 m (SOMMERS (1986) in MCHALE ET AL. (2002)).

2.3. Geology

The geology is mainly similar to the nearby research area of the Huntington Forest where a lot of studies were performed by the State University of New York - college of environmental science and forestry (SUNY ESF) (MCHALE ET AL., 2002; MITCHELL ET AL., 2001; INAMDAR ET AL., 2004, e.g.).

Similar to the Huntington Forest research site, the Fishing Brook Catchment is within an Anorthosite Massif in the central Adirondack mountains. This large igneous intrusion has high amounts of calcium-rich feldspar (MITCHELL ET AL., 2001) which can be solved when the rocks weather. The bedrock consists of pre-Cambrium rock. These rocks are mainly granitic gneiss with some gabbro-amphibolite from the snenitegranite series (FISHER, 1957).

The surficial geology is dominated by glacial till. The till was deposited during the end of the Wisconsian glacial epoch (14 000 years ago). The material was accumulated

on and within the glacier ice and deposited when the ice melted (MITCHELL ET AL., 2001). The glacial origin leads to a high fraction of sand ($\approx 75\%$) and a low proportion of clay in the till. Sand layers are often found between the mineral soils and the underlaying bedrock (SOMMERS (1986) in MCHALE ET AL. (2002)). Numerous cobbels and boulders were observed from (SOMMERS (1986) in MCHALE ET AL. (2002)) in Archer Creek as well as during field investigations in Fishing Brook. Figure 2.3.1 shows the surficial geology of the Fishing Brook Catchment. At higher elevations the bedrock is close to the surface. In the valleys till and glacial deposits are accumulated.

2.4. Climate

The climate of the Fishing Brook Catchment is a typical cool and moist northern continental climate. SHEPARD ET AL. (1989) shows long term data (1951 to 1980) for the Huntington Forest which is about 3.9 km (2.5 mi) away from Fishing Brook: The long term annual temperature is 4.4 °C. For the same location the January mean is -10.2 °C and the July mean is 17.4 °C. The mean precipitation for the period specified above is 1010 mm per year. Due to the relatively cool climate, about 47% of the precipitation during this period fell as snow.

2.5. Hydrology

As described in section 2.1.2 the landscape can be divided into different units. These major landscape units show different hydrological behaviors.

Figure 2.5.1 shows wetlands, open water bodies and the river flowpaths in the research area. The wetland dataset was identified and mapped by the Adirondack Park Agency (APA). The wetlands were delineated from 1 : 40000 and 1 : 58000 scale USGS aerial infrared photos which were taken during different research programs during the 1980s and 1990s (CANHAM ET AL., 2004). The delineation was based on the National Wetland Inventory (NWI) techniques (CANHAM ET AL., 2004). The mapping for rivers, ponds and lakes (flowpath and waterbodys) was taken from a USGS National Hydrography Dataset (NHD).

The drainage density for the Fishing Brook Catchment was calculated by using the NHD dataset. The drainage density was determined as 1.16 km/km^2 . A relatively low value compared to the value of 1.68 km/km^2 given by MCHALE ET AL. (2002) for the Archer Creek catchment.

The reaction time of the Fishing Brook Catchment was determined by comparing



Figure 2.3.1.: Surficial geology of the Fishing Brook Catchment. The till accumulations are mainly in the lower elevations - at the higher elevations bedrock dominates the close-to-surface geology.



Figure 2.5.1.: Wetlands, Rivers and Ponds in the Fishing Brook Catchment. The wetland dataset was mapped by the Adirondack Park Agency.

measured precipitation and temperature datasets as well as observed snowmelt amounts with the response of the outlet (waterlevel). The catchment typically reacts within one day. The time delay in which the highest water level followed an observed melting event was between 9 and 12 hours for most events.

Further different runoff processes were observed. Similar to observations in the Catskills (BURNS ET AL., 1998) and in the Archer Creek Watershed (MCHALE ET AL., 2002) several groundwatersprings can be found. These springs occur most often at the interface of wetlands and upland areas, where strong changes of the slope from the steeper uplands to the nearly flat wetlands occur.

Within the wetland groundwater springs were also observed. These springs seem to depend mainly on flooded/saturated areas upside their location. Flooded areas within wetlands often have their origin in high beaver activity. The beaver dams change the waterlevel and enhance the development of new small channels within the wetlands (DRISCOLL ET AL., 1987).

Another process being observed in the field was overland flow at different locations.

During low flow conditions (August 2007) only a few locations with overland flow were observed within the wetlands but at many places the waterlevel was just below the land surface (2-5 cm). During higher flow conditions (October 2007) most of the wetland areas showed a close to saturation state while most of the upland areas were not saturated.

During the snowmelt period 2008 most of the wetlands were saturated or flooded from the numerous small channels. At different locations the snowpack became saturated from below due to a rising groundwater level. Overland flow also occurred in the forested upland areas. Often the main flowpath was in very small channels between the snowpack and the soil. Most of the times these channels exist just temporarily (hours to days), as long as the snowpack above does not break down.

These observations suggest a high potential for a surface runoff component mixed out of meltwater and soil water of the upper soil horizons.

2.6. Summary

The Fishing Brook Catchment in northern New York State is mainly characterized by the glacial epochs. The granitic gneiss bedrock and the accumulated till indicates that a low mineralization of groundwater can be expected. These low mineralized waters have a low buffering ability which leads to the risk of acidification as shown by LAWRENCE ET AL. (2007) for the west-central Adirondack region.

When comparing the Fishing Brook Catchment to other catchments in the world, a

broad congruence of the properties of other boreal, forested areas can be found. Examples are given for the northern US (Vermont (SCHUSTER ET AL., 2008)), Canada (Ontario (GALLOWAY and BRANFIREUN, 2004)) and Scandinavia (northern Sweden (BISHOP ET AL., 1995)). This confirms that the research in the Fishing Brook Catchment is not only of regional importance.

3. Current State of Research

3.1. The Mercury Cycle

The current conceptual model of the mercury cycle in aquatic ecosystems is based on a mass balance model and on the assumption that the system has known boundary conditions. The model can be described by different pools (storages), fluxes between these pools, and fluxes into and out of the system (KRABBENHOFT ET AL., 2005). In figure 3.1.1 an example for the mercury cycle of a hypothetical watershed in the temperatured northern climate is given. The watershed properties and typical Hg concentrations were collected by KRABBENHOFT ET AL. (2005) from different studies.



Figure 3.1.1.: The Mercury cycle for a hypothetic temperatured northern watershed. The upper value in the pool and flux boxes represents the inorganic Hg fraction. The lower value shows a typical MeHg amount. The units are [g] for the pools and [g/year] for all fluxes. (KRABBENHOFT ET AL., 2005, modified).

Figure 3.1.1 demonstrates, that the likely pools for significant mercury storage in temperatured northern catchments are: (1) vegetation, (2) the organic horizon of upland soils, (3) the mineral horizon of upland soils, (4) wetland soils, (5) lake and pond sediments and (6) stream sediments. Even though the storages 3 and 4 represent only relatively small parts of the soil volume, they can be assumed as a major storage for inorganic Hg and MeHg.

General input (boundary fluxes) to the system would include dry and wet deposition. There is also a difficult-to-quantify flux of gaseous mercury in of Hg^0 and Hg(II) that may be deposited to the aquatic and terrestrial ecosystem. Part of this flux is represented by throughfall and litterfall, but an unknown fraction is not easily quantified. Losses from the system include the gaseous form to the atmosphere as well as the mass of Hg transported by the stream.

Fluxes within the system are complex. There are transport processes from one soil pool to another, transport from the soils to the stream, losses to sediment, and biological uptake. Some of these fluxes within the system are highly variable in space and time.

3.2. Mercury Input to Aquatic Ecosystems

The primary mechanism of mercury input to remote locations is atmospheric Hg transport (SCHUSTER ET AL., 2002). The species found in the atmosphere are elemental Hg⁰, gaseous divalent Hg(II) and particulate divalent Hg (PHg). These different species have very different atmospheric lifetimes. Hg⁰ is assumed to have an atmospheric lifetime of about 1 year. Hg(II) is typically removed from the atmosphere by dry or wet deposition in an much smaller time frame. The particulate mercury is highly variable. It is considered to be deposited slower than Hg(II), but shorter than Hg⁰ (SEIGNEUR ET AL., 2003).

The input to the atmosphere is mainly given by industrial sources (MANOLOPOULOS ET AL., 2007), by volcanoes and by a natural background (SCHUSTER ET AL., 2002). As shown by MANOLOPOULOS ET AL. (2007) the industrial emission can consist of different species.

The emission of these species is assumed to have different potentials for impact. Hg(II) is considered to have a higher potential for impact at the local and regional scale. The long range transport of Hg^0 and PHg is assumed to be the major factor to the global scale atmospheric deposition (SEIGNEUR ET AL., 2003).

The role of different sources at the local and global scale can be summarized by taking records of atmospheric deposition during the last centuries into account. SCHUSTER
ET AL. (2002) probed an ice core from the Upper Fremont Glacier in Wyoming to determine long term atmospheric Hg deposition. In figure 3.2.1 the results of a 270 a record is shown.



Figure 3.2.1.: A 270 year record of Mercury Deposition in the upper Fremont Glacier in Wyoming. The concentrations were determined by analysing 97 samples from an 160m lce core (SCHUSTER ET AL., 2002).

The results of the study of SCHUSTER ET AL. (2002) demonstrate, that there are several effects that influence the Hg concentration in the atmosphere: The pre-industrial background is quantified as 3 ng/l. Additional input of Hg is given by volcanoes. Their input was identified by linking three large eruptions (Tambora, Krakatau, and Mount St.Helens) to the ice records. Anthropogenic input was determined to contribute 52% of the total mercury deposition during the past 270 years and over 70% during the past 100 years. The ice core also showed an decrease of the Hg concentration since the 1990's. This decreasing effect can be explained by the lower industrial input (e.g. the lower emissions of coal burning power plants) SCHUSTER ET AL. (2002).

3.2.1. Deposition of atmospheric Hg

The regional and local deposition in the Adirondack area is specified by a study of SEIGNEUR ET AL. (2003). They used a three dimensional atmospherical model for chemical reactions called the Chemical Transport Model (CTM) to simulate the amount and origin of Hg deposition to the Huntington Wildlife Forest. Three different scenarios were calculated, assuming different levels of perturbation. The nominal base simulation representing the general behavior. The two other scenarios were: the local deposition base simulation, which showed a possible scenario in which a local deposition is more likely to happen and the long range transport base simulation, which represented a scenario in which longer transport ranges of Hg are favored. A detailed description of the input parameters chosen for three different scenarios is given in SEIGNEUR ET AL. (2003).

The results shown in table 3.2.1 indicate, that the total input of Hg deposited to the central Adirondacks is in the range of $18.8 - 19.3 \text{ mg/m}^2 \cdot year$. The dry deposition is dominated by Hg(II). The major input consists of wet deposition, which forms around 63% of the total Hg input for all three scenarios.

Type of deposition	Type of scenario		
	Nominal base simulation	Local deposition base simulation	Long range transport base sim.
Dry deposition of Hg(II) Dry deposition of PHg Wet deposition Total deposition	$6.4 \\ 0.6 \\ 12.2 \\ 19.2$	$6.4 \\ 0.7 \\ 12.2 \\ 19.3$	$6.3 \\ 0.5 \\ 12.0 \\ 18.8$
Unit	$[\mu { m g}/{ m m}^2 \cdot year]$	$[\mu { m g}/{ m m}^2 \cdot year]$	$[\mu { m g}/{ m m}^2 \cdot year]$

Table 3.2.1.: Simulated Hg deposition fluxes for the Huntington Wildlife Forest - Adirondacks, NY (SEIGNEUR ET AL., 2003, modified). Three different simulation scenarios were used. The results of all scenarios show a good congruence.

Another factor influencing the amount and species of Hg deposition is the vegetation. MUNTHE ET AL. (1995) compared the Hg deposition of an open area to the throughfall and litterfall of a coniferous forest in south-west Sweden. The study demonstrated that the total amount of Hg deposition in the forest is about 3 times higher than in the open field. The throughfall Hg input was about 1.5 times higher than the total Hg input to the open area. This effect was explained by MUNTHE ET AL. (1995) as a result of dry deposition on the canopy: Throughfall which passes the canopy washed off some of the dry deposited Hg from the leaves surfaces. The remaining amount on the leaves represent to be the second large input to the forest floor as litterfall. This input is quantified in the same range than the input via throughfall.

Another analysis of the differences between precipitation and throughfall is given by CHOI ET AL. (2008). The study revealed explicit deposition of Hg to the Huntington Forest for the period of December 2004 to December 2006. Figure 3.2.2 shows the wet deposition in the Central Adirondack region.



Figure 3.2.2.: Monthly Mercury concentrations and flux in precipitation and throughfall at the Huntington Wildlife Forest. (a) shows the monthly VWM Hg concentration and the precipitation/troughfall depth. (b) shows the monthly and the cumulative Hg flux. (CHOI ET AL., 2008).

The study indicated that different factors influence the Hg input of the central Adirondack region. In general a higher concentration and flux in the throughfall was observed, but the difference was much smaller than shown by MUNTHE ET AL. (1995). During the 2 year period, the volume weighted mean Hg concentration was 6.6 ng/L in throughfall and 4.9 ng/L in open field precipitation. The 2-year-flux was quantified as 12.0 μ g/L in troughfall and 11.6 μ g/L for the open field. The small difference in flux is explained by the higher amount of precipitation compared to throughfall. Within the measuring period strong variations were observed. In general the input by precipitation as well as by throughfall was much higher during the leaf-on period (from the beginning of May to end of October). A strong difference between throughfall and open field precipitation concentrations was identified during the leaf-on period. The effect of higher Hg concentrations in throughfall during the leaf-on period are explained by four possible processes: (1) the wash off effect of Hg on the leaves from dry deposition as shown by MUNTHE ET AL. (1995), (2) foliar leaching, (3) evaporation of a fraction of precipitation from the canopy, which might increase the Hg mass per water volume and (4) surficial oxidation of atmospheric Hg⁰ on the canopy.

3.3. Hg transformation to MeHg

In general the most important biochemical process of methylation is the reduction of Hg(II) by Sulfate Reducing Bacteria (SRB) (EKSTROM ET AL., 2003). Equation 3.3.1 shows the reaction:

~ ~ ~

$$Hg(II) \xrightarrow{SRB} CH_3Hg^+$$
 (3.3.1)

Two immediate conclusions of equation 3.3.1 are that the reduction process requires anoxic conditions and that the availability of Hg(II) is a major parameter for controlling the methylation rate of SRB. Beside the supply of Hg(II) the major factors affecting the methylation process are those influencing the activity of SRB population. The metabolism of SRB mainly depends on the availability of sulfate and carbon under anoxic conditions (KRABBENHOFT ET AL., 2005) and, therefore, the bioavailability of sulfate (as an electron acceptor) and organic matter (as an electron donor) can be limiting factors.

As described by BENOIT ET AL. (2003) the methylation by SRB is assumed to be a side reaction of the sulfate-reduction process. The rate of methylation of a cell is dependent on the rate of uptake and the rate of Hg being sequestered within the cell. There is strong evidence that the main fraction uptaken by SRB, is Hg which diffused through the cell membrane. In general the neutral Hg complexes are taken up much more likely (BENOIT ET AL., 2003). Therefore the species of Hg has an influence on the uptake of the SRB.

In aerobic waters the most important inorganic Hg ligands are Cl^- and OH^- , but due to the high amount of available DOC, organic bounds are much more likely. Thus DOC is the most important ligand in aerobic freshwater conditions with relatively low Cl^- concentrations (KRABBENHOFT ET AL., 2005) which leads to an two fold relation of Hg and DOC: On the one hand the biodegradable organic matter is required for the methylation process, but on the other hand Hg-DOC-complexes inhibit the mobilization and reduce the amount of bioavailable Hg (BENOIT ET AL., 2003).

Under anaerobic conditions reduced sulfur species are the most common inorganic ligands for Hg. Increasing sulfide concentrations support the genesis of HgS⁰, followed by HgHS⁻₂, HgS²⁻ and finally Hg(HS)⁰₂ (KRABBENHOFT ET AL., 2005). Is is assumed that especially HgS⁰ is the most important Hg species for uptake by bacteria, while Hg(HS)⁰₂ plays a less important role. Other neutral Hg species as for example HgCl⁰₂ are considered to be less important due to the fact that most of these Hg species are rapidly bound to the cell membrane (BENOIT ET AL., 2003). The dependency of the methylation rate to sulfate/sulfide concentrations is also two fold. In general the following pattern is observed: an increasing supply of sulfate mediates higher methylation, but when the amount of sulfide reaches a certain level, the methylation becomes inhibited (BENOIT ET AL., 2003). A hypothesized explanation for this behavior is the higher probability of charged Hg speciation, when sulfide concentrations rise (KRABBENHOFT ET AL., 2005). As a consequence, the factors affecting bioavailability and microbial activity become interdependent (KRABBENHOFT ET AL., 2005) and the modeling of methylation rates becomes critical (BENOIT ET AL., 2003).

Other factors influencing the methylation rate of SRB are temperature and pH. The role of pH on the methylation rate is shown by BENOIT ET AL. (2003) by using a simple model which simulates the complexation of Hg species with a fixed sulfide concentration: In the range of an pH value from 7 to 10, it is assumed that an increase of the pH supports a higher rate of HgS⁰ and less charged Hg complexes, which increases the methylation rate. A pH below 7 is assumed to lower the amount of bioavailable HgS⁰ due to more charged complexes and, therefore, the methylation rate. Another dependency of pH is given by the strong influence of hydrophobic acid fraction(HPOA) which are often a major fraction of the DOC concentration (SCHUSTER ET AL., 2008) and strong ligands to Hg. DITTMAN ET AL. (2007) show stronger relations between HPOA and total Hg than for DOC and UHg for several catchments in the north-eastern US, which indicate, that organic acids influence the pH as well as the mobilization of

Hg. Temperature is also assumed to have a direct influence on the SRB activity when the supply of sulfate and DOC is not limited. But, due to the reason that changes in temperature affect methylation as well as demethylation, the effects of temperature on methylation are not fully understood (BENOIT ET AL., 2003).

3.3.1. Demethylation

In general demethylation occurs in both forms, as an biotic and as an abiotic process. The biotic degradation of CH_3Hg can be done by two different types of processes: The (1) mer-detoxification pathway and the (2) 'oxidative demethylation' (KRABBENHOFT ET AL., 2005). While the degradation via mer-detoxification is assumed to be predominant at locations with higher Hg contamination, the 'oxidative demethylation' is the prevailing mechanism for remote locations with an lower Hg input (KRABBENHOFT ET AL., 2005). The reaction of the 'oxidative demethylation' consists of two chemical reactions, oxidation and reduction, for which the methyl group is altered to CO_2 and CH_4 . The reaction is shown by BENOIT ET AL. (2003) in equation 3.3.2.

$$4CH_3Hg^+ + 2H_2O + 4H^+ = 3CH_4 + CO_2 + 4Hg^{2+} + 4H_2$$
(3.3.2)

Abiotic demethylation is not very well understood. The most important process of abiotic demethylation is photodemethylation which is driven by UV light exposure. In lakes and ponds high rates of photodemethylation are possible. The main dependency is water turbidity, which influences the depth of penetration in a water column (KRABBENHOFT ET AL., 2005).

3.3.2. Hg transformations in the catchment scale

In the catchment scale the distribution of bioavailable organic matter, Hg and sulfate and anoxic conditions leads to the assumption that high methylation rates can be expected in systems as wetlands, recently flooded reservoirs and periodically flooded river plains (BENOIT ET AL., 2003).

These locations are generally described as so called 'hot spots' of elemental cycling. The following definitions for biochemical hot spots and hot moments are given by MCCLAIN ET AL. (2003):

• 'Hot Spots are areas (or patches) that show disproportionally high reaction rates relative to the surrounding area (or matrix).'

• 'Hot Moments are short periods of time that show disproportionally high reaction rates relative to longer intervening time periods.'

Beneath these definitions MCCLAIN ET AL. (2003) also explained, that for hot spots a mixture of complementary reactants is needed. This can be given by an flowpath which converges with another flowpath or another substrate. In terms of hot moments the mobilization of accumulated reactants and/or reactivation of flowpath is the typical way to achieve the additional reactant. Thus, hot spots and hot moments can occur separately, but it is also possible that they overlap since it seems to be unlikely, that hot moments appear at all locations commensurately.

A study by MITCHELL ET AL. (2008b) shows methylation hot spots at the interface of uplands and wetlands. I high number of UHg and MeHg pore-water samples was collected from many different locations within four different headwater peatlands in northern Minnesota and northwestern Ontario. In the study the percentage of MeHg of the total Hg concentration was used as a proxy for the methylation rate at one location. The 90th percentile value (22% MeHg of UHg) of all samples was used to define methylation hot spots. Figure 3.3.1 shows contour plots of typical Hg hot spots at the upland/wetland interface.

The general pattern observed by MITCHELL ET AL. (2008b) is that the highest percentages of MeHg were measured within the first 5 m of the peatlands. Thus, MITCHELL ET AL. suggest that the maximum width of Hg transformation hot spots can be assumed to be 3 m. The variation of the percentage of MeHg with seasonality also indicates that there are additional dependencies on temperature and supply of reactants.

Another paper by MITCHELL ET AL. (2008a) shows the supply dependency of the Hg methylation in hot spots at the upland/wetland interface. In an in situ experiment SO_4 and different organic C sources (glucose, acetate, lactate, coniferous litter leachate and deciduous litter leachate) were added to 44 peatland mesocosms in northern Minnesota. The results show, that an addition of organic C (glucose, acetate, lactate) does not increase the concentration and percentage of MeHg. The addition of coniferous or deciduous leachate, which are both assumed to contribute organic C as well as Hg(II), did not lead to an increasing effect either. A higher production of MeHg was observed when SO_4 was added. The highest MeHg was an effect of combined sulfate and carbon addition. Two different artificial inputs were used: 4 and 10 times annual atmospheric deposition. The lower combined input (4 times) generally resulted in greater net production of MeHg than the higher (10 times) input. Due to low sulfide concentrations after both, high and low combined additions, MITCHELL ET AL. assume that low



Figure 3.3.1.: Contour Plots of the methylation proxy (% MeHg of UHg) for the two peatlands in Minnesota. The dashed line represents the upland/wetland interface characterized by a change in the topography and/or in the soils. The hillslope runoff is from upper right to the lower left for all plots. Spring sampling was done in early June, Summer in August, Fall in early October in 2005 (MITCHELL ET AL., 2008b).

MeHg production is not a result of Hg(II) sulfide complexation. Thus it has to be assumed that other effects than the simple 'delivery of limiting reactants', as indicated by MCCLAIN ET AL. (2003), influence the dynamic of Hg methylation in Hg hot spots (MITCHELL ET AL., 2008a). To the authors the opposed effect of methylation and demethylation at higher SO₄ and organic C levels seems to be more reasonable than sulfide complexation. As shown before, another explanation which was not assumed by the authors could be the Hg complexation with organic C.

3.4. Transport

As shown before, the transport of Hg and other possible reactants for the Hg methylation within the watershed are of major importance. In the following section a number of studies investigating the mobilization of DOC and Hg at different scales will be shown.

3.4.1. DOC Flushing

One of the early papers showing the flushing of organic carbon from upland areas is the paper of HORNBERGER ET AL. (1994). In an alpine catchment in Colorado the flushing of DOC during the snowmelt showed clockwise hysteresis. During several years the DOC concentration peaked between 14 and 36 days before the peak runoff. HORN-BERGER ET AL. (1994) developed a conceptual model for representing the flushing mechanism in the following way: It was assumed, that the variation in the DOC concentration in the stream is a mixing of subsurface flow of lower and higher soil horizons. It was hypothezised that during baseflow conditions the flowpath of the subsurface flow would be mainly in the lower horizons. During high flow conditions it was assumed that subsurface flow would move in the lower horizons as well as in the higher ones. Following this idea, nutrients as DOC can be leached from the upper soil horizons if they are available.

A study by MCGLYNN and MCDONELL (2003) points out, that there are two major sources for DOC: the upper layers of the upland soils and the riparian areas. They demonstrated that the DOC dynamic at the catchment scale is a result of the mixing of DOC from different spatial sources. For the DOC contribution from the hillslopes it was shown, that a wetness threshold has to be reached before measurable contributions to the stream can be observed.

WEILER and MCDONELL (2006) addressed the question of first order controls of the flushing of DOC and other nutrients to virtual experiments using the hillslope model Hill-vi. The general findings showed, that there is an influence of hillslope geometry and antecedent wetness which can produce both, clockwise and counterclockwise flushing patterns. The general result for the mobilization ratio (relative amount of nutrient which gets mobilized) was, that previously wet conditions support a higher export of DOC. Further results are, that for the DOC dynamic at the hillslope scale the mechanism of transmissivity feedback can be assumed to be more important on concave hillslopes than on straight hillslopes. The same effect can be observed for nutrient mobilization. Thus concave and wet hillslopes are assumed to have the highest mobilization ratio for the transport of nutrients to the stream.

A detailed study comparing the contribution of riparian and hillslope DOC and their biochemical properties was investigated by ÅGREN ET AL. (2008). SUVA₂₅₄ (see 4.1.2 for explanation) which is an indicator for the aromaticity fraction (WEISHAAR ET AL., 2003) and the relation between A_{254}/A_{365} which is negatively correlated to the molecular weight of DOC was used to separate different sources of DOC.

In general, the carbon character of forest soils had higher A_{254}/A_{365} values and lower

 $SUVA_{254}$ than the wetland soils. While the DOC character changed with depth of forest soils (strongly decreasing A_{254}/A_{365} , stable $SUVA_{254}$) the character of wetland DOC is more stable (light decrease of A_{254}/A_{365} , stable $SUVA_{254}$).

During winter baseflow the character of DOC in the streams was sensitive to the percentage of wetlands. When the percentage of 10% was reached, the character of DOC was indicated that wetlands were the predominant contributors for DOC to the stream. During the spring flood this dependency became less important and the character changed to more low molecular weight and less aromatic DOC, indicating that higher soil horizons of the forested uplands also contributed to the stream under these high flow conditions.

3.4.2. Mercury Flushing

As shown by different studies (GALLOWAY and BRANFIREUN, 2004; SCHERBATSKOY ET AL., 1998, e.g.) just a small fraction of the Hg input reaches the output of the system by the stream. Wetlands are assumed to support Hg retention. Flux calculations from GALLOWAY and BRANFIREUN (2004) show that about 69% of the UHg input is stored in the soils or lost by deep groundwater fluxes or Hg⁰ evasion. A even higher percentage (95%) was observed by SCHERBATSKOY ET AL. (1998) for an upland catchment. They also observed, that during high flow conditions like snowmelt, a major fraction of the anually Hg flux can be mobilised within one day.

The dynamic of Hg during snowmelt was investigated in Sweden by BISHOP ET AL. (1995). His study showed a general rise of total carbon (TOC) peaking early in the melting period, while total unfiltered mercury (UHg) peaked with the highest peak in discharge. MeHg became deluted and showed the lowest concentration during the second high peak. Another paper by LEE ET AL. (2000) focusing on the same catchment in Sweden showed that the pattern of high total Hg concentrations during the peaks and dilution of MeHg can be observed during several years. A general coupling of DOC and UHg was also observed. This pattern is explained by LEE ET AL. (2000) as a flushing mechanism from the organic rich top soil which also had the highest Hg concentrations. MeHg peaked in summer during several years, when higher flow states were reached by summer storms. As an explanation LEE ET AL. (2000) considered that flowpaths through the riparian zone were the major factors causing the observed MeHg pattern: During low flow the stream channels are below the riparian wetlands. Subsurface flow passes the organic and MeHg rich riparian soils before entering the stream. A fast dilution is assumed to be the result of the limitation in supply of the MeHg pool in these riparian zones during the spring flood.

SHANLEY ET AL. (2002b) showed a strong correlation of DOC concentrations and dissolved total mercury for the Sleepers River Watershed in Vermont. The ratio of UHg/DOC was used to address the effect of a similar flushing of DOC and inorganic Hg from the soil. DOC and inorganic Hg are positively correlated with streamflow, but the relation of UHg to DOC increased, as snowmelt proceeded. SCHUSTER ET AL. (2008) report for the Sleepers River, that the highest Hg concentrations of a 3-year period were observed slightly before peak flows, when the highest organic carbon concentrations were measured. During the snowmelt SCHUSTER ET AL. (2008) assumed that the high UHg concentrations occurring during the springflood can be explained by a combination of processes: A Hg enriched snowpack melts and the water drains to the surficial soil, which has high Hg and organic matter contents, due to the input of litter during autumn. The high water input during melt resulting in saturation excess overland flow in stream-near areas, the 'riparian flushing' is assumed to be the responsible process for the high Hg concentrations during the springflood (SCHUSTER ET AL., 2008).

SCHUSTER ET AL. (2008) also point out, that summerstorms can have a high impact on Hg transport. Even though they are of a shorter duration than the snowmelt, the fluxes are in a comparable dimension (SCHUSTER ET AL., 2008). Similar observations for the Hg export of summerstorms were made by BUSHEY ET AL. (2008) for the Archer Creek catchment in the central Adirondacks.

3.5. Summary

Even though the mercury emissions in the US peaked over the last 20 to 40 years (SHANLEY ET AL., 2002b) and the input of Hg to remote ecosystems is assumed to decrease, the mercury stored in soils is still available and can be mobilized by hydrological events. Thus the question of a Hg threat for remote ecosystems mainly depends on mobilization mechanisms and Hg transformation.

4. Chemistry and Oxygen-18 during the Snowmelt

4.1. Methods

In this chapter the methods applied in this study will be presented. The chapter is subdivided into the field methods, the chemical analysis and the the data analysis. After that the results will be presented and discussed.

4.1.1. Sampling

In this section the methods used in the field are described. The sampling was done in different parts of the catchment.

Continuous measurements at County Line Flow

The gauging station at the Fishing Brook catchments was installed in January 2007. The station consists of a datalogger (campbell scientific) with an pressure transducer. The weir is located at the outlet of a pond. It is installed under a bridge. Around the bridge a dam divides the valley and, thus, it can be assumed that the entire water which drains in the catchment is passing the station. The Bridge has a given cross section made of concrete. In order to obtain the needed rating curve (water level to discharge equation) a standard USGS method using several discharge measurements of different flow conditions was used.

The water level is measured as a 15 minute average value to reduce the influence of short time variations (i. g. waves on the pond near the outlet). Additionally the air temperature is measured. For this study an additional probe for water temperature and specific conductance (campbell scientific CS547A) was installed in mid of march 2008. The measurements of this probe are also available as 15 minute average values.

Additional records of precipitation and temperature (daily max, min and mean) were available from the NCDC meteorological station in Newcomb, New York (43.97°N, 74.19° W).

Chemistry and Oxygen-18 sampling

The sampling for major Ions, DOC and Oxygen-18 at County Line Flow was performed by using an ISCO automated sampler. The time interval of the sampling was varied between 24 and 6 hours depending on flow conditions. The automated sampler was emptied within one week and the samples were stored cool and dark in a fridge in the ISCO bottles. As the automated sampler was frozen several times (especially during a cold period in march 2008) additional samples were taken manually.

Because of the high number of samples only an selection was used for analysis. The selection was done in am manner that all relevant stages of discharge were included. A more detailed description is given in section 4.1.2.

Additional samples for chemistry and Oxygen-18 from different locations within the catchment were taken manually. To get a better insight into the differences of wetlands and uplands, shallow groundwater from three different wells in the sixmile wetland were drawn during the snowmelt. The upland area was sampled at the so-called Unnamed Tributary site, a small tributary which is located at the northern slope of Windfall Mountain. Additional samples of overland flow and deep groundwater were taken as well. The locations of the different sites are shown in the map 4.1.1.

To get an comprehensive view of the chemical conditions during the melt, different in situ measurements were also performed. Air and water temperature, pH, specific conductance, dissolved oxygen and oxygen saturation and barometric pressure were measured with a Hydrolab MS5 coupled to a Hydrolab Surveyor hand held.

The in situ measurements were done two times per day (morning and evening) at the County Line Flow gauging station. At the other locations it was simultaneously to the water sampling.

Snow Sampling

The snowpack was sampled at different locations beginning in mid of March 08. Aim of the sampling was to characterize the snowpack and the melt in the whole Fishing Brook area. An overview of the sites (A to F) is given in the map 4.1.1. The sampling locations were selected to meet different requirements: They had to be accessible within an reasonable time frame. This explains that all sites are located near the major road 28N. The sampling also had to cover the different elevations of the catchment. The sites with higher elevation (C,D) are at the northern slope of Windfall Mountain, within the Unnamed Tributary.

The snow sampling was done by drawing snowcores to determine the depth of the snowpack, the snow-waterequivalent and the snow density. This was performed several times within the melting period for each location. To cover small-scale variation 3 to 5 snowcores were taken during each of these samplings. The snowcores were ran down into the top soil. This ensured that the entire snowpack is sampled. It also allowed to testify, if the top soil is frozen or not.

During all snow samplings the content of the snowcores (without topsoil) was collected and packed into zip-lock bags. subsequently they were melted in a fridge and a selected number was chosen to be analyzed for major ions, DOC and Oxygen-18.

Mercury Sampling

The procedure of the Mercury sampling was done following the specifications of the USGS National Water-Quality Assessment (NAWQA) Program. Four samplings for the different mercury species were performed during the snowmelt 2008. The first samples were taken on 2nd of April to cover the early-melt conditions. A second sampling was done on 04.12.08 (second peak), when the highest flow occurred. The third sampling was performed at the third peak (04.20.08). A final set of samples was done on 1st of May, to represent the late snowmelt conditions.

All samples were taken close to the middle of the stream at the gauging station at County Line Flow. Ultra clean teffon bottles were used. The samples were cooled and brought to the USGS laboratory in Troy, NY, for filtering within several hours.

4.1.2. Sample Analysis and Uncertainty

Analysis of Major lons and DOC

The analysis of the samples was performed at the U.S. Geological Survey's New York District Water-Analysis Laboratory. A full description of the analysis techniques can be found in LAWRENCE ET AL. (1995).

- Anions Chloride, Nitrate and Sulfate: The selected sampled were filtered with an 0.4 μ m polycarbonate filter and stored in the fridge at 4 °C. The anion concentrations were measured by using a ion chromatograph.
- Acid Neutralizing Capacity (ANC): ANC is determined by titration with sulfuric Acid (H_2SO_4) .
- Cations Calcium, Magnesium, Sodium and Potassium: the samples were filtered with an $0.4\mu m$ polycarbonate filter and acidified to a pH < 2 by adding 5ml of reagent grade nitric acid (HNO_3) . The samples were analyzed by using a atomic absorption spectrophotometer.



Figure 4.1.1.: Sampling locations for this study. The deep groundwater sampling location is not shown. It is located 3.2km east of County Line Flow and is used for the water supply of the Huntington Forest research camp.

- Dissolved Organic Carbon (DOC): the samples for DOC were filtered through an Whatman GF/F filter. The DOC concentration is measured by converting all organic carbon into carbon dioxide (ultraviolet radiation and persulfate oxidation). The carbon dioxide is then analyzed by using a infrared detector.
- pH: the negative logarithm of the activity of hydrogen ions (pH) was measured with an pH electrode. The temperature was also measured and pH was compensated for different temperatures.
- Aluminum: samples were acidified and analyzed by using the graphite-furnance atomic absorption spectroscopy to measure the total aluminum concentrations.
- Silicon: the Silicon concentration was measured by using the colorimetric reaction of acidified ammonium molybdate and the silicon. The siliconmalybdate is then reduced by ascorbic acid. The concentration is determined by measuring the intensity of the blue complex.
- UV-Absorbance: The samples were filtered with an Whatman GF/F filter. The UV-Absorbance at 254nm was measured by using a UV Spectrometer.
- SUVA₂₅₄: The SUVA₂₅₄ values were calculated by dividing the UV_{254} Absorbance by the DOC concentration as described by WEISHAAR ET AL. (2003).

The table 6.3.3 gives the uncertainty and the detection limits for the different chemical parameters described above.

Analysis of Oxygen-18

The analysis for Oxygen-18 was performed at the Laboratory of the Institute of Hydrology at the University of Freiburg. The analysis was done by using a Finnigan Delta S stable isotope ratio mass spectrometer. The samples were compared to standards and the measured Oxygen-18 ratios are given as relations (δ) of ¹⁸O to ¹⁶O as given by CLARK and FRITZ (1997):

$$R = \frac{{}^{18}O}{{}^{16}O} \tag{4.1.1}$$

Table 4.1.1.: Uncertainty and reporting limits for different chemical parameters in the low level range analyzed in the USGS Laboratory in New York (LAWRENCE ET AL., 1995, modified). cv = coefficient of variation.

constituent	reporting limit	accuracy	precision
or property		data quality objective	data quality objective
	[umol/l]	[%] error	[%] cv
Cl ⁻	2.0	10	15
NO_3^-	2.0	10	15
SO_4^{2-}	2.0	10	15
ANC	none	10	10
Ca^{2+}	2.0	10	15
Mg^{2+}	1.0	10	15
Na^+	1.0	10	15
K^+	1.0	10	15
DOC	41.0	15	15
pН	none	10	10
Si	6.0	15	15
Al	-	20	10
UV Absorbance	_	-	10
(estimated)			

$$\delta = \frac{R_{sample} - R_{standard}}{R_{sample}} \cdot 1000\%_0 \tag{4.1.2}$$

The standard used in this study is 'Vienna Standard Mean Ocean Water' (V-SMOW). A number of 40 samples from the stream at County Line Flow and samples from snow (18), overland flow (3), uplands (5), wetland water (12), deep groundwater (1) and rain (6) were selected and analyzed.

The uncertainty for the measurements made with the Finnigan Mass Spectrometer is given as $0.1\%_0\delta$ (V-SMOW). This value was determined from long term comparison of different laboratory standards.

Mercury Analysis

The mercury analysis was done by the USGS Mercury Research Laboratory in Wisconsin and was performed for the following species:

• FHg and PHg: The determination of the filtered and particulate total mercury in the water was done by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS). • FMeHg and PMeHg: The filtered and particulate methyl mercury concentrations were measured by distillation of the samples for subsequent determination of methyl mercury by aqueous phase ethylation, followed by CVAFS or by direct aqueous phase ethylation, followed by CVAFS.

A more detailed description of the analysis is given by OLSON and WILD (1999) and WILD ET AL. (2002). Table 4.1.2 gives the uncertainty of the mercury analysis.

Table 4.1.2.: Uncertainty and reporting limits for different Hg species analyzed at the USGS Mercury Research Laboratory in Wisconsin (OLSON and WILD, 1999; WILD ET AL., 2002, modified).

Hg species	reporting limit	accuracy	precision
		data quality objective	data quality objective
	[ng/l]	[%] error	[%] cv
FHg, PHg	0.04	10	10
FMeHg, PMeHg	0.04	<17	< 15.6

4.2. Results

In this section the results of the hydrological and chemical response of the snowmelt 2008 are shown. The entire snowmelt period began in mid of March 2008. As good as all snow was melted until mid of May. The period of highest importance is the high flow period from 1st of April to 5th of May. This period will be called 'spring flood' and is shown in figure 4.2.1.

4.2.1. Hydrological Response

The snowpack in the Fishing Brook catchment was well developed, having a depth between 500 and 1100 mm and a snow waterequivalent between 190 and 410 mm at the lowest site at the edge of the Sixmile Wetland (F) and at the highest, forested sampling site (C) respectively.

The melting generated a springflood, consisting of three major events: the first one (peak I) was mainly forced by the high air temperature from the beginning of April till 10th of April. The second peak (II) was forced by a Rain on Snow (ROS) event. The total amount of rain between the 10th and the 12th of April was 22.5mm. The rain was caused by a warm front from the northwest. After that, a temperature drop from 4.4°C to 0.0°C caused by a cold front arriving on 11th of April was observed. After the cold front another warmer period followed. The third peak (III) is based on this warm period during which all the remaining snow was melted. Some following rain events influenced the falling limb of the hydrograph after the major melting events. Figure 4.2.1 shows the hydrological response and three melting peaks.

4.2.2. Chemical Response

At the outlet at County Line Flow, the stream shows a strong decrease from 44.6 to $18.8 \ \mu\text{S/cm}$ in specific conductance following slightly the hydrograph response. A delay between 13 and 38 hours was observed for the three major peaks.

Another parameter strongly influenced by the melt is the water temperature. In general an increase of the water temperature was observed, when a warming during the day occurred. Cooler air temperatures at night generated a diurnal pattern of warming and cooling down. These patterns changed, when the melt proceeded. Two major changes in the general level of water temperature can be identified: One between the 14th and the 16th of April (1.8° C to 4.2° C) and another one between the 18th and the 20th of April (5.0° C to 10.6° C). Figure 4.2.2 shows the behavior of specific conductance and temperature of the outlet station of Fishing Brook during the melt.



Figure 4.2.1.: The springflood in 2008 occurred from the 1st of April to the 5th of May 2008. The first peak (I) occurred on the 04.10.08, the second peak (II) on the 04.12.08 and the third (III) on 04.20.08. These definitions will be used in the following sections.



Figure 4.2.2.: Water temperature and specific conductance during the springflood 2008.

As already indicated by the conductance, the results of the samples of anion and cation concentrations show a strong general decrease, but just small changes of the relative fractions of the stream water during the melting period. Figure 4.2.3 shows the general fractions of calcium, sodium and potassium, magnesium, and the fractions of sulfate, chloride and hydrogen carbonate.

Samples of shallow groundwater from the wetlands (also called 'wetland water') change their composition strongly during the melt. Samples of wetland water taken during the falling limb after peak III show a chemical composition which is in congruence with the deeper groundwater sample. Upland water shows in general a similar composition as stream water, but has much lower concentrations, except for sulfate. The sulfate concentration of all upland and overland flow samples constitutes a much higher proportion of the total mineralization than the wetland and stream water samples. Tables with the entire chemical data are given in appendix A.1.



Figure 4.2.3.: Piper Diagram with stream water and other typical end members. The stream samples are mainly projected at the same location, showing no major changes in the relative composition. A distinct difference is given for upland water and overland flow as well as for some wetland samples and deep groundwater

4.2.3. Oxygen-18

The stable water isotope Oxygen-18 shows a high dynamic in the stream; values between $-12.44\%_0$ (all values are δ regarding to V-SMOW) between peak I and II and $-11.48\%_0$ at the and of the springflood were observed. During winter baseflow (20th of March) -11.82% were measured. Generally the δ values follow the hydrograph inversely, but during peak II no lowering is observed, whereas during peak III a short increase from -12.14% to -11.96% and back to -12.24% is taking place.

Snow samples show a big spatial variation. Samples taken within a 10×10 m plot at location A at the beginning of the melt show values between $-12.50\%_0$ and $-14.18\%_0$. This variation is similar to the general variation of the snow samples: $-12.35\%_0$ to $-14.18\%_0$. The average snow isotope signature is $-13.14\%_0$. Rain shows much higher values between $-5.32\%_0$ and $-11.42\%_0$ (except for one sample with $-12.63\%_0$).

Upland water and overland flow observations are generally in the range of snow, but showing higher values as melt proceeds. Wetland water of the first two samplings is between the values measured for snow and the stream at the corresponding time. The last wetland sampling (18th of April) shows values between stream water (-12.04%₀) and deep groundwater (-11.40%₀). Figure 4.2.4 shows the dynamic of ¹⁸O of the stream at County Line Flow as well as all other samples taken during the melt.



Figure 4.2.4.: Dynamic of Oxygen-18 during melting period. Samples from Streamwater, Snow, Rain, Upland Water and Overland Flow, Wetlands and Deep Groundwater as well as the Hydrograph are plotted. Note the break in the right Y-axis

A more detailed view on the snow samples demonstrates, that the isotopic composition of the snowpack changes with the elevation. In figure 4.2.5 the samples collected from the sites A (County Line Flow), C and D (both located on the slope of Windfall Mountain) after 4th of April ca be seen. Equation 4.2.1 gives the mean change of δ ¹⁸O dependent on the elevation h in 100 meters.



Figure 4.2.5.: δ ¹⁸O change of the snowpack with elevation of the sites A, C and D after 4th of April 2008.

$$\delta^{18}O(h) = -0.27 \cdot h - 11.16 \tag{4.2.1}$$

4.2.4. DOC, UV Absorbance and SUVA

DOC

The average dissolved organic carbon concentration of the 40 stream samples which were collected during the melt were 5.78 mg/L. The concentrations showed an increase with the rising hydrograph. At the beginning of the springflood the concentrations was rising from 4.08 mg/L to 5.71 mg/L. During the first peak the DOC concentration changed from 4.92 mg/L to 5.56 mg/L; after peak II a concentration of 6.16 mg/L was reached. The lowest concentration between peak II and III was measured on the 18th of April. At this date, the hydrograph was already rising to the third peak. During the third peak the DOC concentration was rising, till a maximum concentration of 6.69 mg/L was reached on the 23th of April, three days after peak III. After that the concentration stayed high at levels in the range of 6.43 mg/L to 7.07 mg/L, which is the highest value measured, occurring on 1st of May.

The general timing pattern of DOC to the hydrograph is delayed. The DOC peaks were between 36 and 45 hours delayed for peaks I and II and 72 hours for the peak III. The following smaller peak showed a delay of 39 hours. The difference in the timing of the lowest flow between peak II and III and the lowest DOC concentration was 51 hours.

Upland DOC concentrations were low (2.23 - 2.89 mg/L) and show an increase during the melt. The highest measured value was from a sample taken on 12th of April (2.89 mg/L). Overland flow samples have different concentrations; while a sample collected uphill between the snow sampling locations C and D shows a higher concentration of 3.94 mg/L. Samples taken at lower elevation have lower values of 2.19 mg/L and 2.23 mg/L for locations near the sampling sites of County Line Flow and Sixmile Wetland respectively.

The highest concentrations were measured in samples containing shallow groundwater from the wetlands: while the samples taken prior to peak I and II have concentrations of 5.47 mg/L to 7.58 mg/L, samples taken at the end of the springflood (5th of May) have much higher concentrations (4.69 - 14.25 mg/L).

Lower values were observed for the snow (0.85 - 2.10 mg/L). The values measured for rain are in the range of 2.81 mg/L to 6.49 mg/L. The deep groundwater sample had the lowest DOC concentration - only 0.79 mg/L were found.

UV Absorbance₂₅₄ and SUVA₂₅₄

UV Absorbance is generally following the delayed pattern of DOC. The UV Absorbance at 254nm shows values between 0.182 to 0.303 $[cm^{-1}]$. The lowest value in the stream was measured for the beginning of the springflood (2nd of April), the highest for the 30th of April. During peak I a change from 0.209 to 0.238 $[cm^{-1}]$, during the second peak 0.268 $[cm^{-1}]$ and during peak III a much stronger delayed peak of 0.264 $[cm^{-1}]$ was observed.

Upland samples and overland flow show a UV Absorbance in the range of 0.070 to 0.106 $[\text{cm}^{-1}]$ while snow samples are between 0.017 and 0.046 $[\text{cm}^{-1}]$. The highest values were measured similar to DOC in the wetlands (0.284 to 0.683 $[\text{cm}^{-1}]$).

The calculated SUVA values for the stream follow a quite different pattern. Very high values occur at the beginning of the springflood (4.45 [L/mgC· m] on the 2th of April), two minimums appear on 17th and 23rd of April with 3.90 and 3.85 [L/mgC· m] respectively. During the main part of the springflood SUVA positively follows the hydrograph of all three peaks and the minimums before and after. There is no delay in the timing of this behavior. Figure 4.2.6 shows the dynamic of DOC, Absorbance₂₅₄ and $SUVA_{254}$ during the springflood 2008 at County Line Flow.

SUVA values for the wetland samples ranged from 3.37 to 5.01 [L/mgC· m], while upland and overland flow ranged ranged from 2.69 to 3.50 [L/mgC· m]. The deep groundwater showed a low value of 2.03 [L/mgC· m]. Rain was between 0.89 and 1.59 [L/mgC· m] and snow between 2.00 and 2.19 [L/mgC· m].



Figure 4.2.6.: Dynamics of DOC, Absorbance₂₅₄ and SUVA₂₅₄ during the springflood 2008. While DOC and UV Absorbance show a strong delay of several hours to days, SUVA shows no time lag.

4.2.5. Mercury

Mercury generally showed an increase during the springflood 2008. Total unfiltered mercury (UHg) increased from 1.768 ng/L (2nd of April) to 2.765 ng/L during peak II and 2.951 ng/L peak III, which is the highest measured concentration. After peak III UHg decreased one slightly to 2.949 ng/L for the sample taken at the end of the melting period.

The fractions of unfiltered total Mercury are dominated by the filtered mercury (FHg) concentrations, which account for 93% of the early sample, 84% for peak II and 89% for peak III as well as for last sample. The total particulate Hg concentrations (PHg) are in the range of (0.128 - 0.445 ng/L) peaking in the sample collected during peak II.

Total methylmercury concentrations (UMeHg) ranged from 0.02 to 0.1 ng/L. The concentration of 0.08 ng/L at the beginning was lowered to 0.02 ng/L during peak II and stayed low during peak III (0.0443 ng/L). The highest MeHg concentration (0.1 ng/L) is measured for the last sample (1st of May). Methylmercury is also dominated by the filtered fraction (FMeHg). The values for particulate MeHg (PMeHg) reported for the early sample, peak II and the sample at the end of the springflood were below the detection limit of 0.004 ng/L. The filtered fraction of peak III is 90.3%. Figure 4.2.7 shows the response of the different mercury fractions in the Fishing Brook catchment during the springflood 2008.

When comparing the Hg behavior to an annual period (06.01.07 to 06.01.08) a decrease of the UHg concentrations from 2.166 ng/L to 1.501 ng/L during the summer low flow (July to October 07) is observed. UHg also shows several peaks in the range of the melting peaks, forced by hydrological events as rainstorms as well as melting events which force a direct reaction of the hydrograph.

UMeHg shows one of the strongest minimums during the melt 2008. Concentrations of the same, low level are only observed during a summer storm sampled on the 13.01.07 and as a result of melting events during the winter (01.02.08 and 03.11.08). Figure 4.2.8 shows the snowmelt compared to UHg and UMeHg samples taken during the previous year (06/01/2007 till 06/01/2008).

Dynamic of methylation factors

Major factors indicating possible reducing conditions and thus the possibility of methylation are a decrease of sulfate, dissolved oxygen and DOC. For sulfate a strong decrease from a concentration of 4.68 mg/L during winter baseflow to 3.29 mg/L during peak I and to 3.13 mg/L during peak II was observed. After peak II sulfate stays at values



Figure 4.2.7.: Mercury fractions during the springflood 2008: Total Hg fractions (Uhg, FHg and PHg) are shown on the left (A), Methylmercury fractions (UMeHg, FMeHg and PMeHg) on right (B). The hydrograph is shown in gray in the background. Note the different scalings of the right y-axis. Error bars are not shown for PMeHg because of values at the detection limit (0.004 ng/L).

between 3.44 mg/L and 3.67 mg/L as melt proceeds. Oxygen also shows a strong decrease during the melt. Short increases are observed during peak II and on the rising limb of peak III. Oxygen saturation values are in the range of 88% to 95%. Nearly saturation is observed at the beginning of the melt as well as for one sample at the end of the springflood (4th of May).

The DOC dynamic is described in section 4.2.4. Figure 4.2.9 shows sulfate, oxygen, temperature and DOC compared to the UMeHg concentration.



Figure 4.2.8.: Mercury dynamic of a one year period (06.01.07 to 06.01.08). The hydrograph is shown in gray in the background.

Mercury relations to Discharge, DOC, Absorbance and SUVA

The question of factors controlling the different Hg concentrations during the snowmelt was investigated by comparing the different patterns of hydrological and chemical parameters.

One major factor which is related to the mercury and methylmercury concentrations is discharge. A non-linear interrelation was found for the one year dataset: Increasing discharge forced a higher stream water UHg concentration, while the UMeHg concentration decreased with increasing discharge. In figure 4.2.10 the relations and fitted equations are shown.

Other positive linear relations were found between UHg and DOC, UHg and UV Absorbance at 254nm as well as between UHg and SUVA₂₅₄ as shown in figure 4.2.11. The pearson correlation coefficients are 0.0843 for UHg to DOC and 0.1868 for UHg to UV Absorbance. The strongest correlation was found for UHg and SUVA ($r^2 = 0.2358$).



Figure 4.2.9.: Dynamic of SO₄, O₂, temperature and DOC at County Line Flow. The hydrograph is shown in gray in the background. A possible period of the beginning of reduction processes is also marked.

4.3. Discussion

The result shown above indicate, that during the springflood different processes like flushing mechanisms as well as hydrological controls influence the concentrations of solutes and Hg. This 'interplay' will now be further discussed.

The chemical response of Fishing Brook catchment can be assumed to be mainly influenced by the hydrological response, especially the high amount of meltwater contributing to the stream. Thus a dilution of the higher mineralized pre-event water with the low mineralized meltwater (event water) from the snowpack can be expected. BUTTLE (1994) shows that for forested catchments a contribution of snowmelt water



Figure 4.2.10.: Relation between UHg and UMeHg concentrations and discharge for the one year dataset. A group of post melt UHg samples (red) show an exceptionally high UHg concentration compared to the fitted curve.



Figure 4.2.11.: Relations of UHg to DOC (A), UHg to Absorbance₂₅₄ (B) and UHg to SUVA₂₅₄ (C) determined from a dataset containing all samples from 06.01.07 to 06.01.08.
 'C' in the formulas is the corresponding chemical parameter.

in the range from 30% to 50% with a mean value of 42%. This dilution explains the major changes in the hydrochemical response regarding to the major ions. All possible chemical differences of water from different sources contributing to the stream are superimposed by this dilution process.

The temperature pattern of the two major warming-up periods can be explained by the melting of the channel-near ice and snow. The first warming can be addressed to a lowering in the water table, which inhibited the melting of ice and snow in the channel surrounding riparian areas. Even though there was a drop down in the air temperature, the temperature of the stream increased. This indicates the lower hydrological connectivity of riparian areas and wetlands during this period. The second warming is simply induced by the complete melt of the remaining ice on the ponds. The strong change in composition (major ions as well as DOC, Absorbance and SUVA) of shallow groundwater samples from the wetlands can be addressed to the effect of flooded piezometers. Additional water from the stream drained into the wells and which caused an irrigation during the major peaks. This effect was observed in the field during the first two samplings.

4.3.1. DOC, UV Absorbance, SUVA

The high concentrations of DOC for the precipitation samples are vague. In general there are two possible explanations: (1) stormy weather with high wind speeds might have contaminated the samples in the open bucket sampler by stirring up water from the nearby pond or (2) an additional input from leaves and coniferous litter might have caused the high values. The last explanation seems to be more reasonable, due to the fact, that the amounts of water collected in the bucket show good congruence to the precipitation data of the meteorological station of Newcomb and due to the reason that some leaves and litter were found in the rain gage.

The relatively high and unsteady DOC concentrations of snow samples can also be explained by two different reasons: (1) The way snow samples were taken and (2) litter and leaves within the snowpack. The snowcores were generally rammed down to the DOC rich topsoil. Afterwards the soil proportion was removed and, therefore, there is a high probability, that some soil remains of the Oi horizon were left and increased the DOC content of the snow sample. Litter and leaves on or within the snowpack were also found in the samples.

In the stream, the rising DOC concentrations with increasing discharge indicate a flushing mechanism of organic matter during the melt. As shown before, possible sources of DOC could be: (1) organic rich wetlands and riparian areas which get connected to the stream (INAMDAR ET AL., 2004) or (2) upland soils following the 'HORNBERGER Hypothesis' (WEILER and MCDONELL, 2006).

During summerstorms INAMDAR and MITCHELL (2006) showed that for an Adirondack catchment three different End-Members were identified as sources contributing to the stream by using an End-Member-Mixing-Analysis: Shallow groundwater which is discharging at seeps in the wetlands, throughfall, and riparian water which originates from the upland benches. During several summer storms the counterclockwise flushing for DOC originated from a contribution of shallow groundwater and throughfall on the rising limb and throughfall and riparian water from the upland bench on the recession limb.

Assuming a similar dynamic for the Fishing Brook Catchment, the counterclockwise

DOC behavior would suggest a higher contribution of DOC from the riparian water source than from the wetland source. Following this conceptual idea, the saturation of the upland benches could be produced by the water output of the snowpack which drains the upland through surficial and subsurface flowpath and generates a saturation state in the channel near riparian/upland bench.

The behavior of SUVA₂₅₄ in the stream supports the conceptual idea described above. Its dynamic indicates a change of the DOC character. Higher SUVA₂₅₄ values indicate a higher aromatic fraction (WEISHAAR ET AL., 2003) and, as observed in Sweden, a higher contribution of DOC from the upland soils which have a lower fraction of aromatic rich DOC (ÅGREN ET AL., 2008). In the Fishing Brook catchment, there is evidence for a similar behavior in the DOC character: Late wetland samples, which are not assumed to be irrigated with stream water show SUVA₂₅₄ values in the range from 4.22 to 5.01 [L/mgC· m] while upland and overland samples are in the range of 2.69 to 3.50 [L/mgC· m].

Assuming a conservative mixing for DOC as done by INAMDAR and MITCHELL (2006), the conceptual model would explain the DOC origin and the End-members contributing to the stream the follow way: During peak I, the lowering of SUVA₂₅₄ on the rising limb and an increase on the falling limb would indicate, that during the rising limb a higher contribution of wetland water and during the falling limb a higher fraction of upland water would contribute. The steep increase of SUVA₂₅₄ during peak II would suggest, that during the ROS event a higher contribution of wetland DOC and wetland water accounts for the response. During the third peak a change from the upland to the wetland (peak flow) DOC source on the rising limb and a domination of upland DOC on the falling limb would be the result.

4.3.2. Oxygen-18

The response of Oxygen-18 shows the general mixing of groundwater and soilwater with a high fraction of meltwater. The decrease during peak I can be addressed to the single contribution of meltwater from the snowpack, while the O-18 behavior observed during peak II suggests a contribution of another source with a higher δ^{18} O value. Possible sources are deeper groundwater with -11.40% and rain water with -5.98%.

Assuming rainwater to cause the effect of lowering Oxygen-18 during peak II, the mechanism of this contribution could be (1) 'through flow' of rain through the snowpack combined with a high melting rate or (2) a direct contribution of rainwater by falling on stream near areas which are close to saturation. The first possibility is in congruence with observations of SINGH ET AL. (1997) who showed that preferential flow path can

be developed within the snowpack supporting high flow velocities up to 6 m/h for rain moving through a ripened snowpack. The second hypothesis seems to be reasonable when taking into account, that the SUVA₂₅₄ showed a strong response to the rain event, indicating a higher contribution of DOC originating from wetland sources. Also considering, that the lowest specific conductivity was observed during peak II, there seems to be a high evidence for a direct contribution of rain water via the wetlands to the stream.

When comparing the change of δ^{18} O of the snowpack with elevation, the gradient of $-0.27 \ \%_0 \delta^{18}$ O /100m is in the same range (-0.15%₀ to -0.5%₀) as the altitude effect for precipitation reported by CLARK and FRITZ (1997) from different studies. A more detailed view of event and pre-event water calculations derived from the δ^{18} O data is given in chapter 5.

4.3.3. Mercury

The increase of the UHg concentrations during the snowmelt indicate the mobilization of inorganic mercury during the springflood, while the MeHg concentrations decreased. These findings are similar to those of BISHOP ET AL. (1995) except for the counterclockwise behavior. BISHOP ET AL. (1995) demonstrated that total organic carbon (TOC) peaked slightly before the peak of the hydrograph, while THg showed the maximum concentration in-time with the hydrograph.

Due to the fact, that the THg concentration consists of PHg as well as FHg, a closer look at the different dynamics is nesessary: BUSHEY ET AL. (2008) shows that for summer storms the PHg percentage of UHg is up to 25%. They also show, that the chemical composition during these events, especially potassium, nitrate and DOC suggest a major contribution of througfall to the stream. In the Fishing brook catchment the PHg fraction during the melt is generally lower (7% to 11%), except for the ROS event generating peak II (16%). Thus, this effect can be adressed to a direct input of PHg with precipitation or to the mobilization of PHg as a response of througfall, which is in accord with the conceptual idea explained above.

The relation found between discharge and UHg is more difficult to explain. Even though the relation shows the strong mobilization of Hg during high flow, the fact that the connectivity of riparian areas, the flooding of wetlands as well as an increase of upland contribution are going along with higher discharge does not allow a linking of the mobilization to processes.

The role of the post-melt samples with higher Hg values regarding to discharge also

stays unclear. The fractions of particulate Hg does not give evidence, that the higher UHg values are only based on an higher input of PHg by throughfall, as assumed above. Thus, a possible explanation could be that an important part of the mercury mobilized during the melt stays in different places at the hillslope as well as in stream near areas. This Hg could be remobilized during post melt rain events. Thus a stepwise transport of Hg through the catchment by events has to be assumed. Such a behavior is also hypothesized by SHANLEY ET AL. (2002b).

The weak correlation between UHg and DOC found in this study is oppositional to findings of SELVENDIRAN ET AL. (2008) in the Archer Creek Watershed during the summer and SCHUSTER ET AL. (2008) in the Sleepers River during the snowmelt. Both assume, that a strong relation would suggest a similar mobilization effect for Hg and DOC. In the Sleepers River Watershed the observed low Y- axis intercept of the relation was also assumed to be an indicator for a short soil contact time and, thus, it was taken as evidence, that a high fraction of Hg from uplands became mobilized by overland flow and contributed to the stream. In the Fishing Brook Catchment the higher Y-axis intercept would consequently suggests a higher soil contact time of the Hg contributing runoff component or an additional DOC source.

More interesting is the slightly better correlation of $SUVA_{254}$ and UHg. It indicates that the chemical character and, thus, the origin of the DOC plays a major role for the mobilization. The higher SUVA values of upland DOC and the congruence of overland flow SUVA samples consolidate the idea of the uplands as the most important contributors for the UHg concentration. An dominating upland contribution is also assumed by SELVENDIRAN ET AL. (2008) for the Acher Creek during high flow events.

MeHg

Assuming a similar mobilization mechanism for MeHg and THg for the snowmelt as done by (BUSHEY ET AL., 2008) for summer storms, the decrease of MeHg concentrations can be addressed to two different mechanisms: A supply limited flushing with a decreasing of the MeHg pool during the event as hypothesized by BRANFIREUN and ROULET (2002) or simple dilution of constant flux with meltwater. This dilution mechanism seems to be less likely, because the MeHg relation to discharge is not linear. The logarithmic decrease indicates a supply limited contribution of MeHg and, therefore, a shrinking pool of available MeHg to the flushing mechanism, when the melt proceeds.

This is also in consistent with the observation of the methylation factors. There are just small indications that new MeHg is produced during the melt. Sulfate shows a decrease, but, as mentioned above, the strong dilution with meltwater complicate an indisputed statement. Oxygen also shows a general decrease, indicating the possibility of reducing conditions. However, the low temperature and the high availability of O_2 as well as the low MeHg values indicate very low MeHg production till the second peak. This is also supported by observations of MeHg production of SCHUSTER ET AL. (2008) that showed, that the production rates in soils and stream sediment are below the detection limit during the snowmelt.

The increase of MeHg at the end of the springflood suggests a higher production of MeHg with the beginning of the following growing season, as also reported by several studies (BRANFIREUN and ROULET, 2002; SELVENDIRAN ET AL., 2008, e.g.).

4.4. Summary

A strong mobilization of the mercury species in the Fishing Brook catchment is observed during the snowmelt 2008. From the measurements a conceptual model of the response was developed. This model describes the response as a mixture of upland and wetland water contributions as well as meltwater. These relative contributions are changing during the three peaks. The relations of Hg to DOC and to SUVA₂₅₄ are weak and indicate different mobilization mechanisms or sources for DOC and mercury. MeHg shows the dynamic of dilution and a supply limited flushing. MeHg production is assumed to increase after the snowmelt.

The further questions are mainly on the role of meltwater and the saturation state of the Fishing Brook catchment. These questions can be formulated as:

- Which role plays the meltwater released from the snowpack for the mercury dynamic during the melt?
- How is the saturation state of the catchment related to the mercury mobilization?

Both questions will be investigated in the following chapters 5 and 6.
5. Modeling of Oxygen-18

The broad measurements of the stable water isotope Oxygen-18 (as described in chapter 4) allow to get a detailed view of meltwater contributions during the springflood 2008.

A modeling approach consisting of two routines was applied. The first routine, the 'Isotope Snowmelt Model' was developed within the work of this thesis. It simulates the water output of a snowpack and its δ^{18} O signature for each time step. A second module, the runCe approach (LAUDON ET AL., 2002), simulates the contribution of meltwater to the stream covering the variation in the meltwater signature. The result of the combined approach is a dynamically calculated isotope hydrograph separation (IHS).

5.1. Isotope Snowmelt Model

5.1.1. Modeling idea and conceptualization

As reported by JOST ET AL. (2007) elevation and land use are the two most important factors for explaining variability in accumulation and melt of the snow water equivalent (SWE) in the catchment scale. For the mainly forested Fishing Brook catchment with his broad elevation range (see chapter 2) a distributed simulation of 12 elevation classes, each covering 50 m in altitude was applied.

The module which is simulating the snowpack for each elevation class is based on the concept of "delayed precipitation" (CHANG, 2006). It is simulated by using the day degree approach (U.S. ARMY CORPS OF ENGINEERS, 1960). If rain occurs during periods with a temperature below the melting temperature (T_m) it is accumulated to the snowpack and cannot contribute to the stream. If a snowpack exists and if the air temperature exceeds T_m , the daily melting rate is calculated as shown in equation 5.1.1.

$$d_m = M \cdot (T_a - T_m) \quad \text{for } T_a \ge T_m \tag{5.1.1}$$

where

 $d_m =$ melting rate [mm]

 $M = melting factor [mm/^{\circ} \cdot day]$

 $T_a = \text{daily mean air temperature [°C]}$ $T_m = \text{melting temperature [°C]}$

Additionally the idea of liquid water storage within the snowpack was included. The retained liquid water content (RLW) allows to store precipitation falling as rain or meltwater from the snowpack to be retained and, if the temperature is falling below T_m , to refreeze. This concept is similar to the HBV-model as described in equation 5.1.2 by MOORE (1993).

$$RF = C_f \cdot (T_a - T_m) \quad \text{for } T_a \le T_m \tag{5.1.2}$$

 $\mathrm{RF} = \mathrm{Refreeze} \; \mathrm{[mm/day]}$ $\mathrm{C}_{f} = \mathrm{refreeze} \; \mathrm{factor} \; \mathrm{[mm/} \;^{\circ} \; \cdot day]$

The maximum amount of retained liquid water, the retained liquid water capacity (RLWC in mm) is calculated as a fraction of the current SWE, using the formula 5.1.3.

$$RLWC = SWE \cdot HC \tag{5.1.3}$$

where

HC = Holding capacity [-]

If the amount of liquid water is higher than the water holding capacity of the snowpack, the water excess is treated as the water output of snowpack.

Due to the fact that in forested catchments a strong parts of the precipitation falling as snow can be intercepted and lost by sublimation (STORCK ET AL., 2002), the amount of net precipitation (P_{net}) [mm] contributing to the snowpack has to be corrected. For its calculation a constant loss factor similar to the HBV model (SEIBERT, 1997) was used. Using equation 5.1.4 yields the calculation of the net precipitation.

$$P_{net} = P \cdot \text{ LF} \tag{5.1.4}$$

where

LF = Loss factor [-]P = precipitation measured in the open field [mm]

Figure 5.1.1 shows the conceptualization of the snowmelt for one elevation class.

The calculation of the snow depths for each elevation class was performed by using



Figure 5.1.1.: Model concept of the Isotope Snowmelt Model for simulating the snowpack of one elevation class. $_{liq}P =$ liquid precipitation, EP = Evaporation. The other abbreviations are explained in the text.

the following assumptions: (1) The air temperature follows a linear decrease with elevation and (2) the change of precipitation with elevation can also be described by a linear gradient.

δ^{18} O calculation

The calculation of the Oxygen-18 signature is based on the following assumptions: (1) all water fluxes are mixed conservatively, (2) all water storages are instantly and completely stirred and (3) the fractionation for the transformations of water from the solid to the liquid phase can be neglected. This allows to perform mixing calculations following the mixing equation (5.1.5) for n different components.

$$Q_m \cdot C_m = \sum_{i=1}^n Q_i \cdot C_i \tag{5.1.5}$$

where

 $\mathbf{Q}_i = \mathbf{W}$ ater volume or flux of i $\mathbf{C}_i = \mathbf{C}$ oncentration of i $m = i + (i + 1) + \dots + (n - 1) + n$

The calculation of the Oxygen-18 signature is done in a daily tiem step. At first the

water fluxes from each storage to the other are quantified. Afterwards the mass flux is calculated and the mass change of each water storage is updated. The entire matlab program code is given in the appendix A.2.1.

5.1.2. Data preparation and fitting

The mean daily air temperature and daily precipitation data used to simulate the snowpack were derived from the meteorological station in Newcomb, which has an elevation of 469.5 m a.s.l.

 δ^{18} O signatures of the snowpack from three different elevations measured at the beginning of the snowmelt (4th of April) were integrated into the model to set the initial signature of the snowpack.

 δ^{18} O values for liquid precipitation were derived from incrementally collected precipitation samples each covering a time interval of 3-7 days. These δ^{18} O values were used to weight the daily precipitation data from the meteorological station in Newcomb. Additionally, precipitation was weighted by the change of δ^{18} O with elevation using the linear gradient determined in chapter 4.

The fitting of the Isotope Snowmelt Model was performed by minimizing the sum of squared errors of simulated and measured SWE of different samplings in different elevations during the melt. The measured values are mean values from 3 to 5 measurements for each site. For the minimization the Matlab function 'fminsearch' was applied (MATLAB 7.3.0, MATHWORKS INC.). The initial values and the best fit parameters are given in table 5.1.1.

Table	5.1.1.:	Initial	and f	fitted	parame	ter s	sets for	the	lsotope	Snow	melt	Model	. The	e fitted	set
		was de	etermi	ined b	y using	the	'fmins	earch	' Matlab	o func	tion \	with a	total	numbe	er of
		304 ite	eratio	ns.											
	D	1		т	ר	l r			ъл		т		ТТ		

Parameter	Р	\mathbf{T}_m	M	\mathbf{T}_{a}	\mathbf{LF}
	${f gradient}$			$\mathbf{gradient}$	
	[mm/100m]	[°C]	$[mm/^{\circ}C^{*}day]$	[°C/100m]	[-]
initial value:	0.2	0.0	3.0	-0.3	0.7
best fit:	0.43	-0.001	4.17	-0.31	0.60

Parameters which were assumed to be constant are (1) the water holding capacity for liquid water of the snowpack, which was set to 10% of the current SWE and (2) the refreezing factor, which was set to 0.05 mm/°C and day. Parameters in a similar range were also used by MOORE (1993). Figure 5.1.2 shows the measured versus the simulated snow water equivalents of the ISM.



Figure 5.1.2.: Measured vs. simulated snow water equivalent of the fitted Isotope Snowmelt Model. The measured SWE originate from measurements at the sampling sites A,B and C as described in section 4.1.1.

5.1.3. Results of the ISM

Between the 16th of November to the 17th of April the ISM simulates a stable snowpack for the lowest elevation class (500 - 550 m a.s.l.). For the highest elevation class (1050 - 1100 m a.s.l.) the simulated snowpack lasts till the 24th of April. The highest snow waterequivalent is simulated as 251 mm for the lowest elevation and as 576 mm for the highest, both on March 31th.

Figure 5.1.3 shows the snow accumulation and melt during the simulation period from the 1st of October 2007 to the 6th August 2008. The results shown below were aggregated by weighting the result of each elevation class by area.

A more detailed view on the melting period is given in figure 5.1.4. The water output during this period shows a similar behavior to the stream. Two peaks dominate the melt. The first one shows water outputs of the snowpack in the range of 4.1 to 38 mm/d (area weighted mean). For the second peak a range from 7.9 mm/d at the beginning, up to 42.6 mm/d during the peak, down to values between 1 mm/d and 5 mm/d at the end of the melt are simulated.

 δ^{18} O was simulated for the period of the 4th of April to the end of the springflood (4th of May). Due to the fact that during this period the air temperature was continuously above T_m there was no refreeze simulated and, therefore, no changes of δ^{18} O signature of the simulated snowpack. The water output of the snowpack changed his composition due to the mixing of the water of the snow with relatively low δ^{18} O values and the liquid precipitation with much higher δ^{18} O signatures. Thus the δ^{18} O of the output



Figure 5.1.3.: Results of the Isotope Snowmelt Model from 1th of October 2007 to the 6th August 2008: precipitation, water output of the snowpack and snow water equivalent of the snowpack. All values are weighted by the percentage of area of the elevation classes.

of the snowpack during the first peak is simulated in the range of -13.2% to -10.1%, when rain occurred. During the second peak, values between -13.2% and -11.5% were calculated. The post melt period (25th of April to 4th of May) is dominated by much higher values (-9.3% to -5.7%) due to the additional rain and as good as no meltwater.

Figure 5.1.5 shows the simulated δ^{18} O signature of the water output compared to the δ^{18} O values of overland flow collected at different locations and samples of upland water collected at the unnamed Tributary site. There is congruence between the first two upland samples. The third one taken during the highest flow on 12th of April (A) does show a lower δ^{18} O value of -10.1 %₀ compared to the simulated δ^{18} O of -12.8 %₀ of the snowpack output. An even stronger incongruity between upland- and simulated δ^{18} O is occurring in the post melt period (C), when the model predicts a much lower δ^{18} O value than the measured one.

When comparing the results to the overland flow samples (B) which would represent the overflow of the liquid water content of the snowpack in the model concept, the



Figure 5.1.4.: Area weighted results of the Isotope Snowmelt Model for the springflood 2008: precipitation, water output of the snowpack, snow water equivalent and Oxygen-18 signature of the melt water.

general increase of δ^{18} O is simulated, though there is an offset of 0.4% to 0.6% between the simulation and the samples.

5.2. RunCe approach

The second module for the calculation of meltwater contributions to the stream is the so-called runCe approach developed by LAUDON ET AL. (2002).

5.2.1. Description

The background of the runCe approach is the two component hydrograph by using stable water isotope tracers (SKLASH and FARVOLDEN, 1979). The pre-event contribution in percent f_p is calculated by using equation 5.2.1.



Figure 5.1.5.: Simulated Oxygen-18 signatures of the melt water by the ISM compared to measured Oxygen-18 of overland flow (different locations) and upland water at the unnamed tributary site. The output of the snowpack is shown in gray in the background. A, B and C are used in the text.

$$f_p = \frac{C_s - C_p}{C_e - C_p}$$
(5.2.1)

where

 C_p = concentration before the event

 C_e = concentration of the event water

 $C_s =$ concentration of the stream

As shown before, there are strong changes of the δ^{18} O signature of water released from the snowpack. Besides that a travel time of the meltwater to the outlet of the system has to be assumed. Thus the event water concentration ($\delta^{18}O_e$) at the outlet is not equal to the meltwater concentration ($\delta^{18}O_m$). The runCe approach takes the effect of a dynamic input signal as well as the travel time into account by calculating the δ^{18} O of the event water within a comparison between cumulative output of the snowpack and the cumulative volume of meltwater that has left the snowpack but not yet discharged to the stream during the event. Equation 5.2.2 shows the calculation of δ^{18} O of the event water at the outlet LAUDON ET AL. (2002).

$$\delta^{18}O_e(t) = \frac{\binom{t}{i=1}\sum M(i)\delta^{18}O_m(i) - \frac{t}{i=1}\sum E(i)\delta^{18}O_e(i))}{\binom{t}{i=1}\sum M(i) - \frac{t}{i=1}\sum E(i))}$$
(5.2.2)

where

- M(i) =incrementally collected meltwater
- E(i) =incrementally collected eventwater

The calculation was performed iteratively for the period of the 4th of April to the 4th of May 2008. The meltwater input was obtained from the simulations of the ISM: the output of the simulated snowpack was taken as the input of meltwater. As an initial value for $\delta^{18}O_e(t) = -12\%_0$ was set. The iteration was stopped (stopping criteria) if the modulus of the difference of the current $\delta^{18}O_e(t)$ to the $\delta^{18}O_e(t)$ of the previous iteration step was below $1 \cdot 10^{-5}$.

For comparison two less complex event water calculations were also performed: The volume weighted average $\delta^{18}O_e$ calculation (VWA) and the current meltwater approach (CMW). The calculation of VWA is given in equation 5.2.3 (SHANLEY ET AL., 2002a). For the CMW it is assumed, that the $\delta^{18}O_e$ of the meltwater and the event water for each time step are equal.

$$\delta^{18}O_e(t) = \frac{t}{i=1} \sum_{i=1}^{t} M(i)\delta^{18}O_m(i)}{t = 1 \sum_{i=1}^{t} M(i)}$$
(5.2.3)

where

n =number of samples/ timesteps of simulated snowpack output

The pre-event water δ^{18} O signature was set to $-11.4\%_0$. This value was measured for the groundwater sample taken at the end of the melting period. The highest $\delta^{18}O$ value measured in the stream during baseflow conditions are in the same range (-11.6%₀ for winter baseflow, -11.5%₀ for summer baseflow).

The program code (Matlab) for the calculations is given in appendix A

5.2.2. Results

The results of the runCe approach show a variation of the $\delta^{18}O_e$ signal in the range of $-13.0\%_0$ to $-12.1\%_0$. At the beginning a value around $-12.5\%_0$ occurs. On the rising limp of the first peak the signature changes to the minimal value of $-13.0\%_0$. With the contribution of rainwater to the snowpack, the event water $\delta^{18}O$ increases to values near the volume weighted average value. During the second peak a decrease to a value of $-12.6\%_0$ is simulated while $\delta^{18}O_e$ becomes strongly lowered to values of $-12.1\%_0$ during the post-melt rain events. The VWA derived $\delta^{18}O_e$ signature is constant at $-12.3\%_0$.

The calculated pre-event contributions to the springflood are 58.0% for the runCe approach and 76.0% for the VWA approach. Both methods indicate a major contribution of pre-event water to the first peak. During the rising limb the runCe approach shows a

much lower contribution than the VWA method, while the falling limb is mainly dominated by pre-event water for both methods. During the second peak VWA indicates generally a higher pre-event contribution than runCe, but both methods show a similar patter of an increasing preevent water on the rising limp, a lowering at the peak and again in increase on the falling part. During the post melt rain events both methods show a major fraction originating from event water.

The hydrograph separation using the CMV method was not successful. The fact that the meltwater contribution δ^{18} O had higher values than the pre-event water during several timesteps and, thus, pre-event water fractions were calculated to be higher than 100% shows the limitations of the CMV approach in catchments in which retention of meltwater occures.

Figure 5.2.1 shows the dynamic of $\delta^{18}O_e$, the fraction of pre-event water as well as the discharge of pre-event water derived from the VWA and the runCe approach.

The role of pre-event water contribution on DOC and $SUVA_{254}$ concentrations is shown in figure 5.2.2. Generally the DOC concentration increases with a higher fraction of pre-event water calculated with the runCe approach following a linear pattern. Only the post melt samples which show extraordinary high DOC concentrations do not follow this structure.

A possible relation between event water contributions and mercury flushing is more difficult to find, due to the fact that the small number of Hg samples taken during the melt does not allow to develop reliable statement.

5.3. Discussion

5.3.1. ISM

The assumption that fractionation during the melt can be neglected presumed for the Isotope Snowmelt Model does generally not represent the physical effect of the transformation of water from the solid to the fluid phase. CLARK and FRITZ (1997) show, that if the snowpack is assumed to be a well mixed, finite reservoir the fractionation can be modeled as a Rayleigh-process. This process can be calculated by equation 5.3.1 (CLARK and FRITZ, 1997):

$$R = R_0 \cdot f^{(\alpha - 1)} \tag{5.3.1}$$

where

R = isotope ratio of the diminishing reservoir



Figure 5.2.1.: Results of the runCe simulations: Shown is precipitation, the eventwater δ^{18} O signal of the runCe as well as of the VWA approach, the calculated fractions of pre-event water and the resulting contribution to the total discharge. For the first three graphs the hydrograph is shown in gray in the background

 $R_0 = initial$ isotope ratio of the reservoir

- $\alpha =$ fractionation factor
- f = remaining fraction of the reservoir

The formula shows, that for the diminishing snowpack an enrichment can be expected



Figure 5.2.2.: Comparison of the runCe event water fractions to DOC and SUVA₂₅₄. The post melt samples were collceted after 26th of April.

during the melt, whereas the water released from the snowpack would show lower δ^{18} O values at the beginning. When the melt proceeds, the meltwater would also increase due to the fact that the isotopic composition of the remaining snow changes.

Assuming a not well mixed reservoir, the fractionation processes become even more complex, as shown by FENG ET AL. (2002) and TAYLOR ET AL. (2002): A physically based 1-D model was used to simulate the change of the isotopic composition of the snowpack during the melt. It was assumed, that the melt only occurs on top of a homogeneous snowpack. The percolation of meltwater trough the snowpack was calculated by using a reduced form of the Richards-Equation. The results indicate, that variations in the range of 1-4%₀ can occur, mainly dependent on the melting rate and the liquid water stored in the snowpack. The behavior observed for the meltwater are comparable to those described above for the simple model assuming well mixed storage and Rayleigh fractionation: During the first part of the melt the simulated meltwater shows lower δ^{18} O values, whereas the δ^{18} O values are increasing if a fraction of more than 0.4-0.6 of the snowpack is melted. The effect causing these changes is the same for both models: The ratio of ¹⁸O to ¹⁶O of the remaining snowpack increases.

EHNES (2006) investigated the influence of the Rayleigh fractionation on the snowpack during the snowmelt in the Dreisam catchment, Germany. His findings show, that the maximum change of the δ^{18} O of the snowpack was below 1%₀ during a 20 day period without rain. The change of the meltwater released from the snowpack compared to the snowpack itself was below 0.33%₀. This suggests a minor role of the Rayleigh fractionation compared to other factors (e.g. rain water contributions during ROS events) in the catchment scale (EHNES, 2006). Even though the simplification of the ISM has be assumed to be critical, the model shows reasonable results when comparing the simulated δ^{18} O with the measured values of samples of overland flow and upland runoff.

While the first two upland samples are in congruence with the simulation, the following samples taken during the ROS event and at the rain dominated end of the melting period (see figure 5.1.5, A and C) show a much lower value than the simulated one.

Whereas the model assumes mainly rain water which drains through the snowpack, the measured values indicate that the upland contribution mainly consists of water with a δ^{18} O signature in the range of the snowpack before the ROS event. A possible explanation for this behavior could be a high melting rate of snow due to the energy input from the rain. Thus the released water would consist of rain water as well as meltwater. Another explanation could be that the processes of runoff generation supporting a higher pre-event fraction in the stream (e.g. groundwater ridging, translatory flow, overland flow (BUTTLE, 1994)) take place in the unnamed tributary subcatchment.

In the conceptual model of the ISM the excessing water in the snowpack is released. Thus a comparison of measured δ^{18} O values of overland flow samples and the model outputs is more reasonable. For overland flow higher values (between 0.4 to 0.6 %₀ higher) were measured during the second peak (figure 5.1.5, B). This can be explained by two different hypothesis: (1) the higher values originates from water released from the snowpack, which was still influenced by stored water from the rain event before, or (2) the measured overland flow is a mixture of meltwater from the snowpack as well as soil water from the upper soil horizon. When taking into account, that the snowpack as well as the upper soil horizon was saturated at several snow sampling locations during the melt, the last explanation seems to be more reasonable. Thus the measured overland flow is also assumed by SHANLEY ET AL. (2002a) for the Sleepers River Watershed.

5.3.2. Hydrograph-Separation

When comparing the different event water calculations, the results of the runCe approach shows a much lower pre-event water contribution than the VWA method. This fact disagrees with the findings of LAUDON ET AL. (2002) who observed a higher contribution of pre-event water from the runCe approach than from the VWA method. An explanation for this behavior is that for the VWA approach pre-event water contributions above 100% were calculated during some timesteps at the beginning of the first peak. As mentioned before the CMW approach showed the same results for many

timesteps, which indicates that both methods cannot account for a retention of meltwater within the catchment. Such a retention causes a mixing of meltwater inputs of different timesteps and, therefore, a smoothing of the eventwater signal.

A critical point for the hydrograph separation performed in this study is that the runCe approach can just account for retention and thus for a delay of meltwater which contributes to the outlet as event water. LAUDON ET AL. (2002) show for the forested 12 ha Västrabäcken headwater catchment in Sweden that the contribution of different units of the catchment (upland, midslope, near stream) does not create statistically different results. Thus, the assumption that the event water reservoir is well mixed does not lead to a systematic error for the small catchment in Sweden, but at the catchments scale this simplification might be more important. Especially the timing of the contribution of the numerous spatially distributed subcatchments, influenced by their flowpaths through wetlands and ponds could play a major role. Hence it has to be assumed that the runCe approach is a strong simplification for IHS in the Fishing Brook catchment.

When comparing the result of the runCe-IHS to other studies, the pre-event water contribution during the two peaks (0.80 during the first peak and 0.5 to 0.6 during the second peak) is generally in the range given by BUTTLE (1994). He reported contributions between 0.6 and 0.85 for forested catchments in the given scale.

A comparison of the DOC mobilization by eventwater is even more difficult. Numerous studies report very different results: Observations of SHANLEY ET AL. (2002a) in the Sleepers River Watershed show a relationship between pre-event water and DOC for two different snowmelt periods. Both melting periods have very different event water contributions (41-74% for the first melt, 30-36% for the second one), but the same SWE. This difference in the event water fractions was explained by soil frost which forced a higher fraction of event water to contribute directly to the stream as well as a higher saturation state which caused saturation overland flow. The DOC concentrations reached the same level for both melts. Thus, the same source for DOC, the upper soil horizons are assumed by the authors. Therefore, the findings support the flushing for DOC following the HORNBERGER hypothesis.

BISHOP ET AL. (2004) refer the fast mobilization of pre-event water in the till dominated Västrabäcken catchment to the transmissivity feedback process. In this catchment the upper soil layers have a much higher lateral saturated hydrological conductivity an, thus, small amounts of additional water can cause a higher lateral runoff in the upper soil layers. In contrast to the concept of SHANLEY ET AL. (2002a), the upper soil horizon is not assumed to be the major source for DOC. The measurement of BISHOP ET AL. (2004) indicate that the DOC originates mainly from a small riparian buffer zone wich becomes connected during high flow conditions.

For the Fishing Brook catchment the relation of DOC and event water is not consistent during the springflood 2008. Generally an increase of DOC with a higher pre-event water fraction can be observed. During the high DOC values measured at the end of the springflood the pattern is oppositional. A very low pre-event water contribution is present. Thus this unlike behavior has to be assumed as an indicator for a more complex mechanism of DOC mobilization. The conceptual model of two DOC sources (upland soils and wetlands) as described in chapter 4 would cover this pattern.

Considering two DOC reservoirs, the special role of the post melt samples indicate, that an additional process of DOC mobilization for the second reservoir, the upland soils, has to be assumed. Due to the fact that the contribution is not strongly dependent on the event water fraction, and that it only occurs after most of the snow is melted, two different hypotheses could explain the observed behavior: (1) an instantaneous production of DOC at the beginning of the growing season as suggested in chapter 4 or (2) a flushing by the post melt rain events which disturb the uncovered upper soil horizon of the upland soils.

The second process would be supported by the fact that the upper soil horizon is no longer covered with snow after the melt and, that the canopy layer is not present. Thus a higher energy of the rain to disturb the soil (e.g. by processes as the 'splash' effect as described by SAINT-JEAN ET AL. (2004) for the canopy) could lead to a physical mobilization from the top soil.

Assuming this hypothesis, the fact that besides the high DOC concentrations the highest mercury concentrations were also measured in this post melt period, the wash-off effect of Hg from the surficial leaves and litter would be the major Hg source.

5.4. Summary

The isotopic hydrograph separation performed in this chapter shows a major contribution of pre-event water during the snowmelt 2008. The combined approach of the ISM used to simulate the release of water to the soil and the runCe approach to simulate the event water signal in the stream shows a practical way to model the mobilization of 'old' water in the catchment scale during the snowmelt. Due to the lack of measured snowpack output data (e.g. by snow lysimeters) the uncertainty of the ISM is not fully revealed. Especially the question if fractionation changes the output δ^{18} O signal during periods with very high melting rates remains unclear. The combined results of the IHS and the changes in DOC behavior suggest that there is an interplay of different sources of DOC during the snowmelt. The question which runoff processes cause a mobilization of DOC and Hg, and, more generally speaking the question, how event water contribution, runoff generating processes and water chemistry are related (KIRCHNER, 2003) stay unrevealed for the Fishing Brook Catchment.

Even though additional mobilization processes were hypothesized in this chapter, a major mobilization caused by a high water level reaching the upper soil horizons seems to be one of the major controls. Hence there is a need to investigate the importance of saturation states regarding to mobilization processes.

6. TOPMODEL

In this chapter the role of the saturation state on the mobilization will be investigated by applying the hydrological model TOPMODEL to the Fishing brook catchment.

The hydrological model TOPMODEL (BEVEN and KIRKBY, 1979) is one of the most often applied rainfall/runoff models. It was developed for humid temperated areas and combines a simple lumped parameter concept with the idea of streamflow generation by the 'variable contributing areas' (DINGMAN, 2002). Thus the hydrological response is dependent on topographical controls and soil properties.

6.1. Model description

Since the model version used within this project is well described by WOLOCK (1993), only a short description is given within this thesis. The model calculations are based on the saturation deficit at the location x (D_x [mm])as given in equation 6.1.1:

$$D_x = \overline{D} + m \cdot (\lambda - I) \tag{6.1.1}$$

where

 \overline{D} = average saturation deficit of the watershed [mm]

I =topographic index at the location x [ln(m)]

 λ = average topographic index of the watershed [ln(m)]

 $m = \text{scaling parameter} = n_{drain}/f \text{ [mm]}$

The exponential decrease of the saturated hydraulic conductivity (in mm/h) with depth is given as $K(z) = K_o \cdot e^{(-fz)}$ with K_0 [mm/h] as conductivity at the soil surface. In the model version used in this study, the K(z) - curve is approximated by three soil parameters: (1) K_D [in/h], which represents the hydraulic conductivity of the C horizon, K_{mult} [-] which describes K_0 as a multiple of K_D . The parameter *m* determines the exponential decrease form the top of the soil to the total soil depth. The topographic index (I) is defined as (equation 6.2.1): $I = ln(\frac{a}{\tan\beta}) \tag{6.1.2}$

where

a = upslope hillslope area per unit contour length [m]

 $\beta =$ surficial slope [°]

The flow delivered to the channel is given as $q_{total} = q_{overland} + q_{subsurface}$ [all in mm]. Subsurface flow is calculated under the following assumptions: (1) the flow follows 'darcy's' law and (2) the hydraulic gradient is similar to the surficial gradient of the landscape. In the spatial aggregated version used in this study, the subsurface flow can then be expressed as 6.1.3:

$$q_{subsurface} = T_0 \cdot e^{-\lambda} \cdot e^{-\frac{D}{m}} \tag{6.1.3}$$

with

$$T_0 = \int_{z_{wt}}^{z_D} K_0 \cdot e^{-fz} dz, \qquad (6.1.4)$$

where

 $T_0 = \text{lateral transmissivity } [\text{m}^2/h]$ $z_{wt} = \text{depth of the water table } [\text{m}]$ $z_D = \text{total soil depth } [\text{m}]$

As long as water in the root zone storage is available evapotranspiration (PET) is calculated by estimating the maximum possible evapotranspiration by using the Hamon formula (6.1.5) as given by CHANG (2006). The root zone is characterized by the root zone depth $(z_{root} [m])$ and the field capacity $(\Theta fc [-])$.

$$PET = C \cdot D_s^2 \cdot \rho \tag{6.1.5}$$

where

C =empirical constant

 $D_s =$ maximum clear sky duration of sunshine [h]

 $ho = {
m absolute humidity} \; [{
m g}/{
m m^3}]$

The snow accumulation is calculated by using the day-degree approach as described in chapter 5, but based on different units. If the air temperature $(T_a \ [°f])$ is below T_m

[°f] snow is accumulated. If snow is present and the air temperature is above T_m , the volume of melt water (d_m) is calculated as given by formula 6.1.6.

$$d_m = Mi \cdot (T_a - T_m) \quad \text{for } T_a > T_m \tag{6.1.6}$$

where

Mi = temp melting factor [in/°f day]

The channel routing is based on the following simple algorithm: At first the number of timesteps t which are needed for the water reaching the stream to flow to the outlet is estimated as described by equation 6.1.7, after which the total flow in a given timestep is divided by the number of time steps which are required for all the water to reach the outlet, as shown in equation 6.1.8.

$$t_{steps} = d_{max} / V_{rout} \tag{6.1.7}$$

$$Q_{portion} = Q_{total} / t_{steps} \tag{6.1.8}$$

where

 $t_{steps} = \text{time steps [days]}$ $d_{max} = \text{maximum stream length [km]}$ $V_{rout} = \text{routing velocity [km/day]}$ $Q_{portion} = \text{water reaching the outlet [m³]}$ $Q_{total} = \text{water reaching the stream [m³]}$

6.2. Input data

TOPMODEL simulations were performed in an daily time step. The input file containing mean daily air temperature, daily precipitation and measured discharge was generated from climate data from the nearby climate station in Newcomb as well as from aggregating daily values from the gauging station.

The calibration was performed for the time period from the 1st of January 2006 to the 16th of June 2008. Due to the fact that the gauging station at Fishing Brook was installed in January 2007, measured discharge data for the first year was not available. To be able to use this period for model calibration, discharge data was derived from surrounding gauging stations (e.g. Archer Creek, Hudson at Newcomb) using multivariate regression (D. BURNS, USGS Troy, unpublished data). The topographic index distribution was calculated by using the GEASY tool (J. SEIBERT, Stockholm University) and a 10mx10m digital elevation model. The tool allows flow direction calculations based on the multiple flow direction algorithm $MD\infty$ ' as described by SEIBERT and MCGLYNN (2007). Figure 6.2.1 shows the relative distribution of the topographic index (I) of the Fishing Brook Catchment.



Figure 6.2.1.: Topographic Index distribution for the Fishing Brook Catchment.

Model parameters

The most sensitive parameters were identified from test simulations and from the results of earlier studies (D.WOLOCK, personal communication). The model fitting was based on the N_{eff} objective function (equation 6.2.1) as given by NASH and SUTCLIFFE (1970).

$$N_{eff} = 1 - \frac{t \sum (Q_{obs}(t) - Q_{calc}(t))^2}{t \sum (Q_{obs}(t) - \overline{Q_{obs}})^2}$$
(6.2.1)

where

Q =observed or calculated discharge at time step t

The fitting was performed by applying 10 000 runs with random parameter sets (Monte-Carlo method) for the 6 most sensitive parameters. Table 6.2.1 shows the parameters and the parameter-ranges used for the Monte-Carlo simulations.

Beside the parameters which were used to fit the model the general catchment properties were specified. Table 6.2.2 gives an overview of all catchment characteristics.

Parameter	K_D	K _{mult}	m	T_m	Mi	V _{rout}
Unit	[in/h]	[-]	[mm]	[°f]	[in/°f day]	$[\rm km/day]$
Range	0.02 - 15	1 - 5000	5 - 100	25 - 33	0.001 - 0.1	3 - 15

 Table 6.2.1.: Parameters and parameter ranges used for the model calibration with the Monte

 Carlo method.

Table 6.2.2.: Catchment properties used for TOPMODEL.

Type	Unit	Value
total area	$[\mathrm{km}^2]$	65.138
lake area	$[\mathrm{km}^2]$	3.35
max. stream lenght	$[\mathrm{km}]$	8.3
field capacity	[%]	0.1136
water holding capacity	[%]	0.16328
porosity	[%]	0.38793
Percent impervious	[%]	0
Percent road impervious	[%]	0
Latitude (for ET calculation)	[°] decimal	43.973
Percent macropore flow	[%]	0.2

Model uncertainty

For uncertainty estimation a 'Generalized Likelihood Uncertainty Estimation' (GLUE) as described by (BEVEN and BINLEY, 1992) was applied. For the probability calculations a dataset consisting of all parameter sets which led to a model result above a given threshold for the objective function $(N_{eff} > 0)$ was aggregated. The dataset consisted of 8640 runs.

For the uncertainty estimation the Matlab tool 'MCAT' developed by T. WAGENER (Pennsylvania State University) was used. Due to the fact that 'MCAT' uses a minimization algorithm, the objective function $N_{eff} \cdot (-1)$ was used instead of the positive NASH-SUTCLIFFE efficiency.

6.3. Results

TOPMODEL was successfully fitted to the observed hydrograph. The simulated hydrograph is in broad agreement with the measured values. For the run with the best fit between the measured discharge at the outlet and the TOPMODEL simulation a N_{eff} of 6.153 and a root mean square error (RMSE) of 0.2286 was obtained. The 10 best parameter sets for all 6 fitting parameters are presented in table 6.3.1. The best model fit generally represents the strongly snow influenced hydrograph as shown in figure 6.3.1. For the first melting period at the beginning of the calibration high differences between observed and predicted values can be found. This can be explained by the fact that the model was not able to accumulate the full amount of snow during the winter 2005/2006. Thus the model underestimates the discharge in the following melting period in may 2006. The second snow accumulation period is simulated in a better manner: The accumulation period and the short melting at the end of December 2006 are reproduced. The melting occurring in April 2007 is simulated slightly too early. In the following phase of summer low flow, the model overestimates the response of the catchment regarding rain events. The simulations for the winter 2007/2008 are also close to the observed discharge in the stream. During the accumulation time some rain events led to short responses of the stream which are not simulated correctly by the model. The springflood 2008 is well simulated. Water amount and timing of both peaks are very close to the observed values.

Rank	KD	K _{mult}	m	T_m	Mi	Vrout	Neff
Unit	 [in/h]	[-]	[mm]	[°f]	[in/°f day]	[km/day]	[-]
	$\cdot 10^3$	$\cdot 10^3$	$\cdot 10^{3}$	$\cdot 10^{3}$		$\cdot 10^3$	
1	0.0131	2.5323	0.0376	0.0263	0.0218	0.0138	0.6153
2	0.0124	4.9303	0.0402	0.0258	0.0196	0.0102	0.6139
3	0.0117	1.8207	0.0376	0.0269	0.024	0.0105	0.611
4	0.0058	1.6556	0.0346	0.0259	0.0196	0.0125	0.6067
5	0.0109	0.7732	0.0366	0.0255	0.0195	0.0117	0.605
6	0.0109	3.9718	0.045	0.0253	0.0192	0.0137	0.6017
7	0.0107	4.1775	0.0424	0.0273	0.0249	0.0145	0.6017
8	0.0075	0.3178	0.0416	0.0263	0.0229	0.0141	0.6013
9	0.004	3.0595	0.0397	0.0269	0.0252	0.0112	0.6008
10	0.0146	3.2054	0.0324	0.0253	0.0185	0.0128	0.6002

Table 6.3.1.: The top 10 Parameter Sets with respect to N_{eff} .

The simulated saturation state is represented by two different output variables which are also shown in figure 6.3.1. The average soil saturation deficit \overline{D} represents the general saturation of the soils of the entire catchment, whereas the calculated saturated area indicates how large the areal extent for surface near runoff generation is.

The simulated average soil saturation deficit \overline{D} is in the range of 100 to 300 mm. The low values are predicted for the melting period 2007 and 2008. A high saturation deficit is assumed by the model for the summer 2006, for the snow accumulation period during the winter 2006/2007 and for the summer 2007. The snow accumulation period 2007/2008 is not characterized by a high deficit, which can be explained by the rain events during the winter which provided water to the soils and to the stream. The evolution of the extend of simulated saturated areas is in general inversely proportional to the simulated average soil saturation deficit. The prediction shows values of 6 to 12% of saturation. The highest extent is calculated for the period with the lowest saturation deficits - the snowmelt 2007 and 2008, whereas a low saturated area extent is predicted for the summers.

The difference between both variables can be described as the sensitivity to the water antecedent moisture state. Though the average saturation deficit \overline{D} reacts more linearly to additional water inputs, the percentage of saturated area is more influenced by antecedent moisture. If the saturation deficit is already high a small amount of rain can force a much higher percentage of saturated area.



Figure 6.3.1.: Best fit of TOPMODEL for the entire modeling period (01.01.2006 to 16.06.2008).

The TOPMODEL runs showed to be highly sensitive to the scaling parameter m and the snowmelt parameters T_m and Mi as displayed in figure 6.3.2, where dotty plots for all 6 parameters are presented. This can be explained by the fact that the high flow





Figure 6.3.2.: Dotty Plots of the Monte-Carlo simulations. The best parameter set is marked.

The uncertainty ranges modeled with the 'GLUE' method are presented in figure 6.3.3. The uncertainty is dominated by the high sensitivity of the parameters which characterize the snowmelt. A high uncertainty interval between the upper and lower confidence limits can be observed for the three melting periods, ranging from 0 to 4 m³/s during the melt 2006, 2 to 10 m³/s for the melting period 2007 and the highest interval from 2 to 25 m³/s for the snowmelt 2008. The snow accumulation period 2006/2007 shows a relatively low uncertainty compared to the range given for the accumulation period 2007/2008 which had rain and melting events.

Relation of saturation state to Hg and DOC

Generally both simulated variables describing the moisture state of the catchment are related to the UHg concentrations in the stream. Figure 6.3.4 shows the simulated average soil saturation deficit as well as the simulated percentage of saturated area. The last variable only includes the newly saturated area of the simulation. Additionally 5.14% are assumed to be countiously saturated and act as open water bodies, which contribute directly to the stream.

The relations show differences between time periods in which the model predicts a snowpack. The relationship between the average soil saturation deficit \overline{D} and UHg is acceptable ($r^2 = 0.721$) for periods without snow. When a snowpack was present a different gradient is observed and the correlation coefficient is lower ($r^2 = 0.534$). The



Figure 6.3.3.: Uncertainty of TOPMODEL calculated with the GLUE method. UCFL = upper confidence limit, LCFC = lower confidence limit, dCFL = normalized difference between upper and lower confidence limits.

Y-axis intercept is the same range for both curves. For the simulated saturated area the relations are similar, but the fitted curve follows a logarithmic scale.

For both simulated saturation variables no significant relations to the DOC concentrations were obtained as displayed in figure 6.3.5. The winter samples generally show lower values than the summer samples but the pattern does not indicate a direct statistical relation between DOC concentrations and soil saturation.

6.4. Discussion

As shown in different studies, TOPMODEL is generally able to calculate satisfying runoff simulations in humid areas after calibration (GÜNTNER ET AL., 1999). The basic assumptions for these simulations are (BEVEN, 1997): (1) That the dynamics of the water table can be approximated by a uniform response of the subsurface runoff production per unit area draining to a point and (2) that the hydraulic gradient can be represented by the local slope of the surface.

Within the TOPMODEL framework the first assumption is mainly present in the lumped soil parameters $(K_D, K_{mult} \text{ and } m)$, whereas the second is implied in the topographic index distribution.



Figure 6.3.4.: Simulated average saturation deficit \overline{D} and additional saturated area of TOP-MODEL compared to UHg concentrations.



Figure 6.3.5.: Simulated average saturation deficit \overline{D} and additional saturated area of TOP-MODEL compared to DOC concentrations.

In the given application TOPMODEL was fitted with the Monte-Carlo method. The soil parameters show very high conductivities at the top soil and, thus, a high transmissivity (most of the 10 best fits use a 1000 - 5000 fold higher lateral transmissivity for the topsoil than for the C horizon).

Obtaining such a high transmissivity from the calibration, the question if this lumped parameters represent the entire catchment is critical. BEVEN (1997) points out that the hydraulic conductivities measured in the field vary in space and that standard deviations as high as 1 unit on a logarithmic scale are common. Therefore the concept of using lumped parameters is limited, but the high values can be assumed as an indicator for a strong anisotropy associated with preferential flow pathways (BEVEN, 1997).

The fitted melting parameter Mi is generally in the range of the values given by other studies (U.S. ARMY CORPS OF ENGINEERS, 1960) and the ones determined in chapter 5 (0.2 in/°f $\approx 2.8 \text{ mm/°C}$). The low value for the melting temperature T_m is also typical for mountainous areas with more than 80% forest cover (CHOW, 1963).

When comparing the melting periods during spring 2007 and spring 2008, a main problem of the melting simulations seems to be the timing. A different development of the snowpack due to different energy fluxes and, thus, a different ripening state of the snowpack (WALTER ET AL., 2005) in both years could account for this problem.

Another critical point of the TOPMODEL application is the topographic index distribution. GÜNTNER ET AL. (2004) compared different factors for the formation of saturated areas. Their results show that if the DEM resolution is high enough (BEVEN, 1997), the major control on continuous surface saturation is upslope contributing area. The slope was identified to be the second important factor, even if its relevance was lower.

For the Fishing Brook Catchment the calculated 'lake' area (defined as areas with β =0) is higher than the area of open water bodies determined with remote sensing (see chapter 2). The difference of about 2% can be accounted by very flat riparian areas. These areas are assumed to contribute directly to the stream. Thus possible processes in these areas can not be simulated by the model.

Saturation and Mobilization

The relations found for UHg and the modeled variables describing the saturation state of the catchment can be taken as evidence for a mercury flushing effect caused by changing flowpath during high flow conditions.

One part of this flushing can be linked to the saturation of wetland areas which become directly connected via surface flow as observed by BUSHEY ET AL. (2008). Within the TOPMODEL framework the simulation of wetland saturated areas is directly given by the areas with the highest topographic index values. These values occur mainly in flat valley bottoms surrounding the largest stream (CHANG and LEE, 2008). The possible reservoirs of the wetland soils could be mobilized, resulting in a combined flushing of Hg and DOC from peatlands.

Besides the flushing from wetlands BRANFIREUN ET AL. (1996) suggest that flushing from upland areas can plays an important role for the mercury input to the stream. When the water table rises, lower topographic index classes become saturated. These areas represent the hillslopes which drain to the stream via surface near subsurface flow. This flowpath is also referred as 'organic layer interflow' (WEILER and MCDONNELL, 2004) and can contribute high amounts of water in the surficial soil where high amounts of mercury are available (SHANLEY ET AL., 2002b).

The observed relationships of UHg concentrations and the saturation state depend on the snow cover. For periods without a snowpack the proportional Hg flushing is higher. Possible explanations for this observed pattern could be: (1) Soil frost affecting the mobilization from the top soil (SHANLEY ET AL., 2002b; SCHUSTER ET AL., 2008), (2) a disturbance of the topsoil by rain events supporting the flushing as suggested in chapter 5 or, assuming a higher availability of recently deposited mercury, the higher input during the leaf-on period (CHOI ET AL., 2008).

The fact that the mobilization of Hg and DOC does not follow the same behavior supports findings of BUSHEY ET AL. (2008) that reject the assumption of a similar flushing mechanism as proposed by DRISCOLL ET AL. (1995, 1998). Besides that, it could be interpreted as an indicator for the dominance of upland Hg contribution: On the hillslopes the available Hg and DOC in the topsoil originates from leaves and litter. While Hg oxidized at the surface of the leaves (CHOI ET AL., 2008) would be directly available, DOC would be limited dependent on decomposition rates. Thus different timing and, therefore, a different mobilization pattern could be observed for the same source.

6.5. Summary

The general aim of this chapter was to investigate the role of the saturation state on the mobilization of Hg and DOC in the catchment scale following the idea of a generalization and simplification of the hydrological system. This concept is generally referred to the 'virtual experiment' term as defined by WEILER and MCDONNELL (2004).

TOPMODEL was applied with limited success in simulating the hydrograph and the snowmelt. But even thought high uncertainties were calculated with GLUE during the melting period, the general patter, the dynamic of the soil saturation deficit, can be assumed to be represented well enough to test mobilization hypotheses. The results of this investigation are: (1) The Hg mobilization is mainly controlled by the saturation state, which can be represented by the average saturation deficit of the catchment or the extend of saturated areas. (2) The mercury flushing follows different patterns during periods without snow compared to times when a snowpack covers the ground. (3) Short mid-winter thaws (often combined with rain) lead to a flushing behavior following the non-snow relation. (4) DOC shows a different mobilization mechanism than mercury in the Fishing Brook Catchment.

7. Conclusions

7.1. Implications for the Mercury cycle

This study indicates that a major time for mercury transport during the year is the snowmelt period. During this state of generally high water levels the Hg species which get flushed were dominated by the filtered fractions of Hg. An increase of particulate mercury up to 25% was observed during one ROS event. UMeHg concentrations generally decreased and were also dominated by the filtered fraction - PMeHg concentrations were most below the detection limit.

Even though DOC concentrations showed a flushing mechanism, the relations found for DOC, Absorbance₂₅₄ and SUVA₂₅₄ to UHg can only explain a small part of the variations. The concept of different DOC sources contributing to the stream (INAMDAR and MITCHELL, 2006) during different periods of the springflood was conceptualized, but remains uncertain due to the lack of tracers which would allow an allocation of DOC sources.

The role of event water contribution was also investigated. A direct mobilization of DOC caused by a higher event water proportion was not confirmed. The modeling results of TOPMODEL support these weak relations of DOC and UHg concentrations and, thus, the assumption that for DOC and mercury different flushing mechanisms are responsible for the dynamic at the outlet of the catchment.

Furthermore the application of TOPMODEL identified additional dependencies of the mercury mobilization processes. The mobilization was lower during periods with a snowpack than without. These different relations might become a question for further research at the hillslope and the plot scale.

Following the idea of 'hot moments' (MCCLAIN ET AL., 2003) for the mercury cycle, snowmelt was identified to be a 'hot moment' of Hg transport, event though the responsible transport processes do not suit the definition given in chapter 3. The dynamic of methylation factors indicated that direct methylation could be expected in the post melt period, but the more important role of the snowmelt regarding to methylation is the stepwise transport (SHANLEY ET AL., 2002b) of Hg and DOC from the uplands via subsurface flowpaths (in particular 'organic layer interflow' (WEILER and MCDONNELL, 2004)) to downstream riparian wetlands, which can act as methylation 'hot spots' during the summer.

7.2. Outlook

The current study should also call the attention of the community of mercury researchers as there might be a high risk for flux calculations based on Hg samplings with a longer time interval. High flow conditions causing high soil saturation of wetlands and uplands with a duration of just several hours to days can be more important for the transport than weeks of summer or winter baseflow conditions.

The ventured hypothesis, that the main variations of mercury and other biochemical parameters are dominated by runoff dynamics instead of chemical reactions (see chapter 1) can be asserted to be valid for a part of the mobilization processes. Thereby high flow conditions are a sufficient condition, but if the surface near flowpaths are activated, the process of dissolution constitute an additional control.

Furthermore this study can be taken as an example, how the question of real generalizations as claimed by MCDONNELL ET AL. (2007) can be attended by field investigations combined with simple conceptualized modeling approaches. Even though the results are limited to a single catchment and the corresponding scale, the general findings of mobilization by saturation could become an important point for larger scale modeling.

A. Appendix

A.1. Chemistry Data

A.1.1. Oxygen-18 data

Sample ID	Date & Time	Location	Туре	$\delta^{18}O$
County Line Flow				
JS096	03.20.08 12:00	CLF	Stream	-11.816
JS098	$03.21.08\ 15:00$	CLF	Stream	-11.896
JS101	$03.22.08\ 13:00$	CLF	Stream	-11.641
JS102	$03.23.08\ 13:00$	CLF	Stream	-11.756
JS100	$03.27.08\ 10.30$	CLF	Stream	-11.793
JS111	$04.02.08\ 10.30$	CLF	Stream	-11.856
JS114	$04.03.08 \ 13.02$	CLF	Stream	-12.095
JS116	04.04.08 13:02	CLF	Stream	-12.100
J5118 JC141	04.05.08 13:02	CLF	Stream	-12.090
JD141 TC149	04.07.08 1:00	CLF	Stream	-12.004
JS145 IS147	04.09.08 7.00	CLF	Stream	-12.271
IS150	04.10.08.1.00	CLF	Stream	-12.135
JS151	04.10.08 7:00	CLF	Stream	-12.286
JS154	04.11.08 1:00	CLF	Stream	-12.307
JS155	04.11.08 7:00	CLF	Stream	-12.413
JS157	$04.11.08\ 19:00$	CLF	Stream	-12.440
JS162	$04.13.08\ 1.00$	CLF	Stream	-12.192
JS163	$04.13.08\ 7.00$	CLF	Stream	-12.184
JS164	$04.13.08\ 13.00$	CLF	Stream	-12.207
JS165	$04.13.08\ 19:00$	CLF	Stream	-12.084
JS167	04.14.08 7:00	CLF	Stream	-12.163
JS187 JC101	04.15.08 1:00	CLF	Stream	-12.110
12106	04.10.08 1:00	CLF	Stream	-12.150
15201	04.17.08 19:00	CLF	Stream	-12.140 12.040
15203	04.19.08.1.00	CLF	Stream	-12.040
JS206	04.19.08 19:00	CLF	Stream	-12.140
JS209	04.20.08 13:00	CLF	Stream	-11.960
JS212	04.21.087:00	CLF	Stream	-12.060
JS222	$04.22.08\ 13.00$	CLF	Stream	-12.240
JS224	$04.23.08\ 13:00$	CLF	Stream	-12.272
JS225	$04.24.08\ 1.00$	CLF	Stream	-12.219
JS227	$04.25.08\ 1.00$	CLF	Stream	-12.143
JS229	04.26.08 13:00	CLF	Stream	-11.849
15231	04.28.08 13:00	CLF	Stream	-11.628
12324	04.30.08 13:00	CLF	Stream	-11.602
15236	05.01.08 13.00	CLF	Stream	-11.536
JS238	05 05 08 13 00	CLF	Stream	-11 485
Snow Samples	00100100 10100	3.21	Stroum	11,100
ICORE	00.00.00.11.05	a b	a	10 50
J 5075 19076	03.20.08 11:35	Snow A	Snow	-12.50
15070	03.20.08 11:35	Snow A	Snow	-14.18
JS078	03 20 08 12 00	Snow A	Snow	-13.30
15079	03.20.08.12.10	Snow A	Snow	-13.82
JS085	03.21.08 12.20	Snow C	Snow	-13.15
JS091	$03.21.08\ 15.45$	Snow E	Snow	-13.45
JS099	$03.21.08\ 15.50$	Snow E	Snow	-12.78
JS103	$03.27.08\ 13.00$	Snow E	Snow Mix	-13.60
JS121	$04.04.08\ 17:40$	Snow A	Snow	-12.6
JS125	$04.05.08\ 13.20$	Snow C	Snow	-13.2
JS127	$04.05.08\ 14.05$	Snow D	Snow	-12.83
JS129	04.06.08 13:00	Snow F	Snow	-12.35
JS131 JC122	04.09.08 15:00	Snow A	Snow	-12.74
J 5 1 3 3 TC 1 97	04.09.08 13:10	Snow D	Snow	-12.93
JS180	04.10.08 11:30	Show P	Snow	-13.00
15183	04.17.08.19.15	Snow C	Snow	-13.02
Pain complex	04.11.00 12.10	Show O	510W	.19.40
nain sampies				
JS168	04.04.08 17:00	Gage @CLF	Rain	-11.42
JS 169	04.11.08 15:00	Gage @CLF	Rain	-11.23

JS170	$04.12.08\ 11:00$	Gage @CLF	Rain	-5.98
JS171	$04.14.08\ 10.45$	Gage @CLF	Rain	-12.63
JS239	$05.01.08\ 10.00$	Gage @CLF	Rain	-7.58
JS240	$05.05.08 \ 9:15$	Gage @CLF	Rain	-5.32
Wetlands				
JS120	04.06.08 13:00	Sixmile wetland	Well 1	-11.99
JS172	04.10.08 11:10	Sixmile wetland	Stream	-12.47
JS173	$04.10.08\ 11:50$	Sixmile wetland	Well 1	-12.35
JS174	$04.10.08\ 12.25$	Sixmile wetland	Well 2	-12.55
JS175	$04.10.08\ 12.55$	Sixmile wetland	Well 3	-12.65
JS216	$04.18.08\ 13.50$	sixmile wetland	Stream	-12.01
JS217	$04.18.08\ 12.40$	Sixmile wetland	Well 1	-11.59
JS218	$04.18.08 \ 13:00$	Sixmile wetland	Well 2	-12.05
JS219	$04.18.08 \ 13:15$	Sixmile wetland	Well 3	-12.16
Other Locations				
JS119	04.05.08 18:00	Unnamed Trib	Stream	-12.57
JS176	04.10.08 17:00	Unnamed Trib	Stream	-12.91
JS177	04.12.08 13.00	Unnamed Trib	Stream	-12.84
JS213	$04.17.08\ 12:40$	near Windfall Mt	overland flow	-12.72
JS214	$04.17.08\ 16:30$	Unnamed Trib	Stream	-12.55
JS215	04.18.08 14:10	half way to sixmile wetland	overland flow	-11.95
JS241	$05.01.08\ 11.00$	Unnamed Trib	Stream	-12.33
JS242	$05.05.08\ 12.15$	Arbutus Cabin Well	Well	-11.40

A.1.2. Major lons and DOC data

Sample ID	Date and Time	Location	Type	DOC	Ηd	Cond.	ANC	Chloride	Nitrate	Sulfate	Calcium	Magn.	Sodium	Pot.	A.	Silicon
				mg/l	Units	uS/cm2	ueq/L	ueq/L	ueq/L	neq/L	ueq/L	ueq/L	neq/L	ueq/L	ueq/L	ueq/L
Stream at County	/ Line Flow															
JS 101	03.22.2008 13:00	CLF	Stream	4.75	6.58	44.20	-96.10	-139.17	-21.53	-98.11	188.12	63.36	147.81	7.18	7.05	55.51
JS 100	03.27.2008 10:30	CLF	Stream	4.80	6.57	46.40	-123.00	-153.72	-21.41	-96.62	202.77	68.68	153.11	7.05	11.78	311.56
JS 111	04.02.2008 10:30	CLF	Stream	4.08	6.58	43.30	-107.30	-139.57	-22.85	-90.58	188.87	62.97	138.39	6.61	10.87	283.10
JS 114	04.03.2008 13:02	CLF	Stream	5.46	6.50	34.70	-60.80	-113.69	-22.74	-76.48	144.43	45.61	116.86	6.15	17.12	205.65
JS 118	04.05.2008 13:02	CLF	Stream	5.70	6.52	36.80	-70.30	-129.84	-20.92	-81.53	156.40	47.07	123.57	5.92	15.91	223.79
JS 143	04.08.2008 01:00	CLF	Stream	5.28	6.44	30.70	-54.60	-107.53	-17.41	-68.64	126.10	36.63	111.35	5.90	17.53	181.99
JS 151	04.10.2008 07:00	CLF	Stream	5.12	6.44	30.00	-52.10	-102.23	-18.32	-68.59	125.69	37.06	104.55	5.66	13.68	179.78
JS 154	04.11.2008 01:00	CLF	Stream	5.43	6.40	27.80	-47.70	-101.67	-18.16	-68.53	120.31	34.85	90.04	5.26	16.68	169.86
JS 157	04.11.2008 19:00	CLF	Stream	5.64	6.30	26.60	-43.50	-81.16	-19.32	-68.16	113.88	33.21	85.38	6.28	18.35	165.81
JS 162	04.13.2008 01:00	CLF	Stream	5.99	6.21	26.40	-37.00	-78.85	-19.03	-66.46	115.31	33.98	87.54	5.81	17.22	161.64
JS 163	04.13.2008 07:00	CLF	Stream	5.91	6.12	25.20	-31.30	-69.78	-18.86	-65.30	109.95	32.33	80.36	6.09	17.55	155.47
JS 167	04.14.2008 07:00	CLF	Stream	6.13	6.22	24.40	-39.90	-57.74	-20.39	-67.24	115.04	32.74	71.64	6.04	20.63	159.44
JS 191	04.16.2008 01:00	CLF	Stream	6.12	6.16	25.50	-39.20	-61.66	-18.81	-71.09	120.77	34.70	74.47	5.94	18.36	171.58
JS 201	04.18.2008 13:00	CLF	Stream	5.34	6.35	26.50	-48.40	-73.69	-15.25	-70.00	118.34	34.33	82.69	5.49	14.93	172.63
JS 209	04.20.2008 13:00	CLF	Stream	5.82	6.30	24.50	-40.20	-54.28	-15.08	-71.78	104.69	31.30	66.27	4.74	16.19	154.95
JS 212	04.21.2008 07:00	CLF	Stream	5.95	6.34	24.00	-46.90	-50.14	-14.75	-71.87	108.17	31.21	62.97	4.86	17.38	151.64
JS 222	04.22.2008 13:00	CLF	Stream	6.26	6.43	24.10	-49.70	-49.08	-12.71	-71.11	114.37	31.89	63.97	4.86	19.12	148.38
JS 229	04.26.2008 13:00	CLF	Stream	6.82	6.54	25.00	-62.40	-49.25	-7.36	-73.17	123.72	35.66	63.25	4.92	18.88	143.65
JS 233	04.30.2008 13:00	CLF	Stream	6.98	6.57	28.80	-69.70	-76.76	-5.73	-70.97	132.40	41.35	86.14	5.27	17.21	155.96
JS 236	05.03.2008 13:00	CLF	Stream	6.96	6.48	30.20	-73.10	-91.90	-5.54	-76.61	134.24	42.67	88.48	5.19	18.72	160.38
Samples from the	Sixmile Wetland															
JS 120	04.06.2008 13:00	Sixmile wetland	Well 1	5.83	6.53	37.00	-112.20	-110.05	-13.16	-74.24	171.25	59.95	119.55	6.31	12.69	265.70
JS 172	04.10.2008 11:10	Sixmile wetland	Stream	7.59	5.97	26.90	-39.30	-85.17	-15.48	-61.24	110.68	33.66	92.72	7.26	18.28	168.07
JS 173	04.10.2008 11:50	Sixmile wetland	Well 1	6.14	6.44	35.00	-79.50	-116.18	-17.52	-69.92	154.82	48.34	118.73	6.36	11.68	215.80
JS 174	04.10.2008 12:25	Sixmile wetland	Well 2	6.31	6.24	34.20	-54.60	-120.48	-18.57	-67.45	147.51	34.43	138.23	6.01	15.22	189.30
JS 175	04.10.2008 12:55	Sixmile wetland	Well 3	5.47	6.46	24.80	-68.30	-26.82	-26.63	-72.98	167.32	29.70	42.70	5.35	17.58	212.06
JS 218	04.18.2008 13:00	Sixmile wetland	Well 2	7.90	6.43	31.80	-75.40	-85.33	-14.39	-78.59	157.94	35.20	93.94	5.45	19.29	214.75
JS 219	04.18.2008 13:15	Sixmile wetland	Well 3	6.73	6.46	32.40	-100.20	-55.94	-16.27	-81.92	164.99	40.53	68.03	4.76	13.75	206.11
JS 243	05.05.2008 10:15	Sixmile wetland	Well 1	4.69	6.82	63.60	-567.40	-10.57	0.00	-69.46	325.63	184.97	96.26	6.59	4.88	710.12
JS 244	05.05.2008 10:30	Sixmile wetland	Well 2	14.25	6.20	51.80	-328.70	-28.72	-6.55	-89.56	356.28	83.53	69.67	5.35	32.87	501.21
JS 245	05.05.2008 11:00	Sixmile wetland	Well 3	10.09	6.66	47.40	-414.50	-9.82	-1.93	-29.42	328.72	123.00	52.27	1.98	18.21	503.19

JS 239	JS 170	JS 168	JS 183	JS 180	JS 103	JS 213	JS 178	JS 241	JS 214	JS 177	JS 176	JS 119	JS 242	Other locations	Sample ID																
05.01.2008 10:00	04.12.2008 11:00	04.04.2008 17:00	04.17.2008 12:15	04.17.2008 13:05	03.27.2008 13:00	04.17.2008 12:40	04.09.2008 18:30	05.01.2008 11:00	04.17.2008 16:30	04.12.2008 13:00	04.10.2008 17:00	04.05.2008 18:00	05.05.2008 12:15		Date and Time																
Gage @CLF	Gage @CLF	Gage @CLF	Snow C	Snow D	Snow E	near Windfall Mt	near CLF	Unnamed Trib	Arbutus Cabin Well		Location																				
Rain	Rain	Rain	Snow	Snow	Snow Mix	erland flo	erland flo	Stream	Stream	Stream	Stream	Stream	Well		Type																
6.49	2.82	3.26	1.07	1.18	2.10	3.94	2.19	2.50	2.75	2.89	2.72	2.23	0.79	y.																	
5.83	6.18	6.56	5.62	5.78	5.82	5.01	6.24	5.93	5.57	5.72	5.88	6.22	7.33		PH																
12.00	14.90	16.90	4.90	4.00	9.00	17.20	13.90	15.60	16.00	16.80	17.60	18.90	100.50		Cond.																
-30.50	-25.40	-66.50	-4.30	-8.70	-14.10	-9.60	-26.00	-17.10	-10.40	-14.00	-18.10	-29.70	-100.50	c C T	ANC																
-6.98	-26.73	-36.91	-4.79	-5.11	-15.83	-5.93	-9.13	-5.22	-8.23	-10.94	-8.51	-8.17	-24.68		Chloride																
-24.22	-21.55	-11.24	-9.58	-5.70	-12.52	-15.63	-8.63	-16.31	-29.08	-35.51	-36.36	-32.74	-11.64	cçç T	Nitrate																
-20.64	-34.18	-23.29	-6.13	-3.11	-16.95	-81.49	-59.43	-79.80	-67.61	-67.73	-68.82	-75.41	-202.80	r	Sulfate																
47.16	47.95	75.70	9.97	7.32	21.06	27.16	79.47	76.13	74.50	81.88	88.77	96.77	675.53	r r	Calcium																
8.70	7.31	15.42	1.47	1.09	7.13	8.65	14.33	21.86	20.29	20.90	22.53	26.27	200.04	c F T	Magn.																
3.44	27.02	39.09	3.77	3.36	14.48	17.16	22.85	22.23	23.07	22.03	25.78	28.15	141.49	r r	Sodium																
14.09	9.16	11.27	2.50	1.81	4.84	7.17	1.94	4.46	5.20	6.50	5.84	4.61	15.58	сц Г	Pot.																
8.22	5.09	6.18	1.70	2.43	5.09	84.51	12.61	18.50	21.66	26.85	23.34	15.04	6.16	сц Г	AI.																
0.12	0.17	1.12	0.00	0.00	0.00	134.24	135.87	161.58	133.34	133.39	145.72	164.90	419.61	r r	Silicon																
	- meas)	-7.33%	-6.55%	-7.86%	-7.45%	-5.26%	-5.03%	-5.37%	-2.34%	-6.30%	-6.01%	-7.62%	-8.20%	-7.50%	-7.05%	-12.48%	-11.74%	-10.81%	-10.42%	-8.64%	-6.60%	-7.67%	-7.25%	-6.71%	-4.78%	-11.50%	-8.26%	-18.06%	-35.77%	-24.97%	-32.60%
-------------	-------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	----------------	--------------------	--------------------	--------------------	--------------------	--------------------	--------------------	--------------------	--------------------	--------------------	--------------------
Cond. Error	meas /(calc	9	6	0	2	9	9	6	5	e	-	8	0	6	e	4	8	6	6	-	-	9	5	5	6	5	7	5	5	7	5
ctence		40.9	43.3	39.9	32.1	34.8	29.1	28.3	27.1	24.9	24.8	23.2	22.4	23.5	24.6	21.4	21.1	21.4	22.3	26.3	28.2	34.1	24.9	32.6	32.5	21.9	29.1	26.5	40.8	38.8	31.9
cal. Condue	calculated																														
alance		6.77%	4.46%	4.83%	6.70%	4.78%	6.02%	6.17%	2.96%	5.90%	9.30%	10.51%	9.79%	10.58%	7.48%	6.60%	6.02%	8.17%	8.43%	8.60%	4.53%	7.11%	9.68%	7.38%	11.08%	11.44%	7.11%	4.50%	-2.70%	6.33%	5.23%
EI.B	%	1.57	6.86	6.54	9.34	0.37	:1.80	1.73	4.41	6.62	-1.30	3.49	0.20	5.12	3.51	5.65	3.55	2.50	5.38	2.01	3.43	-7.41	3.13	5.12	5.08	0.33	8.81	3.98	3.98	1.31	0.31
Sum of lons	req/L	α,							-	C	7	4	4	4		C	C			7	C	4	4	4	U	,			Ŷ	U	4,
Type	_	Stream	c Well 1	(Stream	(Well 1	Well 2	Well 3	Well 2	(Well 3	(Well 1	Well 2	Well 3																			
Location		CLF	mile wetlan	mile wetlan	mile wetlan	rmile wetlan	rmile wetlan	tmile wetlan																							
e and Time		:22.2008 13:00	:27.2008 10:30	.02.2008 10:30	.03.2008 13:02	.05.2008 13:02	.08.2008 01:00	.10.2008 07:00	.11.2008 01:00	.11.2008 19:00	.13.2008 01:00	.13.2008 07:00	.14.2008 07:00	.16.2008 01:00	.18.2008 13:00	.20.2008 13:00	.21.2008 07:00	.22.2008 13:00	.26.2008 13:00	.30.2008 13:00	.03.2008 13:00	.06.2008 13:00 }ix	.10.2008 11:10 Six	.10.2008 11:50 Six	.10.2008 12:25 Six	.10.2008 12:55 Six	.18.2008 13:00 Six	.18.2008 13:15 Six	.05.2008 10:15 3ix	.05.2008 10:30 Six	.05.2008 11:00 Six
Dat		S	S	4	8	8	8	8	8	6	8	8	8	8	8	8	8	8	4	8	05	6	8	8	6	4	4	6	05	05	05

03.22.2008 13:00 03.27.2008 10:30 04.05.2008 13:02 04.05.2008 13:02 04.05.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.11.2008 01:00 04.126.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 04.26.2008 13:00 05.03.2008 13:00 05.03.2008 13:00 05.03.2008 13:00 05.03.2008 13:00 JS 101 JS 101 JS 1111 JS 1114 JS 113 JS 157 JS 162 JS 200 JS 201 JS 201 JS 201 JS 203 JS 222 JS 222 JS 223 JS 233 JS 2333 JS 233 JS 120 JS 172 JS 173 JS 174 JS 175 JS 218 JS 219 JS 243 JS 245 JS 245

Sixmile Wetland

Sample ID

JS 100 JS 111 JS 114 JS 118	JS 101 JS 100 JS 111	Sample ID
03.27.2008 10:30 04.02.2008 10:30 04.03.2008 13:02 04.05.2008 13:02	03.22.2008 13:00 03.27.2008 10:30 04.02.2008 10:30 04.03.2008 13:02	Date and Time
		Location
Stream Stream Stream	Stream Stream Stream Stream	Type S
36.86 39.34 30.37	eq/L 51.57 36.86 36.54 39.34	ium of lons E
4.46% 4.83% 4.78%	% 6.77% 4.46% 6.70%	El. Balance
	alculated	al. Conductenc
43.36 39.90 32.12 34.86	meas 40.96 43.36 39.90 32.12	e Conc
-6.55% -7.86% -5.26%	s /(calc - meas) -7.33% -7.86% -7.45%	1. Error

A.2. Program source-codes

A.2.1. Isotope Snowmelt Model

Matlab code for the Isotope Snowmelt Model:

```
Y----
\H{X} Jakobs Isotope Snowmelt model quick calibration tool using the fminsearch
% function.
% contact: hydrology@schelker.de
%-----
                               _____
clear all
close all
           -----
%-----
%show output as graphs?
Output_flag1=1;
% Output_flag1=0;
Output_flag2=1;
% Output_flag2=0;
Х-----
%initial parameters for fminsearch
    % precip gradient with elevation + 0.2
% cutoff temperature for snow \sim 0.0
% Dardegree factor mm/^{\circ}c 0.2
    \% Daydegree factor mm/^{\circ}c
                                       0.2
    % temp gradient with elevation - 0.1
% interception factor ? ~ ~ 0.7
    %not used
start_parameters =[0.2 0.0 3 -0.3 0.7];
X-----
%run fitting routine
%define function handle (return variable is RMSE)
    RSME = @Isotope_snowmelt_function; %send_return
%run fminsearch on function handle
    continue of the function handle options-optimes('Display','iter'); % ('Display','iter','MaxIter',50);
colibrated_parameters = fminsearch(RSME,start_parameters, options);
%-----
%run with calibrated parameter set:
RSME=Isotope_snowmelt_function(calibrated_parameters);
Υ_____
% Output generation
%---
dlmwrite('OUTPUT/calibrated_parameters.txt',[calibrated_parameters],'delimiter','\t');
%read in variables to from function output file:
precip_station=dlmread('OUTPUT/precip_station.txt');
Output_Snowpack =dlmread('OUTPUT/Isotope_snow_output.xls');
climate_data=load('INPUT/Newcomb_Snowmelt_2008_018.txt');
Х-----
% Plots
%----
       -----
RSME
if Output_flag1==1
    % show graph
    scrsz = get(0,'ScreenSize'); % get screen size
    % create figure
    figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
    hold all % hold figure for additional plots
```

```
title('0-18 - Snowmelt Isotope Model')
      subplot(3,1,1)
      bar(climate_data(:,1),-precip_station(:));
    ylabel('precip (mm)');
% xlim([39540, 39580])
      subplot(3,1,2)
    subjec((3,1,2)
plot(Output_Snowpack(:,1),(Output_Snowpack(:,2)));
ylabel('Water Output(nm/d)');
% xlim([39540, 39580])
%xlabel('date')
%
%
        % create figure
figure('Position',[scrsz(3)*1/10 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
%
        % size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
%
%
      subplot(3,1,3)
  plot(climate_data(:,1),Output_Snowpack(:,5));
ylabel('SWE (mm)');
% xlim([39540, 39580])
%
%
        subplot(4,1,4)
    plot(Output_Snowpack(:,1),(Output_Snowpack(:,4)));
ylabel('0-18, delta VSMOW')
% xlim([39540, 39580])
%
%
%
%
     xlabel('date')
end
if Output_flag2==1
       scrsz = get(0,'ScreenSize'); % get screen size
      % create figure
     % create right = figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
      title('0-18 - Snowmelt Isotope Model')
      subplot(4,1,1)
     subjuct(*,1,1)
bar(climate_data(:,1),-precip_station(:));
ylabel('precip (mm)')
xlim([39540, 39580]);
     subplot(4,1,2)
plot(Output_Snowpack(:,1),(Output_Snowpack(:,2)));
      ylabel('Water Output(mm/d)')
xlim([39540, 39580]);
%xlabel('date')
      subplot(4,1,3)
     plot(climate_data(:,1),Output_Snowpack(:,5));
ylabel('Snowpack (mm)')
xlim([39540, 39580])
      subplot(4.1.4)
  subplot(4,1,4)
plot(0utput_Snowpack(:,1),(Output_Snowpack(:,4)));
ylabel('0-18, delta VSMOW')
xlim([39540, 39580])
% ylim([-14, -5])
xlabel('date')
nd
end
%-----
% 'end of program'
                             -----
function RMSE=Isotope_snowmelt_function(parameters)
test_flag=1;
test_flag=0;
¥-----
%read elevation class table
elevation_levels=load('INPUT/elevation_levels.txt');
h=elevation_levels(:,2); %elevation level
n=elevation_levels(:,3); %number of cells
```

```
dim_elevation=size(elevation_levels);
%plot(n,h)
%title('Höhenverteilung Fishing Brook')
%ylabel('Anzahl Zellen')
 %xlabel('Höhenstufe')
Area = sum(n)*10*10; \% area in \texttt{m}^2
% Area
weight_factor=n(:)*10*10/Area;
%----
\ensuremath{\texttt{X}} write parameters from calibration tool to variables
                                                 \% +0.2; change of rain amount with elevation [mm/100m] \% 0 melting Temperature \%2; [mm/^CC] \% -0.1; change of temperature with elevation in ^\circC/100m
precip_grad=parameters(1);
Tm = parameters(2);
ddf=parameters(3);
temp_grad = parameters(4);
interception_factor=parameters(5);
                                               % 0.7; factor for interzeption losses
%parameters(not fitted)
            X 0.1 holding capacity of snow cover as a fraction of total water equivalent
X 0.05 Xrefreezing factor (Value from HEV)
HC=0.1:
RF=0.05;
 Х-----
\ensuremath{\texttt{'}}\xspace{\ensuremath{\texttt{read}}} temperature and precipitation data
climate_data=load('INPUT/Newcomb_Snowmelt_2008_018.txt');
 dim_climate=size(climate_data);
% dim climate = size of all climate data arrays
date=(climate_data(:,1));
temp_station = ((climate_data(:,7)-32)./1.8); %temp_station = average daily temp in °C
% interception losses
precip_station = (climate_data(:,12)*25.4)*interception_factor;  % precip converted to mm
alt_station = 496.5;
                            % altitude of the climate station [m]
<u>%------</u>
%Elevation Effects:
% change of air temperature with elevation
%define array size:
temp_distrib=ones(dim_climate(1,1),dim_elevation(1,1));
for i=1:dim_climate(1,1) % go thru all rows = timesteps
for j=1:dim_elevation(1,1) % go thru all columns = elevation classes
         \texttt{temp_distrib(i,j)=temp_station(i)+(temp_grad*((h(j)-alt_station)/100));}
     end
end
% change of rain amount with elevation
%define array size:
precip_distrib=ones(dim_climate(1,1),dim_elevation(1,1),2);
for i=1:dim_climate(1,1) % go thru all rows = timesteps
    for j=1:dim_elevation(1,1) % go thru all columns = elevation classes
         if precip_station(i)>0
    precip_distrib(i,j,1)=precip_station(i)+(precip_grad*((h(j)-alt_station)/100));
else
         precip_distrib(i,j,1)=0;
end
    end
end
%snow accumulation and melting routine (Day Degree, HBV - Style ...)
٧-----
 % initial values for Snow storage and water fluxes
% third dimension used for O18 concentrations
% fourth dimension for area weighting
```

```
SWE=zeros(dim_climate(1,1),dim_elevation(1,1),3);
                                                                        % Snow Water equivalent
refr=zeros(dim_climate(1,1),dim_elevation(1,1),3);
melt=zeros(dim_climate(1,1),dim_elevation(1,1),3);
                                                                         %refreezing water
                                                                         %melting water
% max storage of liquid water
LWRC=zeros(dim climate(1.1).dim elevation(1.1));
%apply snow melt routine
for i=2:dim_climate(1,1) % go thru all timesteps
for j=1:dim_elevation(1,1) % run thru all elevation classes
          % snowmelt
          if (temp_distrib(i,j)<=Tm) % if temp lower than zero
  refr(i,j,1)=RF*ddf*(Tm - temp_distrib(i,j)); % refreezing from retained liquid water (from HBV)
  SWE(i,j,1)=SWE(i-1,j,1)+precip_distrib(i,j,1);</pre>
                melt(i, j, 1) = 0;
                if ((refr(i,j,1)<RLW(i-1,j,1)) && (RLW(i-1,j,1)>0)) % if not all refreezes
    RLW(i,j,1)=RLW(i-1,j,1)-refr(i,j,1);
    SWE(i,j,1)=SWE(i-1,j,1)+precip_distrib(i,j,1)+refr(i,j,1);
                     WaterOutput(i,j,1)=0;
                elseif ((refr(i,j,1)>=RLW(i-1,j,1)) && (RLW(i-1,j,1)>0)) % if all refreezes
refr(i,j,1)=RLW(i-1,j,1);
                     RLW(1,j,1)=0;
SWE(i,j,1)=SWE(i-1,j,1)+precip_distrib(i,j,1)+refr(i,j,1);
WaterOutput(i,j,1)=0;
                elseif (RLW(i-1,j,1)==0) % if there is no liquid water
                     RLW(i,j,1)=0;
SWE(i,j,1)=SWE(i-1,j,1)+precip_distrib(i,j,1);
                     WaterOutput(i,j,1)=0;
                     refr(i,j,1)=0;
                end
           elseif ((temp_distrib(i,j))> Tm)
                                                        % if temp higher than zero
               melt(i, j, 1) = ddf * (temp_distrib(i, j) - Tm);
refr(i, j, 1) = 0;
                if ((melt(i,j,1)<SWE(i-1,j,1)) && (SWE(i-1,j,1)>0)) % if not all melts
                     SWE(i,j,1)=SWE(i-1,j,1)-melt(i,j,1);
                     \texttt{RLW}\,(i,j,1) = \texttt{RLW}\,(i-1,j,1) + \texttt{precip_distrib}\,(i,j,1) + \texttt{melt}\,(i,j,1);
                     %LWRC(i,j)=SWE(i,j,1);
LWRC(i,j)=SWE(i,j,1)*HC;
                                                           %amount of water which can be retained in the snowpack
                     if (RLW(i,j,1)>LWRC(i,j))
WaterOutput(i,j,1)=RLW(i,j,1)-LWRC(i,j);
                          RLW(i,j,1)=LWRC(i,j);
                     end
                elseif ((melt(i,j,1)>=SWE(i-1,j,1)) && (SWE(i-1,j,1)>0)) % if all melts
    melt(i,j,1)=SWE(i-1,j,1);
    WaterOutput(i,j,1)=melt(i,j,1)+RLW(i-1,j,1)+precip_distrib(i,j,1);
                     SWE(i,j,1)=0;
                     RLW(i,j,1)=0;
                elseif (SWE(i-1,j,1)==0)
                     SWE(i,j,1)=0;
                     RLW(i,j,1)=0;
melt(i,j,1)=0;
                     WaterOutput(i,j,1)=precip_distrib(i,j,1);
               end
          end
     end %end elevation and timesteps
end
%-----
% water Balance calculation
sumWaterOutput=sum(sum(WaterOutput(:,:,1)));
```

```
sumPrecip=sum(sum(precip_distrib(:,:,1)));
waterBalance = sumPrecip-sumWaterOutput;
waterBalancePercent = sumWaterOutput/(sumPrecip);
%waterBalance
%waterBalancePercent
                            %-
% Q18 Mixing calculations
%-----
                _____
% All 018 concentrations are calculated as masses(conct* water volume)
% The masses of all fluxes/storages are in the third dimension of the data arrays.
% i.e. SWE (*,*,1) contains all water volumes/masses, SWE (*,*,2)contains conct* water volume
%
" X In the (*,*,3) layers all concentrations are calculated at the end of the mixing calculations X by dividing (*,*,2) by (*,*,1) for each element
% set starting date for O18 simulation
start_date=39542; % date = 04.04.2008 (=39542 as excel date)
% set end_date for O18 simulation
end_date=39572; %39572; % = 04.05.08
% altitude 180 effect equation
% values measured in the field
018_grad = -0.287; %elevation factor
018_intercept = -11.073; % y intercept
018_alt=zeros(dim_elevation(1,1));
for j=1:dim_elevation(1,1)
     018_alt(j) = 018_intercept+((h(j)/100)*018_grad);
end
% calculation of precip 018 input
for i=1:dim_climate(1,1) % all timesteps
    for j=1:dim_elevation(1,1) % all elevation classes
          % (climate_data(i,17)) = measured 018 signature of rain
         if climate_data(i,17)~=0 && j==1¼ if a measured 018 concentration is available
    precip_distrib(i,j,2)=(climate_data(i,17)*precip_distrib(i,j,1));
         elseif climate_data(i,17)~=0 && j>1  % add elevation effect to hiher elevation classes
precip_distrib(i,j,2)=((climate_data(i,17)+(((h(j)-alt_station)/100)*018_grad))*precip_distrib(i,j,1));
         precip_distrib(i,j,2)=0;% 0;
end
         if test_flag==1
%Use test data for Precip
             precip_distrib(i,j,2)=-14*precip_distrib(i,j,1); %
          end
     end
end
if test_flag==1
'test value for rain isotope signature in use !'
end
Υ_____
% run 018 simulation
for i=2:dim_climate(1,1) % all timesteps
    for j=1:dim_elevation(1,1) % all elevation classes
         if climate_data(i,1)< start_date
                                                    %Period before 018 simulation
             SWE(i,j,2)=0;
WaterOutput(i,j,2)= 0; %0;
```

```
% concentration for 018
    % concentration for U18
SWE(i,j,2)=SWE(i,j,1)*018_alt(j);
RLW(i,j,2)=RLW(i,j,1)*018_alt(j);
melt(i,j,2)=melt(i,j,1)*018_alt(j);
refr(i,j,2)=refr(i,j,1)*018_alt(j);
WaterOutput(i,j,2)=WaterOutput(i,j,1)*018_alt(j);
elseif climate_data(i,1)> start_date && climate_data(i,1)<=end_date</pre>
     % 180 mixing calculation with all fluxes in the time period
     % between start date and end date:
     if temp_distrib(i,j)<=Tm
         \% what happens if there is no RLW in the timestep before \% what happens if RLW(i-1)==0
         if RLW(i-1,j,1)==0
refr(i,j,2)=0; % last term = concentration of SWE-1
          else
         refr(i,j,2)=refr(i,j,1)*(RLW(i-1,j,2)/RLW(i-1,j,1)); % last term = concentration of RLW-1
         end
         RLW(i,j,2)=RLW(i-1,j,2)- refr(i,j,2);
melt(i,j,2)=0;
          if SWE(i-1,j,2)==0
         SWE (i,j,2)=precip_distrib(i,j,2);
          else
         SWE (i,j,2) = (SWE(i-1,j,2)+refr(i,j,2))+precip_distrib(i,j,2);
          end
         WaterOutput(i,j,2)=0; % 0;
     elseif ((temp_distrib(i,j))>Tm)
         refr(i,j,2)=0;
         if melt (i,j,1)>0
              if melt(i,j,1)>=SWE(i-1,j,1) % if all melts
                   melt(i,j,2)=SWE(i-1,j,2);
                   WaterOutput(i,j,2)=RLW(i-1,j,2)+melt(i,j,2)+precip_distrib(i,j,2);
RLW(i,j,2)=0;
                  % SWE(i,j,2)=(SWE(i,j,1)*(SWE(i-1,j,2)/SWE(i-1,j,1)));
                   SWE(i,j,2)= SWE(i-1,j,2) - melt(i,j,2);
              elseif melt(i,j,1)<SWE(i-1,j,1) % if not all melts</pre>
                   melt(i,j,2)=melt(i,j,1)*(SWE(i-1,j,2)/SWE(i-1,j,1)); % last term = concentration of SWE-1
                  SWE(i,j,2) = (SWE(i-1,j,2)-melt(i,j,2));%
                   %SWE(i,j,2)= (SWE(i,j,1)*SWE(i-1,j,2)/SWE(i-1,j,1));
                   \label{eq:RLW(i,j,2)=RLW(i-1,j,2)+precip_distrib(i,j,2)+melt(i,j,2); % Mass of RLW before abstraction of output
                   WaterOutput(i,j,2) = WaterOutput(i,j,1)* ...
                        (RLW(i,j,2)/((RLW(i,j,1)+precip_distrib(i,j,1)+melt(i,j,1))));
                   \texttt{RLW}(\texttt{i},\texttt{j},\texttt{2})=\texttt{RLW}(\texttt{i},\texttt{j},\texttt{2})-\texttt{W}\texttt{aterOutput}(\texttt{i},\texttt{j},\texttt{2}); \ \texttt{\%} \ \texttt{Mass} \ \texttt{of} \ \texttt{RLW} \ \texttt{after} \ \texttt{abstraction} \ \texttt{of} \ \texttt{output}
              end
         elseif melt (i,j,1)==0
             melt (i,j,2)= 0; % 0;
             WaterOutput(i,j,2)=precip_distrib(i,j,2);
         end
    end
```

% end of 180 mixing calculation

%-----

%

```
elseif climate_data(i,1)>end_date %end of simulation period reached
               SWE(i,j,2)=0;
              RLW(i,j,2)=0;
melt(i,j,2)=0;
              WaterOutput(i,j,2)=0; %0;
         end % end of start_end date loop
    end % end climate. elevation loop
end
     _____
%
\% Q18 concentrations and Mass Balance calculation
sumMassOutput=0;
sumMassInput=0;
for i=1:dim_climate(1,1) % all timesteps
    for j=1:dim_elevation(1,1) % all elevation classes
          % calculation of output concentrations as a third array in the
         % data Arrays
         if refr(i,j,1)>0
    refr(i,j,3)=refr(i,j,2)/refr(i,j,1);
end
         if SWE(i,j,1)>0
    SWE(i,j,3)=SWE(i,j,2)/SWE(i,j,1);
end
         if RLW(i,j,1)>0
          if precip_distrib(i,j,1)>0 
 precip_distrib(i,j,3)=precip_distrib(i,j,2)/precip_distrib(i,j,1); end
         if melt(i,j,1)>0
          ______melt(i,j,3)=melt(i,j,2)/melt(i,j,1);
end
          % Mass balance calculation
          %note: all calculations are not area weighted
         if climate_data(i,1)== start_date % initial concentrations
    sumMassInput=sumMassInput+SWE(i,j,2)+precip_distrib(i,j,2)+RLW(i,j,2);
              sumMassOutput = sumMassOutput + Water Output (i, j, 2);
          elseif climate_data(i,1)>start_date && climate_data(i,1)<=end_date
% if not(isnan(precip_distrib(i,j,2)))
sumMassInput=sumMassInput+precip_distrib(i,j,2);</pre>
           summass.input=summass.input+precip_distric(1, j, 2)
% end
% if not (isnan(WaterOutput(i, j, 2)))
sumMassOutput=sumMassOutput+WaterOutput(i, j, 2);
% end
end
    end
end
```

massBalance = sumMassInput-sumMassOutput; massBalancePercent = sumMassInput/sumMassOutput;

%sumMassInput %sumMassOutput

%massBalance %massBalancePercent

%------% compare simulated SWEs with measured SWE

% read in measured SWE measured_SWE=load('INPUT/measured_SWE.txt');

% 1 = station % 2 = elevation

```
% 3 = elevation class
% 4 = date
% 5 = measured SWE
\% define array size for measured/simulated SWE comparison
dim meas SWE=size(measured SWE);
compare_SWE= zeros(dim_meas_SWE(1,1),dim_meas_SWE(1,2)+1);
%compare measured and
for k=1:dim_meas_SWE(1,1)
   for l=1:dim_meas_SWE(1,2)
       compare_SWE(k,1) = measured_SWE(k,1);
   end
   for i=1:dim_climate(1,1) % all timesteps
          for j=1:dim_elevation(1,1) % all elevation classes
              end
          end
   end
end
%calculate sum of squared errors
for k=1:dim_meas_SWE(1,1)
    \label{eq:RMSE} \texttt{RMSE(k)} = (\texttt{compare}\_\texttt{SWE(k,5)} - \texttt{compare}\_\texttt{SWE(k,6)}^2;
end
RMSE=sum(RMSE(:));
RMSE = RMSE^{(1/2)};
_____
% Area weighting for all Outputs:
% Output has water volume in mm, (m^3/s) and O18 concentrations for the entire catchment
Output_Snowpack=zeros(dim_climate(1,1),5);
for i=1:dim_climate(1,1) % all timesteps
    for j=1:dim_elevation(1,1)
         Output_Snowpack(i,1)=date(i);
         Output_Snowpack(i,2)=Output_Snowpack(i,2)+WaterOutput(i,j,1)*weight_factor(j); % Output in mm/day
         Output_Snowpack(i,3)=Output_Snowpack(i,3)+WaterOutput(i,j,1)*weight_factor(j)*Area/(1000*3600*24); % Output in m<sup>3</sup>/s
Output_Snowpack(i,4)=Output_Snowpack(i,4)+WaterOutput(i,j,2)*weight_factor(j);
Output_Snowpack(i,5)=Output_Snowpack(i,5)+SWE(i,j,1)*weight_factor(j); % Snow amount in mm
         % weight_factor=n(:)*10*10/Area; %n= number of cells
    end
    %calculation of Output concentration
     if Output_Snowpack(i,2)>0
         Output_Snowpack(i,4)=Output_Snowpack(i,4)/Output_Snowpack(i,2);
     else
         Output_Snowpack(i,4)=0; % should be no data
     end
end
%------
% Output generation
%------
% Write Output Files:
    dlmwrite('OUTPUT/Isotope_snow_output.xls',[Output_Snowpack],'delimiter','\t');
dlmwrite('OUTPUT/precip_station.txt',[precip_station],'delimiter','\t');
dlmwrite('OUTPUT/compare_SWE.xls',[compare_SWE],'delimiter','\t');
dlmwrite('OUTPUT/SWE.xls',[SWE],'delimiter','\t');
```

%'end of function'

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% IHS Program

A.2.2. runCe - Isotope Hydrograph Separation

Matlab code for the runCe approach:

```
----
% hydrograph separation tool by Jakob Schelker -
% hydrology@schelker.de
"This program contains: runCe, CMV, VWA - all described by
% (Hjalmar Laudon, WRR 2002, Vol 38)
ÿ_-----
clear all;
close all;
y_____
% set the part of the simulation
runCe_flag=1; % turns on the runCe iterative calculation
% runCe_flag=0;
CMW_flag=1; % turns on the Current Melt Water IHS calculation
% CMW_flag=0;
VWA_flag=1;
% VWA_flag=0;
                % turns on the Volume Weigthend average IHS calculation
Output_flag=1; % turns on the output plotting (part one)
% Output_flag=0;
Output_flag2=1;
                       % turns on the second graph
% Output_flag2=0;
test_flag=1; % turns on the usage of a generated test dataset
 test_flag=0;
  -----
% set simulation period for IHS
% set starting date for 018 fitting
start_date=39542; % date = 04.04.2008 (=39542 as excel date)
% set end_date for 018 fitting
end_date=39572; %39572; % = 04.05.08
start_end=end_date-start_date;
X-----
%load needed data:
outlet_measured=load('INPUT/Outlet_measured.txt');
%date=outlet_measured(:,1); %date of measured flow and 018
S=outlet_measured(:,2); %measured discharge
Cs=outlet_measured(:,3); %measured 0-18 signature
%set preevent water concentration
Cp=-11.40; % = measured GW Isotope signature
% Cp=-11.485; % = summer baseflow
% Cp=-11.81; % = winter baseflow
Output_snowpack=load('OUTPUT/Isotope_snow_output.xls');
M=zeros(start_end,1);
Cm=zeros(start_end,1);
% loop to read the needed Snowpack output
for i=1:length(Output_snowpack)
     if Output_snowpack(i,1)>=start_date
         j=j+1;
         \texttt{Xdate=Output\_snowpack(i,1); Xdate of simulated snow output and O18 <math display="inline">\texttt{M}(j)=\texttt{Output\_snowpack(i,2); Xmeltwater in mm} \texttt{Cm}(j)=\texttt{Output\_snowpack(i,4); XO -18 signature of snowpack output}
     end
end
```

X------X testing event water by using 50% of Streamwater and a given 018 signature

```
if test_flag==1
    M=S/2;
Cm(:)=-13;
    for i=1:30
         Cm(i)=Cm(i+1)*(1-0.05*rand(1,1));
         % Cm(i)=Cm(i+1)*(1-0.002*sin(i));
    end
end
x-----
runCe=zeros(start_end,1);
E=zeros(start_end,1);
f_runCe=zeros(start_end,1);
sumE=zeros(start_end,1);
sumE_by_Ce=zeros(start_end,1);
sumM=zeros(start_end,1);
sumM_by_Cm=zeros(start_end,1);
% calculate given (measured) sum variables
for t=1:start_end %loop thru all timesteps % \left[ \left( {{{\left( {{{\left( {{{\left( {{{\left( {{{\left( {{{c}}}} \right)}} \right.}
     t=1:state_ong _____
if t==1
      sumM_by_Cm(t)=(M(t)*Cm(t));
eise
sumM_by_Cm(t) = (sumM_by_Cm(t-1)+(M(t)*Cm(t)));
sumM(t) = sumM(t-1)+M(t);
end
end
%------
% runCe approach
%----
             ·
if runCe_flag==1;
     counter=0;
     for t=1: start_end %loop thru all timesteps
         Diff_runCe=1;
         runCeOld=0;
         %initial values for runCe
          if t==1
          \texttt{runCe(t)=-12.0;} %isnt that a reasonable value ;) elseif t>1
         runCe(t)=runCe(t-1); % use runCe value from the timestep before as a starting value end
         %run iterative optimisation loop
         while (Diff_runCe>0.000001)% (counter<100)%
              \% stopping criteria: difference in runCe between \% the two last runs will be less then the given value
              % count total number of iterations
              counter=counter+1;
              % store old runCe in variable
              runCeOld=runCe(t);
              % calculate event Water fraction f and event water amount E
              f_runCe(t) = (Cs(t) - Cp) / (runCeOld - Cp);
              E(t) = S(t) * f_runCe(t);
              % calculate sum variables
              if t==1
                  sumE(t) = E(t);
                  sumE_by_Ce(t) =E(t)*runCeOld;
```

```
elseif t>1
                       sumE_by_Ce(t)=sumE_by_Ce(t-1)+E(t)*runCeOld;
sumE(t)=sumE(t-1)+E(t);
                  end
                 %calculate new (fitted) runCe
                 f(t) = sumM_by_Cm(t)-sumE_by_Ce(t);
g(t) = sumM(t)-sumE(t); % normally <0</pre>
                 runCe(t) = f(t)/g(t);
                 % calculate difference of the old and the new runCe value
Diff_runCe=sqrt((runCeOld-runCe(t))^2);
            end
            %t
           %counter
      end
end
% Volume Weigtend Average approach:
%------
if VWA_flag==1
      % initialise variables
     % initialise variables
Ce_VWA=0; % VWA evet water concentration
VWA_M=0; % sum of Meltwater
E_VWA=zeros(start_end,1); % Amount of eventwater
f_VWA=zeros(start_end,1); % fraction of eventwater
     % calculate weigthend Average
for t=1:start_end %loop thru all timesteps
           Ce_VWA=Ce_VWA+(M(t)*Cm(t));
VWA_M=VWA_M+M(t);
      end
      Ce_VWA=Ce_VWA/VWA_M;
     % calculate event water fraction
for t=1:start_end %loop thru all timesteps
    if Ce_VWA~=0
    f_VWA(t)=((Cs(t)-Cp)/(Ce_VWA-Cp));
           E_VWA(t)=S(t)*f_VWA(t);
           end
      end
end
X-----
".
%Current Melt Water approach:
%-----
                                  ------
if CMW_flag==1
     Ce_CMW=zeros(start_end,1); %signature of event water
f_CMW=zeros(start_end,1); % fraction of event water
E_CMW=zeros(start_end,1); %amount of event water
     for t=1:start_end %loop thru all timesteps
    Ce_CMW(t)=Cm(t);
           if Ce_CMW(t)~=0
                 f_CMW(t)=((Cs(t)-Cp)/(Ce_CMW(t)-Cp));
                 E_CMW(t)=S(t)*f_CMW(t);
           else
                 E_CMW(t)=0;
     end
end
end
```

X-----Xcalculate total amount of contribution:

```
Х-----
% calculate total event water contributions and fractions
total_amount=zeros(4,2);
for t=1:start end
      %(...,1) gives the sums
     x(..,) gives the sums
total_amount(1,1)=total_amount(1,1)+ S(t);
total_amount(2,1)=total_amount(2,1)+ E(t);
total_amount(3,1)=total_amount(3,1)+ E_CMW(t);
total_amount(4,1)=total_amount(4,1)+ E_VWA(t);
                                                                              %Streamwater
                                                                              % runCe Event Water
                                                                               .
% CMW Event Water
% VWA Event Water
end
total_amount(1,2)=total_amount(1,1)/total_amount(1,1); %percentage stream of stream (=1)
total_amount(2,2)=total_amount(2,1)/total_amount(1,1); %percentage runCe
total_amount(3,2)=total_amount(3,1)/total_amount(1,1); %percentage CMW
total_amount(4,2)=total_amount(4,1)/total_amount(1,1); %percentage VWA
y_____
%ploting results:
%-----
   scrsz = get(0,'ScreenSize'); % get screen size
if Output_flag==1
      % Show all used approaches in one graph
      % create figure
     n create rague
figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
      subplot(1,1,1)
title('0-18 - Hydrograph Separation')
      hold all
     hold all
plot(S(:));
if VWA_flag==1
    plot(E_VWA(:));
end
if CMW_flag==1
if CMW_flag==1
     plot (E_CMW(:));
end
     if runCe_flag==1
    plot(E(:));
end
ylim([0,20])
end
if Output_flag2==1;
      if VWA_flag==1 % show VWA graph
            % create figure
           % create right=
figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
           subplot(3,1,1)
title('0-18 - Hydrograph Separation with VWA')
            hold all
           plot (S(:));
plot (E_VWA(:));
            xlim([1 50])
            ylabel('Discharge (mm/d)')
            subplot(3.1.2)
           subplot(3,1,2)
hold all
t=1:30;
plot(t,Ce_VWA);
ylabel('Eventwater 0-18')
            xlim([1 50])
           subplot(3,1,3)
hold all
plot(f_WWA(:));
ylabel('Fraction of preevent water')
xlim([1 50])
xlabel('days after starting date')
      end
```

```
if CMW_flag==1
```

end

```
% create figure
figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
                subplot(3,1,1)
title('0-18 - Hydrograph Separation with CMW')
                hold all
plot(S(:));
plot(E_CMW(:));
                xlim([1 50])
ylabel('Discharge (mm/d)')
               subplot(3,1,2)
hold all
plot(Ce_CMW(:));
ylabel('Eventwater 0-18')
xlim([1 50])
                subplot(3,1,3)
hold all
plot(f_CMW(:));
ylabel('Fraction of preevent water')
xlim([1 50])
xlabel('days after starting date')
         end
         if runCe_flag==1
                % create figure
                % close rights figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
                subplot(3,1,1)
title('0-18 - Hydrograph Separation with runCe')
hold all
                plot(S(:));
plot(E(:));
                xlim([1 50])
                ylabel('Discharge (mm/d)')
                subplot(3,1,2)
hold all
plot(runCe(:));
                ylabel('Eventwater O-18')
xlim([1 50])
                 subplot (3,1,3)
                subjoc(s,1,3)
hold all
plot(f_runCe(:));
ylabel('Fraction of preevent water')
xlim([1 50])
xlabel('days after starting date')
         end
% create figure
figure('Position',[scrsz(3)*1/20 scrsz(4)*1/10 scrsz(3)*8/10 scrsz(4)*8/10])
% size& position vector= [left, bottom, width, height]
hold all % hold figure for additional plots
subplot(2,1,1)
title('Runoff and meltwater 0-18')
hold all
plot(Cs(:));
plot(Cm(:));
xlim([1 40])
 subplot(2,1,2)
title('Runoff and meltwater Discharge')
hold all
plot (S(:));
plot (M(:));
```

xlim([1 40])

%-----%Write Output to File

% Output has water volume in mm, (m^3/s) and O18 concentrations for the entire catchment

```
IHS_Output=zeros(start_end,17);
```

```
for i=1:start_end % all timesteps
```

```
IHS_Output(i,1)=i+start_date-1; % write data
IHS_Output(i,2)=M(i); % Meltwater
IHS_Output(i,3)=Cm(i); % Meltwater signature
IHS_Output(i,4)=S(i); % Streamwater signature
IHS_Output(i,5)=Cs(i); % Streamwater signature
IHS_Output(i,7)=runCe(i); % runCe signature
IHS_Output(i,3)=E(1); % runCe Event Water
IHS_Output(i,9)=f_runCe(i); % runCe Fraction of total runoff
IHS_Output(i,10)=0;
IHS_Output(i,11)=Ce_CMW(i); % CMW signature
IHS_Output(i,12)=E_CMW(i); % CMW signature
IHS_Output(i,13)=f_CMW(i); % CMW fraction
IHS_Output(i,14)=0;
IHS_Output(i,15)=Ce_VWA(i); % VWA signature
IHS_Output(i,16)=E_VWA(i); % VWA signature
IHS_Output(i,17)=f_CWA(i); % VWA fraction
```

```
end
```

% Write Output File:

dlmwrite('OUTPUT/IHS_Output.xls',[IHS_Output],'delimiter','\t');

%-----% messages:

if test_flag==1
 'test data for meltwater and meltwater signature in use '
end

'end of program'

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Ehrenwörtliche Erklärung:

Hiermit erkläre ich, dass die Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt wurde.

Ort, Datum

Unterschrift