Institut für Hydrologie
der Albert-Ludwigs-Universität Freiburg im Breisgau

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The spatio-temporal distribution of $\delta^{18}O$ and $\delta^{2}H$ of precipitation in Germany
-
an evaluation of regionalization methods

Diplomarbeit unter der Leitung von
Prof. Dr. Ch. Leibundgut
Freiburg im Breisgau, Oktober 2007

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Referent: Prof. Dr. Ch. Leibundgut
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List of Abbreviations

^2H	Deuterium	
^{18}O	Oxygen 18	
$\overline{\delta^2 H}_{month/year}$	precipitation weighted monthly/annual mean $\delta^2 H$	[‰]
$\overline{\delta^{18} O}_{month/year}$	precipitation weighted monthly/annual mean $\delta^{18} O$	[‰]
ANIP	Austrian Network of Isotopes in Precipitation	
DWD	Deutscher Wetterdienst (German Weather Service)	
GMWL	Global Meteoric Water Line	
GNIP	Global Network of Isotopes in Precipitation	
IAEA	International Atomic Energy Agency	
MWL	Meteoric Waterline	
MLR	multiple linear regression	
SEP_{cv}	standard error of prediction for full cross validation	
SEP_{DWD}	standard error of prediction when using the DWD stations as a test dataset	
VSMOW	Vienna Standard Mean Ocean Water	[‰]
A	altitude	[m asl]
asl	above sea level	
LA	latitude	[°]
Lo	longitude	[°]
P	amount of precipitation	[mm]
T	temperature	[°C]
Jan (J)	January	
Feb (F)	February	
Mar (M)	May	
Apr (A)	April	
May (M)	May	
Jun (J)	June	
Jul (J)	July	
Aug (A)	August	
Sep (S)	September	
Oct (O)	October	
Nov (N)	November	
Dec (D)	December	

Summary

The objective of this work is to evaluate regionalization methods determining the spatio-temporal distribution of the isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of precipitation in Germany (expressed with $\delta^{18}O$ and $\delta^{2}H$ in [‰]). Using the most suitable methods the spatial distribution of monthly and annual mean isotope ratios shall be calculated and presented in maps for Germany.

The regionalization was performed by multiple linear regressions (MLRs) on monthly and annual amount-weighted mean values of $\delta^{18}O$ and $\delta^{2}H$ of precipitation, observed at 17 German GNIP (Global Network of Isotopes in Precipitation) stations, 12 DWD (German Weather Service) stations and 4 stations of the Austrian Network of Isotopes in Precipitation (ANIP) (all provided by Willibald Stichler, GSF, Neuherberg), as well as at the GNIP station in Groningen, Netherlands (IAEA/WMO, 2004). Latitude (as well as the squared latitude), longitude, altitude, temperature and precipitation are used as regression parameters. Although there is a clear physical effect of these regression parameters on the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation, multicollinearity of the parameters prevents the corresponding coefficients in the regression equations from getting the meaning of a physical gradient. So the MLR equations can not be seen as physical models and must not be used for places outside of Germany.

To find the most suitable regression equations for the prediction of monthly and annual mean isotope ratios of precipitation regressions were performed with different combinations and numbers of the parameters mentioned above and then sorted by their adjusted R^2. The adjusted R^2 was chosen as the overall measure of quality because, in contrast to the simple R^2, it is adjusted to the number of explanatory variables in the regression equations.

As the influence of the different parameters on the isotopic ratios of precipitation changes through the year the quality of the predictions of monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation could be significantly improved by setting up a separate regression equation for each season instead of using one equation for all months.
For the prediction of amount-weighted annual mean isotope ratios the best results were obtained when the MLR equations were set up on observed annual mean δ values, using only geographic parameters for the regression. Calculating annual mean $\delta^{18}O$ and $\delta^{2}H$ values from the predicted monthly means leads to worse results.

The standard errors of prediction, giving the average deviation between observed and predicted δ values, were calculated for full cross validation including all the stations available. The results show that the monthly and annual mean isotope ratios predicted by the regression equations are of sufficient precision to enable a spatial and temporal (summer - winter) differentiation of $\delta^{18}O$ and

δ^2H values of precipitation in Germany.

Based on the best MLR equation for each season maps of mean $\delta^{18}O$ and δ^2H values of precipitation in Germany were created for every month. The same was done for the annual mean isotope ratios calculated with the respective regression equations.

Keywords:

$\delta^{18}O$ - δ^2H - oxygen 18 - deuterium - precipitation - spatio-temporal distribution - Germany

Zusammenfassung

Das Ziel dieser Arbeit ist die Ermittlung geeigneter Regionalisierungsmethoden zur Bestimmung der räumlichen und zeitlichen Verteilung der $^{18}O/^{16}O$ und $^{2}H/^{1}H$ Isotopenverhältnisse des Niederschlags in Deutschland (ausgedrückt durch $\delta^{18}O$ und $\delta^{2}H$ Werte in [‰]). Mithilfe der am besten geeigneten Methoden soll die geographische Verteilung der Monats- und Jahresmittel der $\delta^{18}O$ und $\delta^{2}H$ Werte berechnet und in Karten für Deutschland dargestellt werden.

Die Regionalisierung wurde mithilfe von multipler linearer Regression auf der Basis von niederschlagsgewichteten Monats- und Jahresmittelwerten der $\delta^{18}O$ und $\delta^{2}H$ Werte des Niederschlags durchgeführt. Die Daten stammen von 17 deutschen GNIP (Global Network of Isotopes in Precipitation) Stationen, 12 DWD (Deutscher Wetterdienst) Stationen und 4 Stationen des österreichischen Isotopenmessnetzes ANIP (Austrian Network of Isotopes in Precipitation) (allesamt von Willibald Stichler, GSF, Neuherberg zur Verfügung gestellt), sowie von der GNIP Station in Groningen, Niederlande (IAEA/WMO, 2004). Als Regressionsparameter wurden Breitengrad (auch die quadrierte Form), Längengrad, topographische Höhe, Temperatur und Niederschlag verwendet. Obwohl diese Parameter einen eindeutigen physikalischen Einfluss auf die $\delta^{18}O$ und $\delta^{2}H$ Werte des Niederschlags haben, können die zugehörigen Koeffizienten in der Regressionsgleichung aufgrund der Multikollinearität unter den Parametern nicht als physikalische Gradienten interpretiert werden. Daraus ergibt sich, dass die Regressionsgleichungen nicht als physikalische Modelle angesehen werden dürfen, und ihre Gültigkeit nur innerhalb Deutschlands gewährleistet ist.

Um die geeignetsten Regressionsgleichungen zur Vorhersage der monatlichen und jährlichen mittleren Isotopenwerte des Niederchlags zu finden, wurden Regressionen mit verschiedenen Kombinationen und unterschiedlicher Anzahl von Parametern durchgeführt, und anschließend die Gleichungen nach dem zugehörigen angepassten R^2 sortiert. Das angepasste R^2 wurde als übergeordnetes Gütemaß ausgewählt, da es, im Gegensatz zum einfachen R^2, nach der Anzahl der erklärenden Variablen in der Regressionsgleichung korrigiert wird.

Da sich der Einfluss der verschiedenen Parameter auf das Isotopenverhältnis im Niederschlag im Verlauf des Jahres verschiebt, konnte die Vorhersage von Monatsmitteln der $\delta^{18}O$ und $\delta^{2}H$ Werte des Niederschlags durch das Aufstellen einer gesonderten Regressionsgleichung für jede einzelne Jahreszeit, anstelle einer einzigen Regressionsgleichung für alle Monate, deutlich verbessert werden. Für die Vorhersage der niederschlagsgewichteten Jahresmittel der Isotopenverhältnisse wurden die besten Ergebnisse dann erzielt, wenn die Regressionsgleichungen auf Basis der Jahresmittel der gemessenen δ Werte und nur mit geographischen Parametern aufgebaut wurden. Die Berechnung der Jahresmittelwerte aus den vorhergesagten Monatsmitteln führt zu schlechteren Ergebnissen.

Die Standardfehler der Vorhersage, die eine durch vollständige Kreuzvalidierung ermittelte mittlere Differenz zwischen den gemessenen und den vorhergesagten δ Werten angeben, zeigen, dass die aufgestellten Regressionsgleichungen eine räumliche und zeitliche (Sommer - Winter) Unterscheidung der Monats- und Jahresmittel der $\delta^{18}O$ und $\delta^{2}H$ Werte des Niederschlags in Deutschland ermöglichen.

Mithilfe der besten Regressionsgleichungen für die jeweilige Jahreszeit wurden für jeden Monat Karten der mittleren $\delta^{18}O$ und $\delta^{2}H$ Werte des Niederschlags in Deutschland erstellt. Auch die mittleren Jahreswerte von $\delta^{18}O$ und $\delta^{2}H$ wurden unter Verwendung der entsprechenden Regressionsgleichungen in Karten dargestellt.

Stichworte:

$\delta^{18}O$ - $\delta^{2}H$ - Sauerstoff 18 - Deuterium - Niederschlag - räumliche und zeitliche Verteilung - Deutschland

1. Introduction

1.1. Motivation

TRACE (Tracing the origin of food) is a 5 year project (2005-2010) sponsored by the European Comission through the Sixth Framework Programme. It aims to deliver improved traceability of food products with the first focus being on mineral water, cereals, honey, meat and chicken (URL1). The objective of the "Food Origin Mapping" workpackage within the "Analytical Tools Group" is to correlate geological and groundwater composition, in terms of natural tracers (stable isotopes and trace elements), with that of local mineral water or food (URL2).

As the isotopic composition of local groundwater and food is mainly controlled by the local precipitation, there is a strong interest in the spatio-temporal distribution of the isotopic ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ (expressed in $\delta^{18}O$ and $\delta^{2}H$) of precipitation in Germany.

1.2. Objectives

The objectives of this work are
- to evaluate regionalization methods determining the spatio-temporal distribution of $\delta^{18}O$ and $\delta^{2}H$ of precipitation in Germany and
- to use the most suitable methods to calculate the spatial distribution of the predicted monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation and present the results in maps for Germany.

The study is based on monthly values of $\delta^{18}O$ and $\delta^{2}H$ of precipitation and on the corresponding monthly mean temperatures and amounts of precipitation from 17 German GNIP (Global Network of Isotopes in Precipitation) and 12 DWD (German Weather Service) stations, as well as from 4 stations of the Austrian Network of Isotopes in Precipitation (ANIP) (all provided by Willibald Stichler, GSF, Neuherberg) and the GNIP station in Groningen, Netherlands, (IAEA/WMO, 2004).

1.3. State of the Art

1.3.1. The spatio-temporal distribution of the isotopic composition of precipitation

In 1961 the International Atomic Energy Agency (IAEA) started measuring the isotope contents of precipitation at 151 globally distributed stations on a monthly basis. This was the beginning of the Global Network of Isotopes in

Precipitation (GNIP) which, in 2005, consisted of 183 stations contributing monthly or daily samples from 53 countries (Gourcy et al., 2005).

Craig (1961) discovered that the isotopic concentrations of ^{18}O and ^{2}H in precipitation correlate on a global scale and are fairly well aligned along the so called Global Meteoric Water Line (GMWL). Using data from the GNIP Dansgaard (1964) analysed the global distribution of oxygen and hydrogen isotopes in precipitation and discovered several effects on isotope variations. Typical gradients for some effects are given below:

Altitude effect: Kullin and Schmassmann (1991) published a stable isotope average recharge altitude gradient of -0.19‰/100m for $\delta^{18}O$ and of -1.07‰/100m for $\delta^{2}H$ for the region of the northeastern Jura and the south-eastern slope of the Black Forest. These relationships are based on data from the Nagra (Nationale Genossenschaft für die Lagerung radioaktiver Abfälle) and the Swiss National Energy Research Foundation (NEFF) programmes published in Schmassmann et al. (1984) and Dubois and Flück (1984).

Latitude effect: Dansgaard (1964) reported global gradients for mean $\delta^{18}O$ and $\delta^{2}H$ values of coastal and polar stations at different latitudes of 0.7‰/°C and 5.6‰/°C respectively. Expressed with respect to latitude typical gradients for $\delta^{18}O$ are about -0.6‰/degree of latitude for coastal and continental stations in Europe and the USA (Gat et al., 2000).

Seasonal effect: The temperature dependence of $\delta^{18}O$ and $\delta^{2}H$ due to the change of the seasons is weaker than due to the change in latitude. For $\delta^{18}O$ gradients are between 0.5‰/°C for some higher-latitude stations and ultimately 0‰/°C for tropical ocean islands (Gat et al., 2000).

Small-scale temporal variations: Even during short rainstorms the isotpic composition of the rain can vary considerably. Ambach et al. (1975) reported a change in $\delta^{18}O$ and $\delta^{2}H$ of 4.5‰ and 31.4‰ respectively for a two-hour rainstorm.

1.3.2. Predicting the isotopic composition of precipitation

1.3.2.1. Rayleigh model

According to Sturm et al. (2005) Dansgaard (1964) was the first to develop a conceptual model for isotopes in precipitation. This model was based on the assumption that the vapour mass moves from the oceanic origin to the condensation site without further mixing. Thus the isotopic composition of vapour and rain mainly depend on the equilibrium fractionation factor and the fraction of vapour lost by the rainout process due to the temperature gradient between the source region and the precipitation site. This can be modeled by the Rayleigh distillation equation, which has been improved by incorporating the kinetic fractionation during evaporation from the ocean (Merlivat and Jouzel, 1979) or during the formation of ice crystals (Jouzel and Merlivat, 1984). Even mixed cloud processes between 0°C and -30°C (Ciais et al., 1995) and the meteorological evolution of individual air parcels (Covey and

Haagenson, 1984) were included into the model. Although the high-latitude isotope - temperature dependence is modelled realistically by these models they are not able to describe the mixing of different air masses, the influence of evapotranspiration over continental surfaces or convective cloud processes (Sturm et al., 2005).

1.3.2.2. Atmospheric circulation models

To take into account the complexity of the hydrologic cycle as far as possible fractionation processes were built into atmospheric general circulation models (AGCMs). AGCMs numerically solve the equations of motion on a discretized three-dimensional grid. Boundary conditions are the solar insolation at the top of the atmosphere, the concentration of greenhouse gases and the sea-surface temperatures (Hoffmann et al., 2000). According to Hoffmann et al. (2000) Joussaume et al. (1984) were the first to build a water isotope module into an AGCM. While Joussaume et al. (1984) embedded the isotope module into an AGCM from the Laboratoire de Meteorologie Dynamique (LMD), Hoffmann et al. (1998) used the European Centre model Hamburg (ECHAM) GCM with a horizontal resolution of about 2.8°*2.8° and 19 vertical levels.

As the relatively coarse resolution of the AGCMs makes them inappropriate for regional studies, Sturm et al. (2005) developed and validated a stable water isotope module in the REMO regional circulation model, a modified version of the weather forecast model system EM/DM from the German Weather Service. They conducted a 2 year case study over Europe and compared their results with $\delta^{18}O$ measurements of precipitation at an annual, monthly (GNIP database, IAEA-WMO 2001) and event timescale (GSF stations Norderney, Arkona, Hohenpeissenberg). The REMO model was set up with a horizontal resolution of 0.5° ($\sim$ 55 km) and 19 vertical levels. The best results were obtained when climatic and isotopic boundary conditions were derived from the ECHAM_{iso} general circulation model. Annual mean $\delta^{18}O$ values as well as the tendencies of the isotopic effects were reproduced correctly but REMO failed to simulate their magnitude on annual and seasonal timescales.

1.3.2.3. Interpolation methods

Yurtsever and Gat (1981) tried to find relationships between the mean isotopic composition of precipitation and geographical and climatological parameters by performing multiple linear regression analyses on the GNIP database. Beginning the regressions with the parameters precipitation, latitude, altitude and temperature and then eliminating them one by one, they found out that the use of precipitation, latitude and altitude besides temperature did not lead to a considerably better correlation between observed and predicted monthly mean $\delta^{18}O$ values (for simple and for amount-weighted means). So temperature was the only parameter of importance. However Yurtsever and Gat (1981) stressed that these regression equations were calculated on a global scale. On a regional scale the amount effect or evaporation effect might become equally important factors. The poor correlation between mean $\delta^{18}O$ values and altitude was most likely caused by the fact that most of the GNIP stations used are located at low altitudes.

In a joint IAEA - University of Waterloo project BIRKS ET AL. (2002) re-evaluated and reconfigured GNIP station-based data to produce global and regional maps of the amount-weighted annual and monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation. They interpolated the GNIP station data using the Cressman objective analysis. In the Cressman objective analysis multiple passes are made through the grid at subsequently lower radii of influence. The analyses starts with a first guess. With each pass new values are obtained for all the grid points by applying a distance-weighted formula to all the errors of the first guess field or the previous pass at the locations of observation within the radius of influence. The decreasing radii of influence allow the analysis of different scales (CRESSMAN, 1959). However, according to BIRKS ET AL. (2002), the new maps have not been ground-truthed for interpolation between the GNIP stations.

BOWEN and WILKINSON (2002) empirically modelled relationships between amount-weighted annual mean $\delta^{18}O$ values of modern precipitation and latitude and altitude using the third release of the GNIP database (IAEA/WMO 1998). As the isotopic composition of precipitation is controlled by Rayleigh distillation, which in turn mainly depends on temperature, BOWEN and WILKINSON (2002) believed that one has to include the geographic parameters that control temperature, i.e. latitude and altitude. Looking at the spatial distribution of the residuals between observed and calculated values BOWEN and WILKINSON (2002) concluded that the $\delta^{18}O$ values of precipitation primarily depend on latitudinal and altitudinal temperature variations. However, at northern middle to high latitudes there are regions showing high residuals. According to the authors this is most likely due to the zonal heterogeneity of vapour transport.

As there is no standardized method for creating an accurate representation of stable isotopes in modern precipitation BOWEN and REVENAUGH (2003) evaluated four interpolation schemes:
- Triangulation, a simple spatial interpolation with reference only to the nearest stations.
- Inverse distance weighting, where all available stations were used.
- Cressman objective analysis, as used by BIRKS ET AL. (2002) with slightly different radii of influence.
- The method used by BOWEN and WILKINSON (2002) (BW model), i.e. a regression with latitude and altitude.

BOWEN and REVENAUGH (2003) estimated the error of interpolated $\delta^{2}H$ and $\delta^{18}O$ values of precipitation by subsampling the amount-weighted annual GNIP station data and using these subsamples to predict the isotopic composition at the excluded measurement sites. They found out that the average error of the estimates calculated with the method used by BOWEN and WILKINSON

(2002) (BW model) and modified by themselves was 10-15 % lower than that of the other methods. This was true for a wide range of data densities. For all methods the average error increased substantially as the number of stations in the subsample (training set) decreased. Bowen and Revenaugh (2003) assumed that the inclusion of the altitude effect into the BW model is an important reason for the lower average error obtained by this method compared to the others. Triangulation, inverse distance weighted interpolation and the Cressman objective analysis performed almost equally well, with a slight improvement of triangulation relative to the other two methods for high data densities.

Liebminger et al. (2006b) predicted the $\delta^{18}O$ values of precipitation for Austria using multivariate regressions. Based on Liebminger et al. (2006a) they selected 8 basic local climatic and geographic regression parameters (latitude, longitude, elevation, relative humidity, fresh snow, wind speed, precipitation and air temperature), with the climate parameters being long term monthly mean values from the period 1971-2000. The monthly $\delta^{18}O$ values of precipitation used for model calculation and validation with partial least squares regression (PLS) had been measured at 30 stations of the Austrian Network of Isotopes in Precipitation (ANIP). To compare the performance of the models Liebminger et al. (2006b) calculated the standard error of prediction for full cross validation (leave one out) and for a test set. To improve the performance of the regression equations mathematical operations like inversion, logarithm and multiplication were applied on the basic parameters. By creating separate equations for each season the performance of the regressions could be improved considerably. According to Liebminger et al. (2006b) this is due to the changing importance of the different parameters from season to season.

Darling and Talbot (2003) provided a background for understanding the hydrological cycle of the British Isles by investigating the isotopic composition of rainfall over a variety of timescales and locations. As rainfall isotopic composition changes in response to alterations in climate they also tried to find a relation between the annual NAO (North Atlantic Oscillation) Index and the $\delta^{18}O$ values of rainfall at Wallingford (England) and Valentia (Ireland) for the period 1982-1999. The correlation however was poor. Darling and Talbot (2003) believe that this is mostly due to the relatively short duration of the isotope records.

Based on water samples from 480 water supplies in Western Germany Förstel and Hützen (1984) performed multiple linear regressions on the $\delta^{18}O$ values, using elevation, distance to the coast and annual precipitation as regression parameters. As water samples that were obviously not controlled by local precipitation (e.g. filtered river water) were excluded from the regression Förstel and Hützen (1984) expected the regression equation obtained to give a good representation of the long term mean annual $\delta^{18}O$ values of precipitation.

A similar study was done by Kortelainen and Karhu (2004) on 983 groundwater samples taken in Finnland. They found out that the $\delta^{18}O$ values, interpolated by IDW (inverse distance weighting), showed a good correlation with the mean annual surface temperature. When comparing mean annual $\delta^{18}O$ and $\delta^{2}H$ values of local precipitation with the ones of local groundwater Kortelainen and Karhu (2004) could not find significant differences. Thus isotope data from local groundwater seem to be a good approximation of the mean annual isotopic composition of precipitation in this region.

2. Data

2.1. Isotope Data

The original dataset provided by Willibald Stichler, Institute of Groundwater Ecology, GSF, Neuherberg, included monthly values of $\delta^{18}O$ and $\delta^{2}H$ of precipitation as well as the corresponding monthly temperatures and amounts of precipitation from 17 German GNIP (Global Network of Isotopes in Precipitation) and 12 DWD (Deutscher Wetterdienst) stations. To improve the availability of data along the German border, monthly data from the ANIP (Austrian Network of Isotopes in Precipitation) stations Kufstein, Reutte, Salzburg and Scharnitz, which were also provided by Willibald Stichler, and from the GNIP station in Groningen, Netherlands (IAEA/WMO, 2004) were added to the dataset.

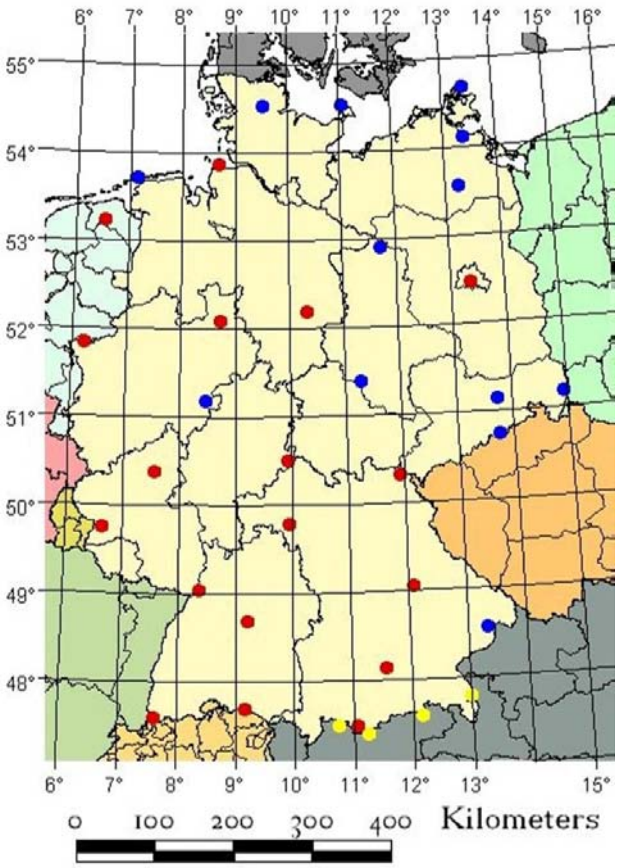


Figure 2.1.1.: Locations of the isotope stations used within this study. Data from the German GNIP (red) and DWD (blue) stations and the Austrian ANIP stations (yellow) were provided by Willibald Stichler, GSF, Neuherberg. Data from the GNIP station at Groningen, Netherlands (red) were downloaded from IAEA/WMO (2004).

Table 2.1.1.: Isotope stations included in this study.

Station	Network	Altitude [m asl]	Latitude [°]	Longitude [°]
Arkona	DWD	42	54.68	13.43
Artern	DWD	164	51.38	11.3
Dresden	DWD	227	51.13	13.75
Fehmarn	DWD	9	54.53	11.07
Fürstenzell (near Passau)	DWD	476	48.55	13.35
Görlitz	DWD	238	51.17	14.95
Kahler Asten	DWD	839	51.18	8.48
Neubrandenburg	DWD	15	53.56	13.26
(+ Greifswald	DWD	2	54.1	13.4)
Norderney	DWD	11	53.72	7.15
Schleswig	DWD	43	54.53	9.55
Seehausen	DWD	23	52.9	11.73
Zinnwald	DWD	877	50.73	13.75
Bad Salzuflen	GNIP	84	52.09	8.74
Berlin	GNIP	48	52.47	13.4
Braunschweig	GNIP	86	52.19	10.34
Cuxhaven	GNIP	12	53.87	8.7
Emmerich	GNIP	17	51.84	6.24
Garmisch-Partenkirchen	GNIP	720	47.48	11.07
Hof	GNIP	567	50.32	11.93
Karlsruhe	GNIP	145	49.03	8.37
Koblenz	GNIP	70	50.37	7.58
Konstanz	GNIP	447	47.68	9.18
Neuherberg	GNIP	495	48.13	11.58
Regensburg	GNIP	371	49.05	12.1
Stuttgart	GNIP	391	48.68	9.23
Trier	GNIP	273	49.75	6.67
Wasserkuppe-Rhön	GNIP	925	50.5	9.95
Weil am Rhein	GNIP	249	47.58	7.63
Wuerzburg	GNIP	272	49.77	9.97
Groningen	GNIP	1	53.23	6.55
Kufstein	ANIP	495	47.57	12.17
Reutte	ANIP	870	47.48	10.75
Salzburg	ANIP	435	47.78	13
Scharnitz	ANIP	960	47.38	11.25

Except for Neubrandenburg-Greifswald and Dresden-Zinnwald all stations cover the time period from January 1998 to December 2002. This time period was chosen to maximise the number of stations with isotope data available. For the Dresden station (220m asl) data were only available fom January 1998 to December 2000. Data from January 2001 to December 2002 were taken from the Zinnwald station (877m asl), which is located about 50 km south of the

Dresden station in the Erzgebirge. Due to the difference in elevation of about 660 m these two stations were not put together in this study. For Neubrandenburg (15m asl) the observations lasted from January 1998 to June 2002. For the missing six months from July 2002 to December 2002 data were taken from the Greifswald station (2m asl), about 60 km north of Neubrandenburg. As there is no big difference in topography between these two stations and climate data is very similar, the data from Greifswald were added to the one from Neubrandenburg to allow calculations of average values for Neubrandenburg.

A couple of stations showed missing temperature and precipitation values. To complete the datasets these values were taken from the website of the DWD (German Weather Service) (URL3), the climate calculator from wetteronline (URL4), and, for Weil am Rhein, from a station in Basel-Binningen (URL5). For the two Austrian stations at Reutte and Scharnitz temperature values are missing partly and completely respectively.

Monthly and annual means of $\delta^{18}O$, $\delta^{2}H$, temperature and precipitation were calculated from the monthly measurements for all stations listed in table 2.1.1. To take into account the change in the amount of monthly precipitation, the monthly and annual mean values of $\delta^{18}O$ and $\delta^{2}H$ were weighted with precipitation, according to equation 2.1.1. As the local temperature only influences the isotope ratio in precipitation during rainfall the mean temperature values were amount-weighted, too:

$$\overline{V}_w = \frac{\sum V_i * P_i}{\sum P_i} \tag{2.1.1}$$

where $\overline{V}_w$ is the amount-weighted mean variable, V_i is the monthly value of the variable, P_i is the monthly amount of precipitation and i the index for the number of values included into the calculation.

2.2. Spatial data of regression parameters

In order to produce maps of $\delta^{18}O$ and $\delta^{2}H$ of precipitation in Germany with the help of regression equations, spatial distributions of the regression parameters are needed:

Elevation: The digital elevation model (DEM) of Germany was downloaded freely from the U.S. Geological Survey's EROS Data Center (URL6). The spatial resolution of the global DEM GTOPO30 is 30 arc seconds (approximately 1 kilometer). It was developed to meet the needs of the geospatial data user community for regional and continental scale topographic data. In figure 2.2.1 you can see the northern lowland as well as the low mountain range and the northern part of the Alps (in the south-east).

Temperature and precipitation:

Temperature and precipitation grids for Germany were created according to the procedure given by Müller-Westermeier (1995). Station data (1998-2002) of all stations listed in table 2.1.1, except for Reutte and Scharnitz, were reduced on 0 m asl by fixed gradients. As proposed by Müller-Westermeier

(1995) a gradient of -0.6°C/100m was taken for temperature. The gradient for precipitation was calculated by regression of precipitation on elevation for the station data described above, giving gradients of 6.3mm/100m for monthly means and 75mm/100m for annual means. The reduced station data were then interpolated by inverse distance weighting (IDW) (with power 2) on a grid with a spatial resolution of 30 arc seconds and counted back to the elevation given by the DEM afterwards. The maps obtained for the annual mean temperature and the annual amount of precipitation are shown in the figures 2.2.2 and 2.2.3. Maps of monthly mean temperatures are presented in figures A.0.1 to A.0.3 in the appendix.

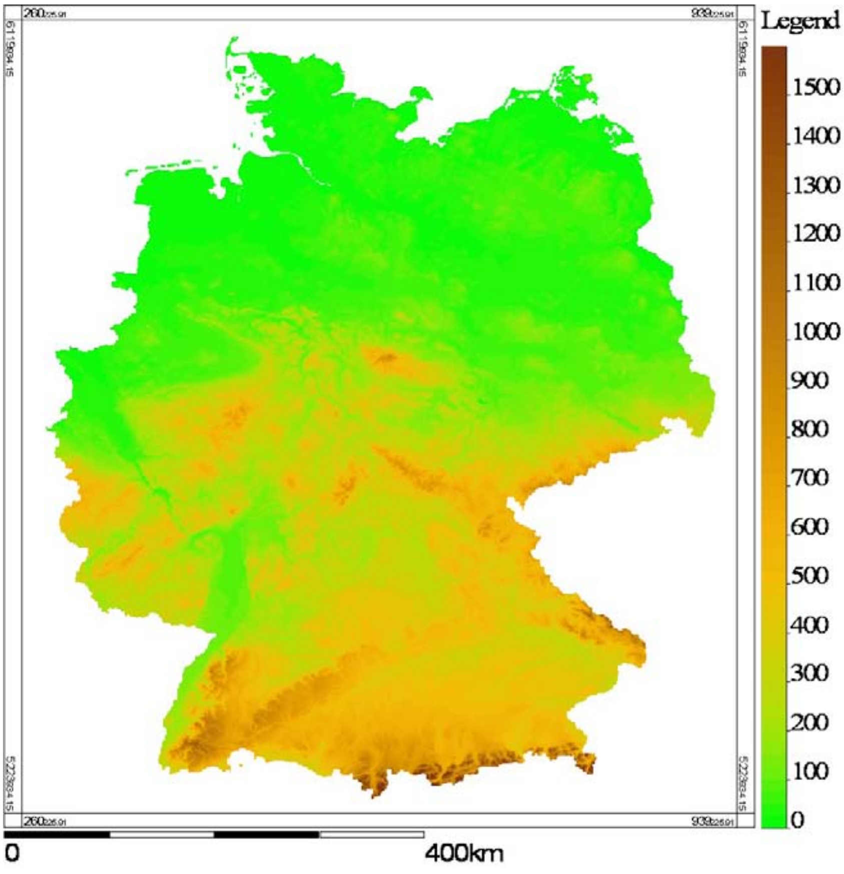


Figure 2.2.1.: Map of the digital elevation model (DEM) of Germany with a spatial resolution of 30 arc seconds. The legend shows the elevation in [m asl]. The DEM was downloaded from the U.S. Geological Survey's EROS Data Center (URL6).

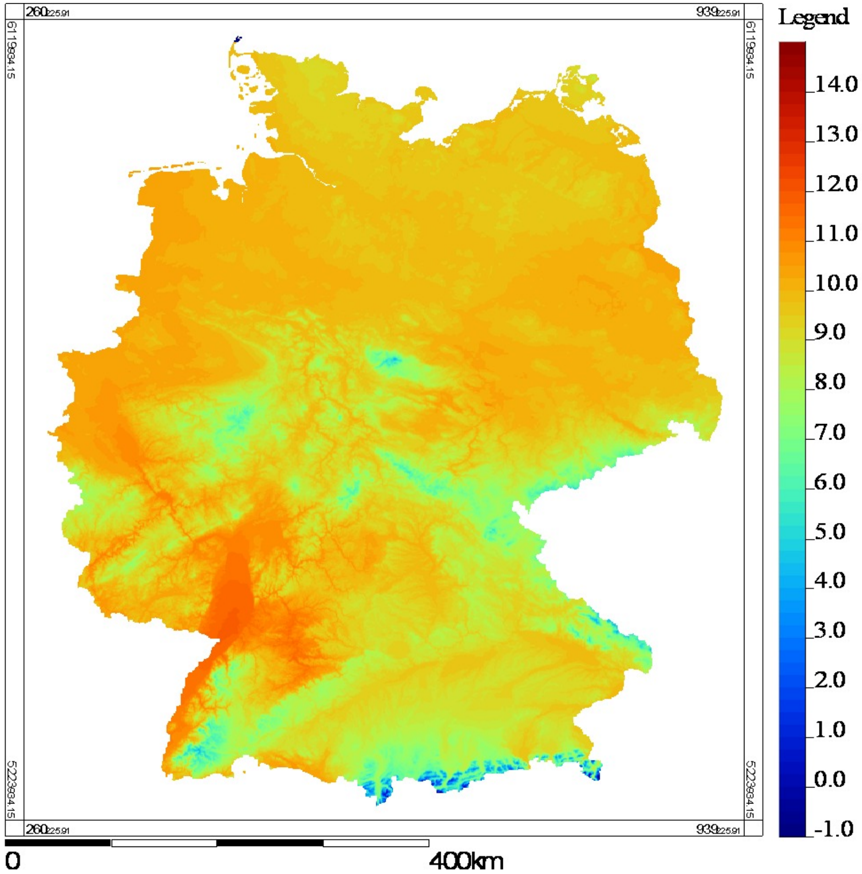


Figure 2.2.2.: Map of the annual mean temperature for Germany, created by inverse distance weighting (IDW) on the temperature data from the stations listed in table 2.1.1. The legend shows the temperature values in [°C].

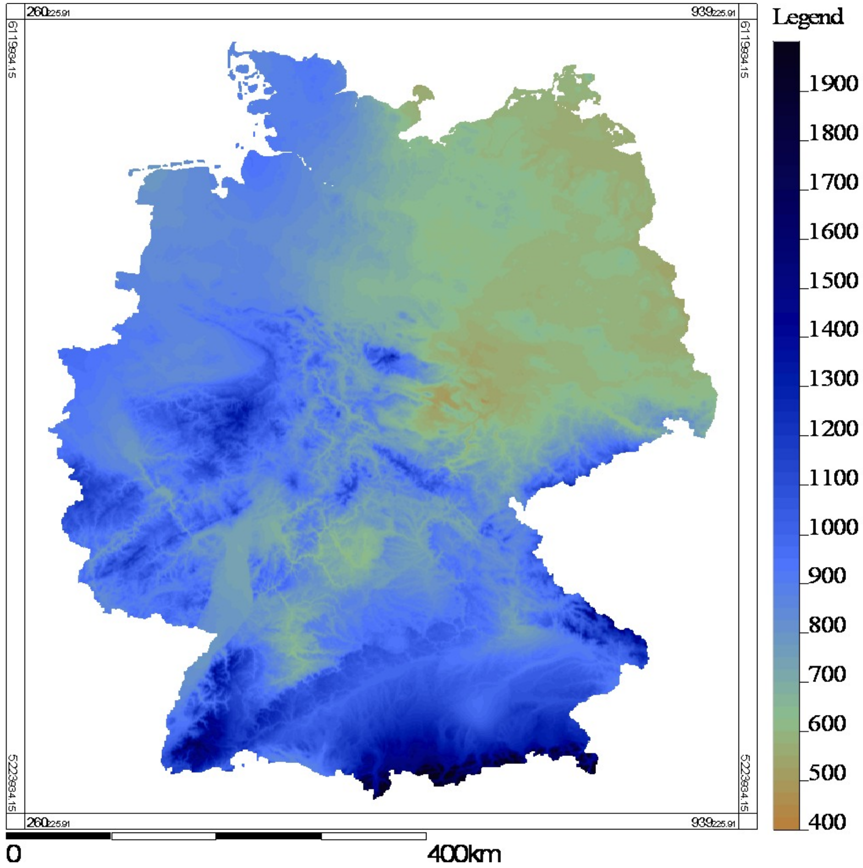


Figure 2.2.3.: Map of the annual amount of precipitation for Germany, created by inverse distance weighting (IDW) on the precipitation data from the stations listed in table 2.1.1. The legend shows the amount of precipitation in [mm].

3. Methodology

3.1. Isotope fractionation in the hydrological cycle

3.1.1. The delta notation

Isotopic concentrations of oxygen and hydrogen are generally expressed in [‰ VSMOW] using the delta notation:

$$\delta^{18}O = [\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{reference}} - 1] * 10^3 \tag{3.1.1}$$

$$\delta^{2}H = [\frac{(^{2}H/^{1}H)_{sample}}{(^{2}H/^{1}H)_{reference}} - 1] * 10^3 \tag{3.1.2}$$

with the VSMOW (Vienna Standard Mean Ocean Water) used as the reference material. If the concentrations of ^{18}O and ^{2}H in the sample, with respect to ^{16}O and ^{1}H, are lower than in the VSMOW the δ values become negative, otherwise they are positive (Clark and Fritz (1997), p. 6f).

3.1.2. Isotope fractionation

The varying isotopic composition of natural waters is mainly caused by the fact that the volatility of the light molecule $^{1}H_2^{16}O$ is higher than that of the heavier ones. The difference in volatility leads to fractionation in condensation and evaporation processes, which turns the isotopic composition of water into an interesting hydrological tool (Dansgaard, 1964). Isotopic fractionation is expressed by the fractionation factor α:

$$\alpha = \frac{R_{reactant}}{R_{porduct}} \tag{3.1.3}$$

with R representing the ratio of the abundance of the rare isotope (e.g. ^{18}O or ^{2}H) to the abundance of the abundant isotope (e.g. ^{16}O or ^{1}H). The fractionation factors generally decrease with increasing temperature and depend on the difference in the rates of reaction for different molecular species. One can distinguish between fractionation by physicochemical reactions under equilibrium or non-equilibrium (kinetic) conditions and fractionation by molecular diffusion:

Physicochemical fractionation is based on the difference in the strength of bonds formed by the light and the heavier isotopes (different volatility), which leads to different reaction rates.

Under equilibrium conditions the forward and backward reaction rates are the same. As the stronger bonds are broken less frequently than the weaker ones the heavy isotopes (forming the stronger bonds) usually are enriched in the more condensed phase.

Under kinetic (non-equilibrium) conditions the forward reaction rate exceeds the backward one. Depending on the reaction pathways the fractionation process can be enhanced or diminished. Kinetic conditions can e.g. be caused by sudden changes in temperature or the addition or removal of a reactant.

Diffusive fractionation is based on the different diffusive velocities between different isotopes. By the nature of diffusion, diffusive fractionation is a kinetic process (Clark and Fritz (1997), pp. 21-30).

3.1.3. Change of the isotopic composition through the hydrological cycle

Craig (1961) discovered that the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation correlate on a global scale and are fairly well aligned along the so called Global Meteoric Water Line (GMWL) (in [‰ VSMOW]):

$$\delta^2 H = 8 * \delta^{18}O + 10 \tag{3.1.4}$$

Variations in $\delta^{18}O$ and $\delta^{2}H$ in the global water cycle are mainly influenced by the evaporation of surface ocean water and the progressive rainig out of the vapour masses moving towards regions with lower temperatures.

During evaporation of seawater equilibrium as well as kinetic processes take place. Equilibrium fractionation occurs between the seawater and the thin boundary layer with 100% water saturation. Between the boundary layer and the mixed atmosphere, which is under-saturated with respect to water vapour, the isotpic composition of water molecules is changed by kinetic diffusive fractionation. Both, the equilibrium and the kinetic fractionation, lead to a depletion of the heavy isotopes in the vapour compared to the water it originates from (Clark and Fritz (1997), pp. 39-43).

When the vapour moves towards regions with lower temperatures water saturation is reached and the rainout process produces an isotopically enriched condensate (rain). Thus the remaining vapour becomes isotopically depleted as the rainout process proceeds. Subsequent rains from the same vapour mass will therfore be depleted with respect to earlier ones. This temperature-isotope evolution during rainout can be modeled with the help of the Rayleigh distillation equation:

$$R = R_0 * f^{\alpha - 1} \tag{3.1.5}$$

with R_0 being the vapour's initial isotope ratio ($^{18}O/^{16}O$ or $^{2}H/^{1}H$) and R representing the ratio when the fraction f of the initial vapour reservoir is left. α is the fractionation factor for equilibrium water vapour exchange at the given temperature (Clark and Fritz (1997), pp. 46-49).

Dansgaard (1964) introduced the deuterium excess or d-value given by:

$$d = \delta^2 H - 8 * \delta^{18}O \tag{3.1.6}$$

This value is a useful index to detect variations in the relation between $\delta^{18}O$ and δ^2H of precipitation, which can be caused by local variations in humidity, wind speed and sea surface temperature during evaporation (Clark and Fritz (1997), p. 45).

The isotope fractionation in the hydrological cycle can also be described by a number of isotope effects, as it was done by Dansgaard (1964) for the first time:

Continental effect:

The continental effect describes the depletion of the $\delta^{18}O$ and δ^2H values of precipitation with increasing distance from the coast due to the raining out process mentioned above (Rayleigh effect). The observed gradients vary broadly from area to area and season to season as they depend on the topography as well as on the climate regime (movement of air masses) (Gat et al., 2000). In winter the continental effect over Europe is much more pronounced than in summer. According to Rozanski et al. (1993) this has been explained by the increased return of water to the atmosphere through transpiration during the summer, leading to a reduced effective degree of rainout of air masses moving eastwards.

Altitude effect:

In general, $\delta^{18}O$ and δ^2H values of precipitation decrease with increasing altitude, as the drop in temperature leads to condensation (Rayleigh effect). But the isotopic depletion of rain with increasing elevation is also affected by the increase of the fractionation factor between vapour and water with dropping temperature (Ingraham, 1998). Due to the decrease in pressure with increasing elevation a larger drop in temperature is needed to reach the saturated water vapour pressure compared to isobaric condensation (see latitude effect). Besides the basic Rayleigh effect other processes can change the isotopic composition with altitude: Evaporative enrichment of ^{18}O and ^2H in raindrops during their fall beneath the cloud base ("pseudo-altitude effect") (Moser and Stichler, 1971) as well as the contribution of air masses with different source characteristics to precipitation at different altitudes (Gat et al., 2000).

Latitude effect:

The latitude effect is the observation that the $\delta^{18}O$ and δ^2H values of precipitation decrease with increasing latitude due to the evolution of an airmass along negative temperature gradients, leading to Rayleigh fractionation (see altitude effect) (Ingraham, 1998).

Amount effect:

Water collected during smaller rainstorms is generally more enriched in the heavy isotopes than water collected during larger rainstorms. This is due to the different degrees of evaporation of the raindrops falling to the ground. During light rains or the beginning of storms the atmosphere is undersaturated with respect to vapour, which leads to evaporation of the raindrops. During large rainstorms the saturation of the atmosphere beneath the cloud base is higher. Consequently the evaporative enrichment of the raindrops is reduced

(INGRAHAM, 1998).
Seasonal effect:
The seasonal effect describes the change in the content of the stable isotopes in precipitation due to the seasonal temperature pattern. The lower temperature dependence of the seasonal effect compared to the latitude effect can be explained by the seasonal change of the temperature in the source region of the vapour, the evaporative enrichment of falling raindrops during warm and dry months and the different isotopic composition of snow or hail (GAT ET AL., 2000).
Small-scale temporal variations:
Even during short rainstorms the isotopic composition of the rain can vary considerably. AMBACH ET AL. (1975) attributed this to the Rayleigh process, the contribution of different storm cells and the influence of evaporation.

So the isotopic content of precipitation is determined by a complex interrelation between geographic and meteorologic factors (MOSER and STICHLER, 1971).

3.2. Regression methods

As atmospheric circulation models are too complex to model local concentrations of ^{18}O and ^{2}H in precipitation within this work and the Rayleigh models hardly perform well on a regional scale (LIEBMINGER ET AL., 2006b) regression methods were chosen to predict the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany. According to the different effects on isotope fractionation described in section 3.1.3 and the literature on regression methods cited in section 1.3.2 it is to be expected that multiple explanatory variables are required to set up regression equations for the spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation. That is why muliple linear regression (MLR) methods are used in this study.

A general MLR equation is given by:

$$y = \beta_0 + \beta_1 * x_1 + \beta_2 * x_2 + ... + \beta_k * x_k + \epsilon \tag{3.2.1}$$

where y is the response variable (e.g. $\delta^{18}O$), β_0 is the intercept, β_1 is the slope coefficient for the first explanatory variable, β_2 is the slope coefficient for the second explanatory variable, β_k is the slope coefficient for the kth explanatory variable, and ϵ is the remaining unexplained noise in the data (the error) (HELSEL and HIRSCH (2002), p. 296).

The adjusted R^2 was chosen as the overall measure of quality of the regression equations in this study. This is an R^2 value that is corrected for the number of explanatory variables in the regression equation. The R^2 value is defined as:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \epsilon_i^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2} \tag{3.2.2}$$

where ϵ_i is the difference between the predicted and the observed values, y_i is the ith observed value out of the n observations, and $\overline{y}$ is the average of the observed values. The R^2 is a good measure of qualtity for simple linear regressions. But for multiple linear regressions (MLRs) the problem with the R^2 is that it does increase whenever an additional variable is added to the regression, even if this variable has no explanatory power. As the adjusted R^2 (R^2_a) accounts for the loss in degrees of freedom by including the ratio of the total degrees of freedom (n-1) to the error degrees of freedom (n-p) as a weighting factor, it can be used as an overall measure of quality for MLR. It is defined as:

$$R_a^2 = 1 - \frac{(n-1)}{(n-p)} \frac{\sum_{i=1}^{n} \epsilon_i^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2} \tag{3.2.3}$$

where n is the number of observations and p the number of explanatory variables (regression parameters) plus 1 (Helsel and Hirsch (2002), p. 313f).

To build a good regression equation Helsel and Hirsch (2002) (p. 315f) suggest, among other things, to take a look at the (adjusted) R^2 and to plot the residuals versus the predicted values to check for heteroscedasticity. If the variance of the residuals is not constant over the entire range of the predicted values (heteroscedastic), a transformation of the variables might improve the regression equation.

To test the performance of a regression equation for locations that did not contribute to the setup of the regression equation itself one can calculate the standard error of prediction for full cross validation (each station is left out once for the calculation of the regression equation) (SEP_{cv}) or for a test data set (SEP_{Test}):

$$SEP_{cv}(SEP_{Test}) = \sqrt{\frac{\sum (Y_i - \widehat{Y}_i)^2}{n-1}} \tag{3.2.4}$$

where Y_i is the observed value at the station that was not used for the setup of the regression equation, $\widehat{Y}_i$ the predicted one, and n the number of samples (Liebminger et al., 2006b).

For the interpretation of the regression coefficients it is important to know that multicollinearity of the variables can lead to unrealistic signs of the coefficients (e.g. increase of $\delta^{18}O$ with altitude) and to unstable slope coefficients (small changes of a few data values can lead to significant changes of the coefficients) (Helsel and Hirsch (2002), p. 305).

The regressions were performed with *R*, a free software environment for statistical computing and graphics (URL7). The version used in this work is *R 2.5.0*. *R* was initially written by Robert Gentleman and Ross Ihaka of the Statistics Department of the University of Auckland. But many other programmers have contributed to the current version.

Maps were produced with the help of SAGA GIS (System for Automated Geoscientific Analyses Geographical Information System), a free GIS with a user-friendly graphical user interface (GUI) (URL8). Vector and especially raster data are supported. SAGA GIS has been developed by Olaf Conrad and some other programmers from the Goettingen University (Olaya, 2004).

3.3. Conclusions

The spatio-temporal distribution of concentrations of ^{18}O and ^{2}H in precipitation is mainly controlled by the original isotopic composition of the vapour mass and the fraction of vapour lost due to rainout. Thus, assuming that the isotopic composition of the original vapour masses is fairly constant on a monthly basis, it should be possible to predict the concentrations of ^{18}O and ^{2}H in precipitation with the help of parameters affecting rainout. As oversaturation of the vapour is obtained by a decrease in temperature, parameters describing spatial changes in temperature (latitude, longitude, altitude) and the local temperature itself, indicating seasonal changes, are used within this study. To consider changes of the isotopic composition of precipiation due to evaporation during rainfall as well as the depletion of the heavy isotopes in the vapour mass with proceeding rainout the amount of precipitation was added to the set of parameters.

Multiple linear regressions (MLRs) based on the parameters mentioned above turned out to be the most suitable way for predicting monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany within this study. The adjusted R^2 was chosen as the overall measure of quality as, in contrast to the simple R^2, it is corrected for the number of explanatory variables in the regression equations. To test the performance of the regression equations the standard error of prediction can be calculated for full cross validation or for a test data set.

As the chosen parameters are subject to multicollinearity an interpretation of the regression coefficients in terms of isotope effects is difficult.

4. Results

4.1. General survey of the dataset

4.1.1. Scatterplot

In order to see how monthly $\delta^{18}O$ and δ^2H values of precipitation of all German stations are correlated δ^2H values were plotted against $\delta^{18}O$ (figure 4.1.1). By fitting a line with a fixed slope of 8 (slope of GMWL, see equation 3.1.4) through the dataset the axis intercept gets the meaning of the average deuterium excess (see equation 3.1.6), which, for Germany, seems to be close to 8 ‰.

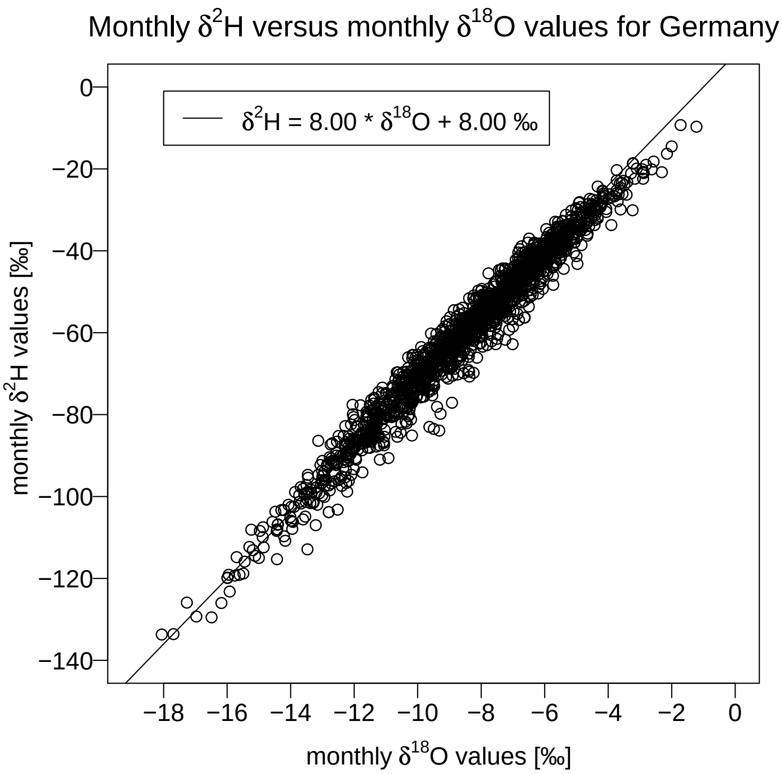


Figure 4.1.1.: Scatterplot of monthly $\delta^{18}O$ versus δ^2H values of precipitation of all German stations. The line through the data points is obtained by fitting the axis intercept for a fixed slope of 8.00. This turns the axis intercept into a measure for the deuterium excess.

4.1.2. Boxplots

To get a summary of the spatial and temporal distribution of the whole dataset boxplots of different groups of the data were created with the help of the statistic software *R* (URL7). A boxplot in *R* consists of a thick line representing the median and a surrounding box that indicates the space between the first and the third quartile. The lines ("whiskers") extend to the largest/lowest value within a distance of 1.5 times the box size form the nearest end of the box. Values outside of this range are indicated by extra points.

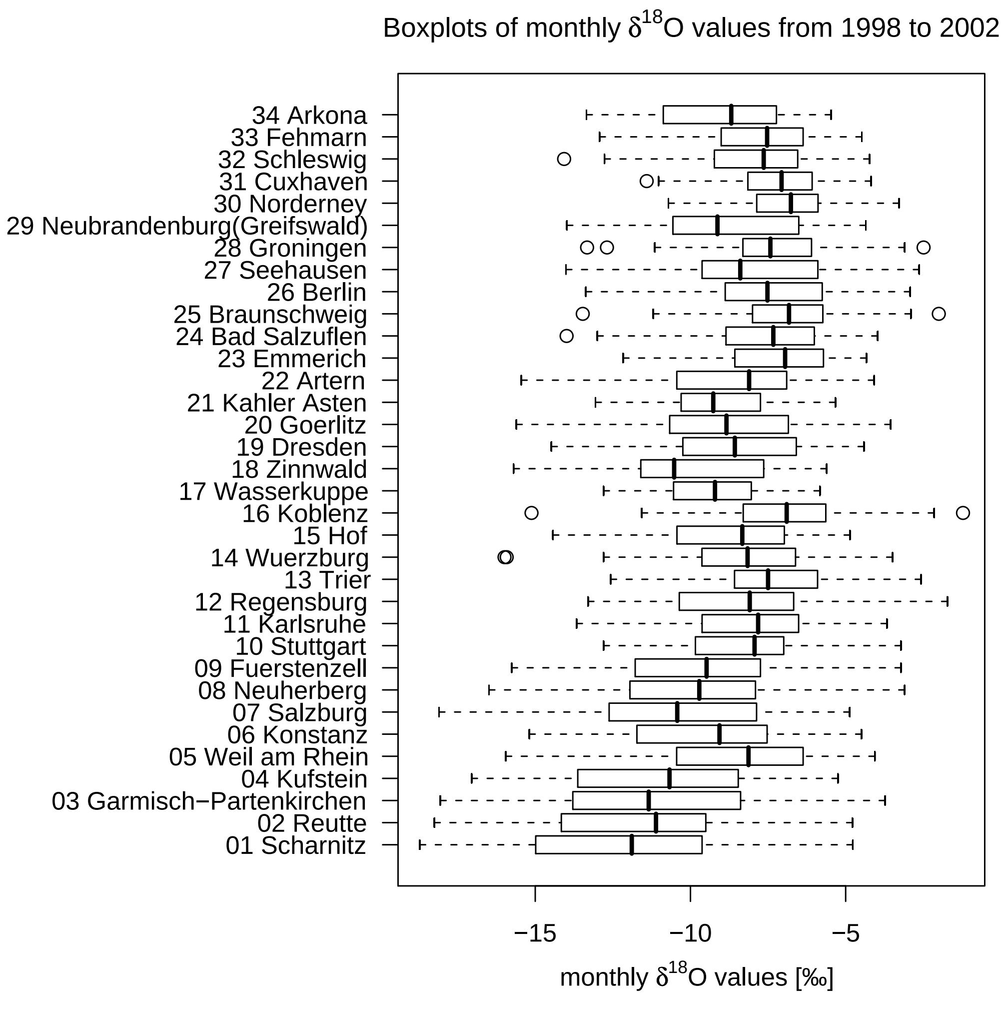


Figure 4.1.2.: Boxplots of monthly $\delta^{18}O$ values of precipitation from January 1998 to December 2002 of all stations listed in table 2.1.1, except for Dresden (January 1998 - December 2000) and Zinnwald (January 2001 - December 2002). Data for Neubrandenburg are only available from January 1998 to June 2002 and is completed by data from Greifswald from July 2002 to December 2002. Stations are sorted by latitude form north (top) to south (bottom).

Figures 4.1.2 and 4.1.3 show boxplots of monthly $\delta^{18}O$ and δ^2H values of precipitation from January 1998 to December 2002 for all stations listed in table 2.1.1, except for Dresden (January 1998 - December 2000) and Zinnwald

(January 2001 - December 2002). As the stations are sorted by latitude form north (top) to south (bottom) it can be seen that both, $\delta^{18}O$ and δ^2H values, tend to decrease from north to south while the seasonal variation seems to increase in the same direction.

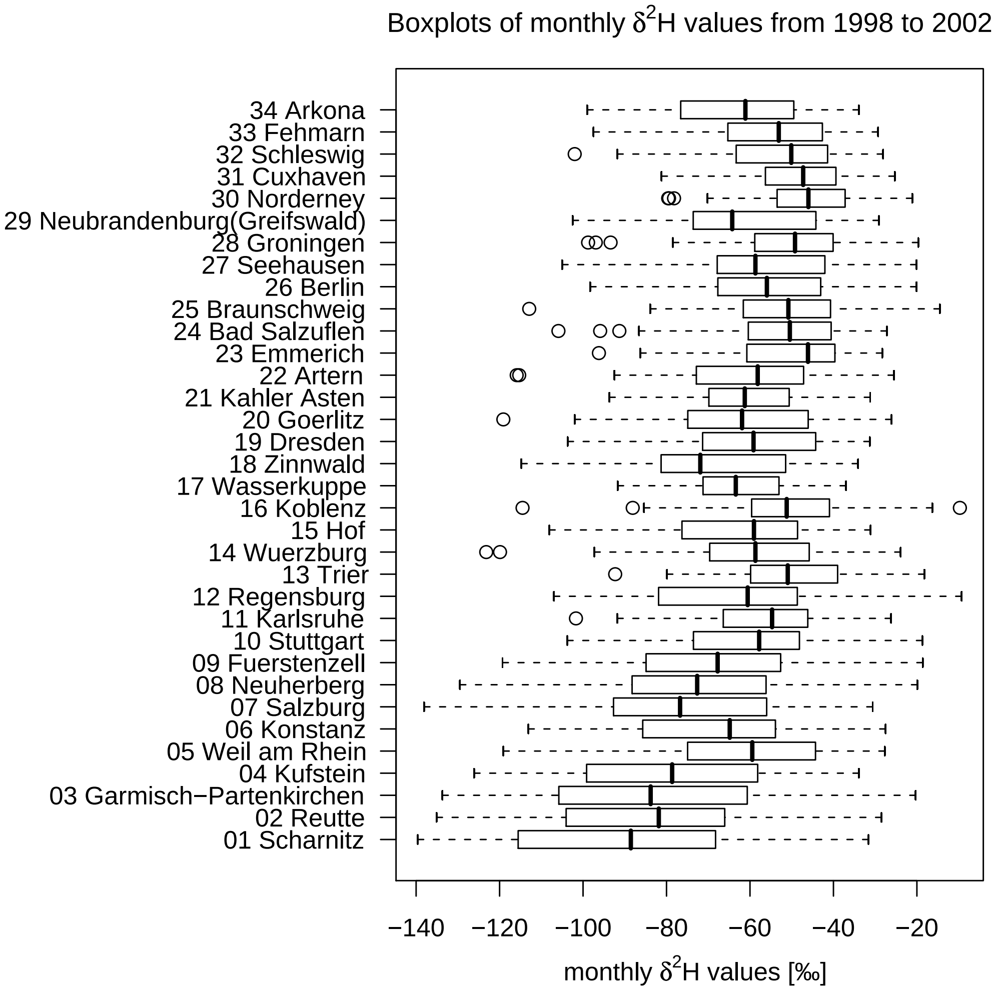


Figure 4.1.3.: Boxplots of monthly δ^2H values of precipitation from January 1998 to December 2002 of all stations listed in table 2.1.1, except for Dresden (January 1998 - December 2000) and Zinnwald (January 2001 - December 2002). Data for Neubrandenburg are only available from January 1998 to June 2002 and is completed by data from Greifswald from July 2002 to December 2002. Stations are sorted by latitude form north (top) to south (bottom).

As done for the monthly $\delta^{18}O$ and δ^2H values, boxplots of monthly deuterium excess (d) values (equation 3.1.6) for each station were sorted by latitude (figure 4.1.4).

Figures 4.1.5 and 4.1.6 show two different types of seasonal variations of monthly $\delta^{18}O$ and δ^2H values of precipitation and the corresponding monthly temperature values. At Norderney, a small island near the coast of the North Sea, the seasonal variation of monthly $\delta^{18}O$ and δ^2H values is very low while temperature does show some seasonal variation. At Garmisch-Partenkirchen, situated at 720 m asl in the Alps far in the south of Germany, the monthly isotope ratios of precipitation show a clear seasonality, close to the one of the monthly temperature values.

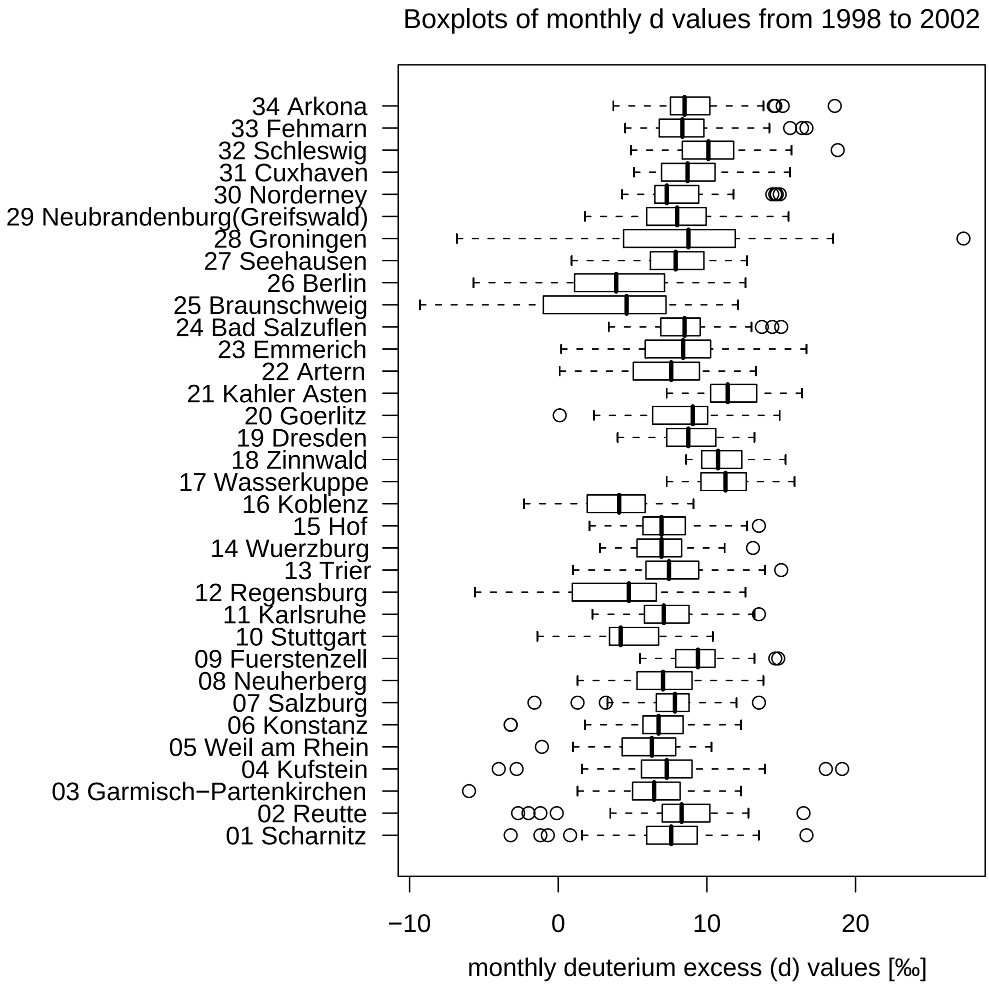


Figure 4.1.4.: Boxplots of monthly deuterium excess (d) values of precipitation from January 1998 to December 2002 of all stations listed in table 2.1.1, except for Dresden (January 1998 - December 2000) and Zinnwald (January 2001 - December 2002). Data for Neubrandenburg are only available from January 1998 to June 2002 and is completed by data from Greifswald from July 2002 to December 2002. Stations are sorted by latitude form north (top) to south (bottom).

4.1.2.1. Interpretation of the boxplots

The $\delta^{18}O$ and $\delta^{2}H$ values of precipitation seem to decrease from the north of Germany towards the south (figures 4.1.2 and 4.1.3). This is most likely due to the increase in continentality from the north-west of Germany (North Sea) towards the south-east (continental effect) and a strong increase in altitude in the south of Germany (Alps) (altitude effect). So, for Germany, the latitude effect, describing the decrease of $\delta^{18}O$ and $\delta^{2}H$ values with increasing latitude

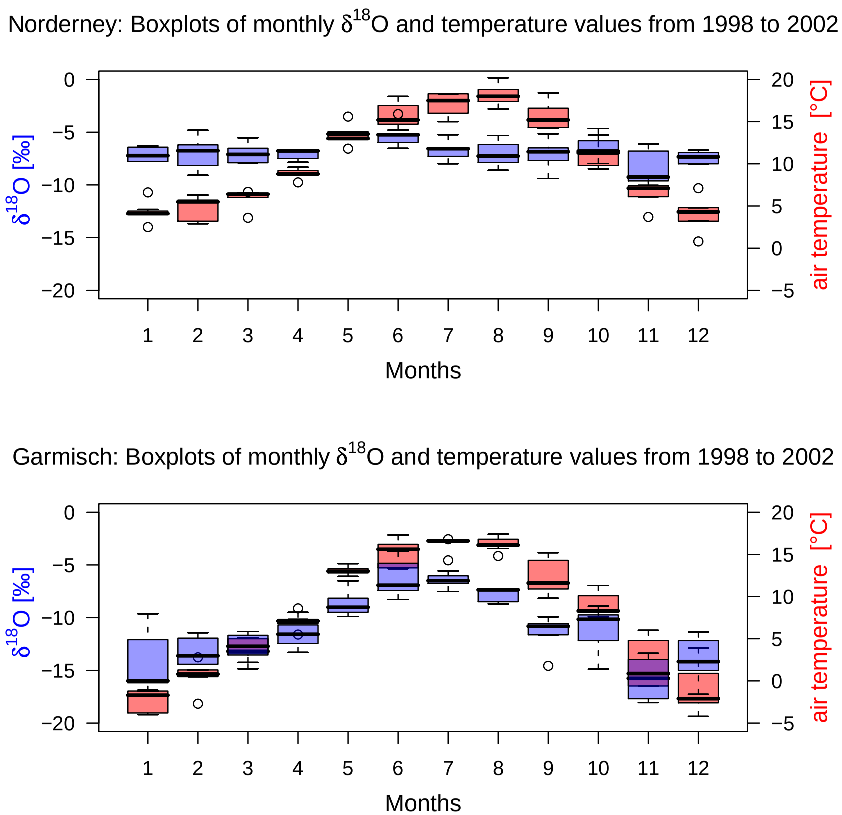


Figure 4.1.5.: Boxplots of monthly $\delta^{18}O$ values of precipitation (blue) and temperatures (red) observed at Norderney and Garmisch-Partenkirchen between 1998 and 2002, and sorted by months from January (1) to December (12).

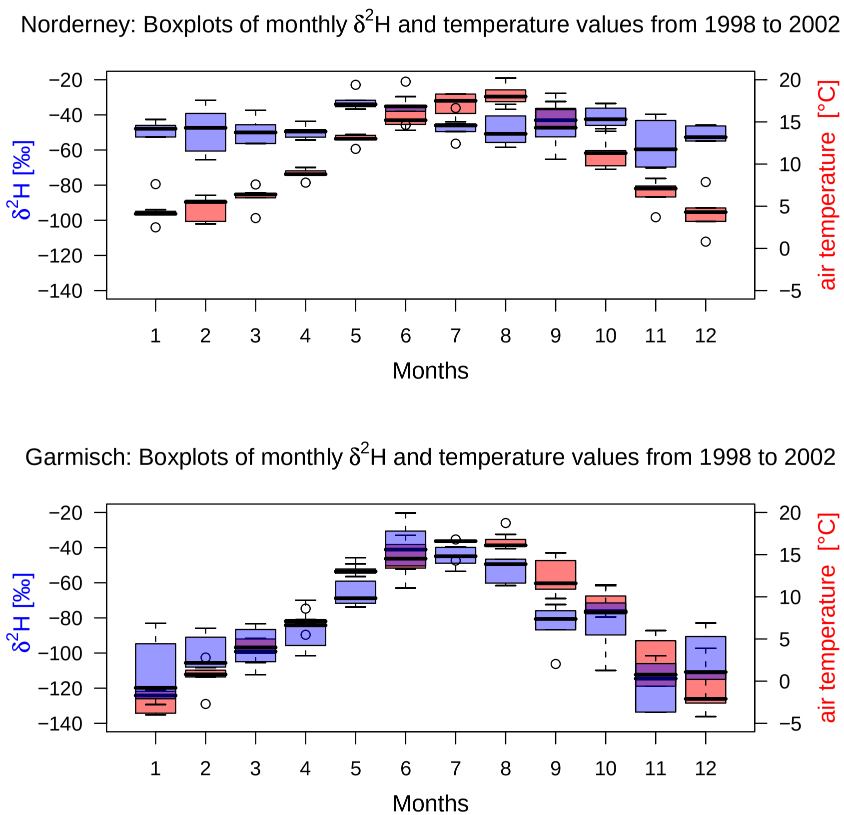


Figure 4.1.6.: Boxplots of monthly $\delta^{2}H$ values of precipitation (blue) and temperatures (red) observed at Norderney and Garmisch-Partenkirchen between 1998 and 2002, and sorted by months from January (1) to December (12).

due to a decrease in temperature, is inverted by an increase in continentality and altitude towards south. The seasonal variations seem to increase with decreasing latitude which can also be explained with the increase in continentality leading to higher variations in temperature through the year.

As the deuterium excess is influenced by primary evaporation in the source area of the vapour and secondary evaporation during rainout or sampling, variations cannot be explained by the parameters availabe for this study. It can however be seen that the stations at the low mountain range (Kahler Asten, Zinnwald, Wasserkuppe), where air masses coming from the sea are forced to rainout, show high deuterium excess values (figure 4.1.4).

The differences in seasonal variations of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation at Norderney and at Garmisch-Partenkirchen, shown in figures 4.1.5 and 4.1.6, can again be explained by the strong difference in continentality between the maritime station at Norderney and the highly continental station at Garmisch-Partenkirchen, where the strong change of temperature through the year seems to control the isotope ratios of precipitation (seasonal effect).

4.2. Multiple linear regression methods

As discussed in section 3.2 multiple linear regression (MLR) equations seem to be the most suitable interpolation methods to predict local values of $\delta^{18}O$ and $\delta^{2}H$ of precipitation in Germany.

The regression parameters used to predict precipitation weighted monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values ($\overline{\delta^{18}O}_{month/year}$, $\overline{\delta^{2}H}_{month/year}$) within this study are monthly and annual means of temperature ($\overline{T}_{month/year}$ [°C], weighted with the amount of precipitation, see equation 2.1.1) and precipitation ($\overline{P}_{month/year}$ [mm]), as well as latitude (La [°]), longitude (Lo [°]) and altitude (A [m asl]) (see table 2.1.1). As all these parameters stand for known isotope effects we decided not to use mathematical operations like inversion, logarithm and multiplication to improve regression results. The only exception to this rule is the use of the squared latitude in addition to the simple latitude, as it was successfully done by Bowen and Wilkinson (2002).

Multiple linear regressions with different combinations and numbers of the parameters mentioned above were performed on monthly and annual means. As the influence of the parameters changes through the year different regression equations were set up for the different seasons, as it was done by Liebminger et al. (2006b). To compare the performance of the multiple linear regression (MLR) equations the adjusted R^2 (equation 3.2.3) was chosen as the overall measure of quality. The equations with the highest adjusted R^2 were taken as the most suitable ones. Residuals between the observed values and the ones predicted with the most suitable MLR equations were plotted against the predicted values to check for heteroscedasticity (figures A.0.6 and A.0.7). In all cases the variance of the residuals seems to be constant over the entire range of the predicted values (homoscedastic), which means that the parameters do not need to be transformed.

To get an estimate of the uncertainty of the values predicted by the best regression equations the standard error of prediction (SEP), showing the average deviation between observed and predicted δ values, was calculated for full cross validation (SEP_{cv}), including all stations available (equation 3.2.4). In order to investigate how the quality of the MLR equations changes when only data of the GNIP stations are used for setup, regressions were based on the German GNIP stations and tested for the observations at the DWD stations (SEP_{DWD}) (equation 3.2.4).

No regressions were performed on deuterium excess data, as the parameters available were not sufficient to obtain good results. According to Liebminger et al. (2006a), who analysed isotope data form the Austrian Network of Isotopes in Precipitation (ANIP), relative humidity and wind speed at the sampling site are important parameters to predict the deuterium excess, as these parameters influence subcloud evaporation.

As the regressions are only based on data from German and near border stations the quality of prediction will decrease when using the MLRs for locations outside of this area. Thus it is important to keep in mind that the MLR equations set up within this study to predict monthly and annual mean $\delta^{18}O$ and δ^2H values of precipitation are to be used for places within Germany alone.

The unit of all MLR results is [‰ VSMOW].

4.2.1. All Months MLR equations

Based on monthly mean values of all months and all stations listed in table 2.1.1, except for the two Austrian stations at Reutte and Scharnitz (missing temperature values!), that means 32 stations in total, multiple linear regressions (MLRs) with different combinations of parameters were performed. The 4 MLRs with the highest adjusted R^2 for the prediction of $\delta^{18}O$ and δ^2H values respectively are listed in table A.0.1 in the appendix.

Table 4.2.1.: R^2 values of all pairs of amount-weighted monthly mean $\delta^{18}O$ and δ^2H values of precipitation of all months with each of the regression parameters (La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; $\overline{T}_{month}$: amount-weighted monthly mean temperature; $\overline{P}_{month}$: mean monthly amount of precipitation). Data are taken from all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria).

all months	La^2	La	Lo	A	$\overline{T}_{month}$	$\overline{P}_{month}$
$\overline{\delta^{18}O}_{month}$	0.0828	0.0847	0.0824	0.1362	0.5578	0.0006
$\overline{\delta^{2}H}_{month}$	0.1114	0.1137	0.0819	0.1157	0.5553	0.0004

In order to investigate the correlation between monthly mean $\delta^{18}O$ or δ^2H values of precipitation of all months and the different regression parameters the R^2 (equation 3.2.2) was calculated for all pairs (table 4.2.1). When performing a regression on all months monthly mean temperature clearly shows the highest linear correlation with the isotope ratios. However, as the parameters are multicollinear, the MLR equation with the highest adjusted R^2 does not necessarily include the variables showing the highest linear correlations with the isotope ratios.

$\delta^{18}O$ values:

Looking at the MLR equations with different sets of parameters in table A.0.1 and the R^2 values in table 4.2.1 one can see that, when predicting monthly $\delta^{18}O$ values with one MLR equation for all months, latitude squared, latitude, longitude and temperature are the most important regression parameters. If altitude is added to these 4 parameters the adjusted R^2 does only show a slight improvement. The best adjusted R^2 is obtained by including precipitation to the 4 basic parameters. If both parameters, altitude and precipitation, are added to the 4 basic ones the adjusted R^2 becomes lower than for the MLR without altitude. This is due to the reduction in the error degrees of freedom. The MLR equation with the highest adjusted R^2 is:

$$\overline{\delta^{18}O}_{month} = -0.08229 * La^2 + 8.627 * La - 0.2034 * Lo + 0.2685 * \overline{T}_{month} - 0.006326 * \overline{P}_{month} - 234.10 \quad (4.2.1)$$

($\overline{\delta^{18}O}_{month}$: amount-weighted monthly mean $\delta^{18}O$ [‰]; La^2: latitude squared [°^{2}]; La: latitude [°]; Lo: longitude [°]; A: altitude [m asl]; $\overline{T}_{month}$: amount-weighted monthly mean temperature [°C]; $\overline{P}_{month}$: mean monthly amount of precipitation [mm])
For this set of parameters the standard error of prediction for full cross validation (SEP_{cv}), showing the average deviation between the observed and the predicted monthly mean values of $\delta^{18}O$, is 1.19 ‰ (table 4.2.5). Using only the 17 German GNIP stations to set up the regression with these parameters the standard error of prediction for the 12 DWD stations (SEP_{DWD}) is 1.35 ‰ (table 4.2.8).

By averaging the predicted monthly $\delta^{18}O$ values of all months an annual mean value can be calculated, with a SEP_{cv} of 0.51 ‰ (table 4.2.5) and a SEP_{DWD} of 0.59 ‰ (table 4.2.8).

δ^2H values:

For the MLR equations predicting the monthly mean δ^2H values for all months the parameters latitude squared, latitude, longitude and temperature are the most important ones, too. But in contrast to the regression equations for $\delta^{18}O$ values the adjusted R^2 decreases if altitude or precipitation are included into the regression. The best MLR equation found is:

$$\overline{\delta^2H}_{month} = -0.68020 * La^2 + 71.7846 * La - 1.5049 * Lo + 2.0246 * \overline{T}_{month} - 1953.38 \quad (4.2.2)$$

The corresponding SEP_{cv} is 8.86 ‰ (table 4.2.6), the SEP_{DWD} is 9.60 ‰ (table 4.2.9).

The SEP_{cv} for the annual mean $\delta^2 H$ value derived from the monthly means is 3.51 ‰ (table 4.2.6), the SEP_{DWD} is 3.28 ‰ (table 4.2.9).

4.2.2. Seasonal MLR equations

To take into account the seasonal variation in the correlation of the different regression parameters with the $\delta^{18}O$ and $\delta^2 H$ values of precipitation MLR equations were also based on monthly mean $\delta^{18}O$ and $\delta^2 H$ values within one single season, as it was done by Liebminger et al. (2006b). December, January and February are classified as winter, March, April and May as spring, June, July and August as summer and September, October and November as autumn months. Regressions were performed on monthly mean values of all stations listed in table 2.1.1, except for Reutte and Scharnitz. The MLRs with the 4 highest adjusted R^2 values for $\delta^{18}O$ and $\delta^2 H$ respectively are listed in tables A.0.1 and A.0.2 in the appendix. The MLRs with the highest adjusted R^2 were used to create the maps of the spatial distribution of monthly mean $\delta^{18}O$ and $\delta^2 H$ values of precipitation in Germany that are shown in figures 4.2.5 - 4.2.10.

Table 4.2.2.: R^2 values of all pairs of amount-weighted monthly mean $\delta^{18}O$ or $\delta^2 H$ values of precipitation, sorted by seasons, with each of the regression parameters (La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; $\overline{T}_{month}$: amount-weighted monthly mean temperature; $\overline{P}_{month}$: mean monthly amount of precipitation). Data are taken from all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria).

		La^2	La	Lo	A	$\overline{T}_{month}$	$\overline{P}_{month}$
winter	$\overline{\delta^{18}O}_{month}$	0.3663	0.3724	0.1601	0.2920	0.4551	0.0094
months	$\overline{\delta^2 H}_{month}$	0.4455	0.4523	0.1569	0.2637	0.4110	$0.58*10^{-6}$
spring	$\overline{\delta^{18}O}_{month}$	0.1570	0.1607	0.0904	0.2196	0.3960	0.1436
months	$\overline{\delta^2 H}_{month}$	0.1910	0.1951	0.0957	0.1803	0.3699	0.1339
summer	$\overline{\delta^{18}O}_{month}$	0.0001	0.0002	0.1642	0.2217	0.0524	0.2672
months	$\overline{\delta^2 H}_{month}$	0.0010	0.0014	0.1645	0.1787	0.0277	0.2530
autumn	$\overline{\delta^{18}O}_{month}$	0.1244	0.1270	0.2127	0.2343	0.4387	0.0113
months	$\overline{\delta^2 H}_{month}$	0.1773	0.1804	0.1976	0.2056	0.3920	0.0054

To see how the monthly mean $\delta^{18}O$ and $\delta^2 H$ values of precipitation are correlated with the different regression parameters for the different seasons, the R^2 was calculated for all pairs (table 4.2.2) and scatterplots were produced for the monthly mean $\delta^{18}O$ values of the winter and the summer months (figures 4.2.1 and 4.2.2). While temperature shows fairly high linear correlations with the monthly $\delta^{18}O$ and $\delta^2 H$ values of precipitation during winter, spring and autumn, the R^2 is low for the summer months. Linear correlations with

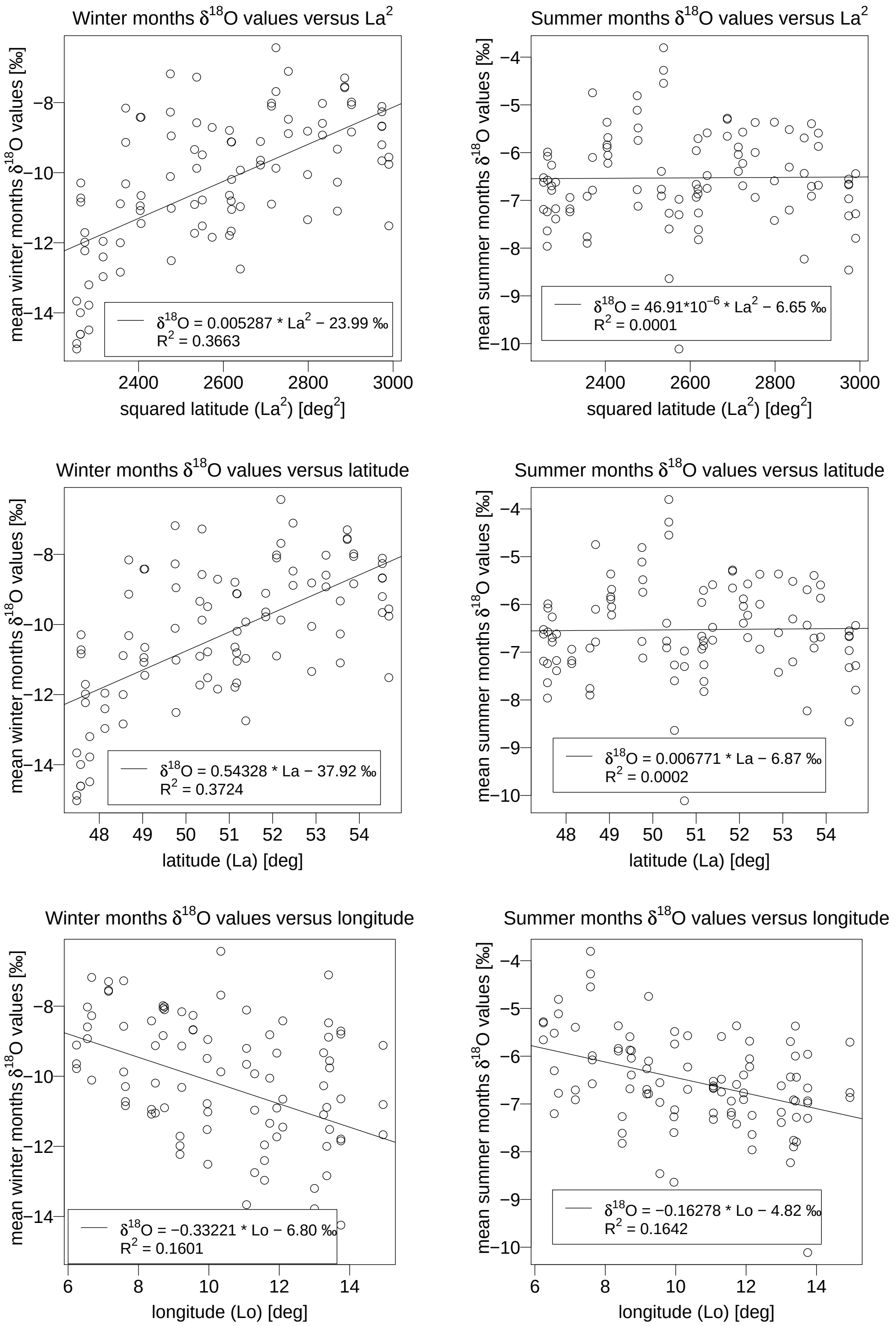


Figure 4.2.1.: Scatterplots of monthly mean $\delta^{18}O$ values versus latitude squared, latitude and longitude of all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria), for winter and for summer months. The regression equations and the corresponding R^2 values are shown in the plots.

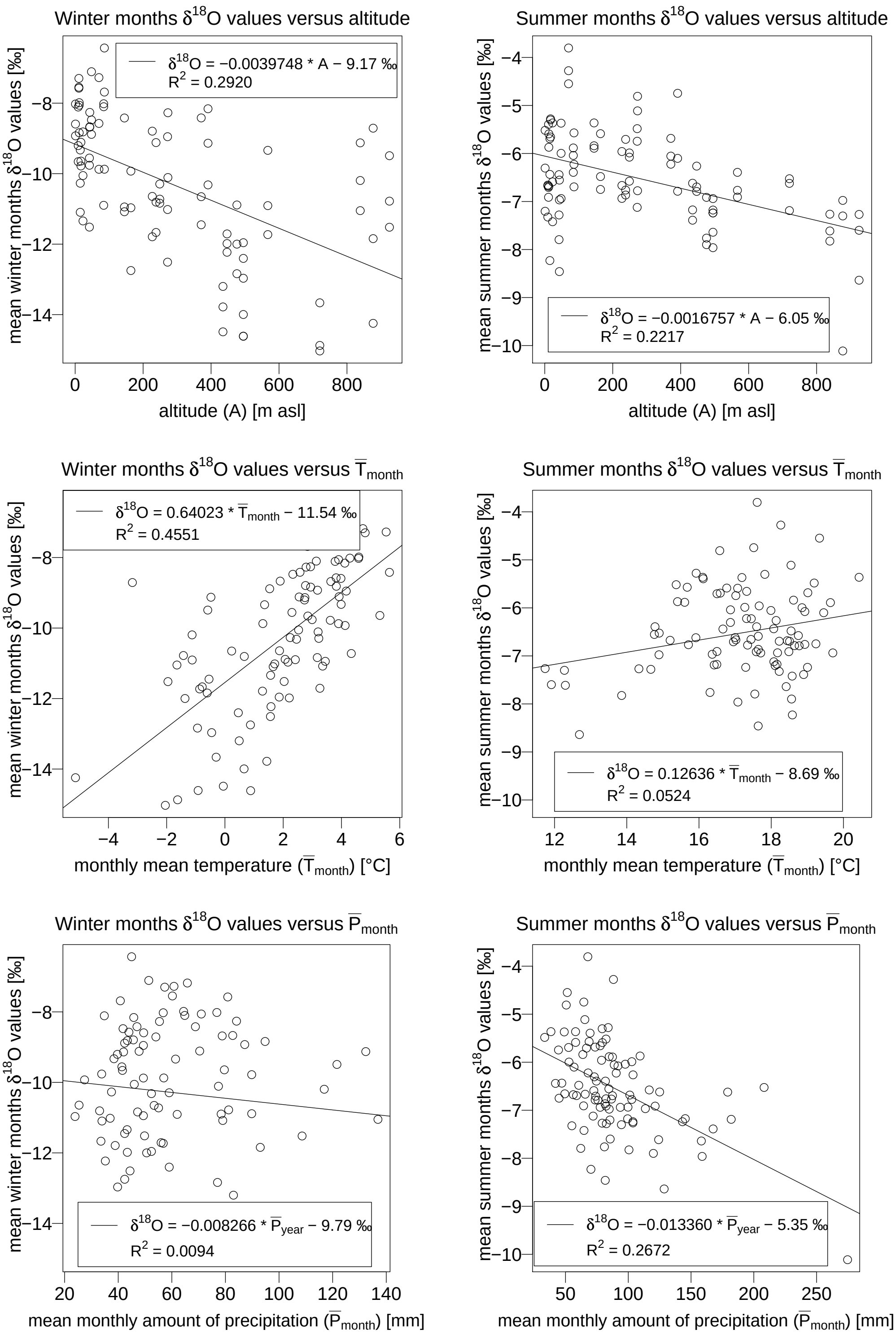


Figure 4.2.2.: Scatterplots of monthly mean $\delta^{18}O$ values versus altitude, monthly mean temperature and mean monthly amount of precipitation of all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria), for winter and for summer months. The regression equations and the corresponding R^2 values are shown in the plots.

the monthly amount of precipitation, however, are highest for summer, compared to very low R^2 values during autumn and winter. Latitude and latitude squared show the highest linear correlation with $\delta^{18}O$ and δ^2H values for the winter months and almost no correlation for the summer months. Longitude seems to be most important during autumn. The differences between linear correlations of the $\delta^{18}O$ values with the parameters for winter and for summer months can well be seen in figures 4.2.1 and 4.2.2. The correlations of the different parameters with $\delta^{18}O$ and δ^2H values show similar patterns for both, $\delta^{18}O$ and δ^2H. For the squared latitude and latitude the R^2 values are generally higher for δ^2H, while correlations with $\delta^{18}O$ are slightly stronger for altitude, temperature and precipitation.
However, as mentioned before, variables showing high linear correlations with the isotope ratios do not necessarily have to be part of the MLR equations producing the best results. This is due to the multicollinearity of the parameters.

4.2.2.1. Winter Months MLR equations

$\delta^{18}O$ values:
By trying out different combinations of parameters (table A.0.1) and looking at table 4.2.2 it can be seen that the most important regression parameters for the MLRs on $\delta^{18}O$ values of the winter months are latitude squared, latitude, altitude and temperature. So, in contrast to the MLRs on all months, longitude is not of great importance, whereas altitude plays an important role. However, including precipitation and longitude into the regression leads to a slight improvement of the adjusted R^2:

$$\begin{aligned}\overline{\delta^{18}O}_{month} = & -0.1042 * La^2 + 11.200 * La - 0.08608 * Lo + 0.004141 * A \\ & +0.7915 * \overline{T}_{month} - 0.010380 * \overline{P}_{month} - 311.00\end{aligned} \tag{4.2.3}$$

For this set of parameters the standard error of prediction for full cross validation (SEP_{cv}), showing the average deviation between the observed and the predicted monthly mean values of $\delta^{18}O$, is 1.14 ‰ (table 4.2.5). Using only the 17 German GNIP stations to set up the regression with these parameters the standard error of prediction for the 12 DWD stations (SEP_{DWD}) is of 1.63 ‰ (table 4.2.8) are obtained for this set of parameters. The frequency distribution for the estimation error for full cross validation (difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations) is shown in figure 4.2.3.
In figure 4.2.4 monthly mean $\delta^{18}O$ values predicted for the German GNIP and DWD stations for the winter months, using equation 4.2.3, are plotted against the observed values.

δ^2H values:
As for the $\delta^{18}O$ values the most important regression parameters for the prediction of mean δ^2H values are latitude squared, latitude, altitude and tem-

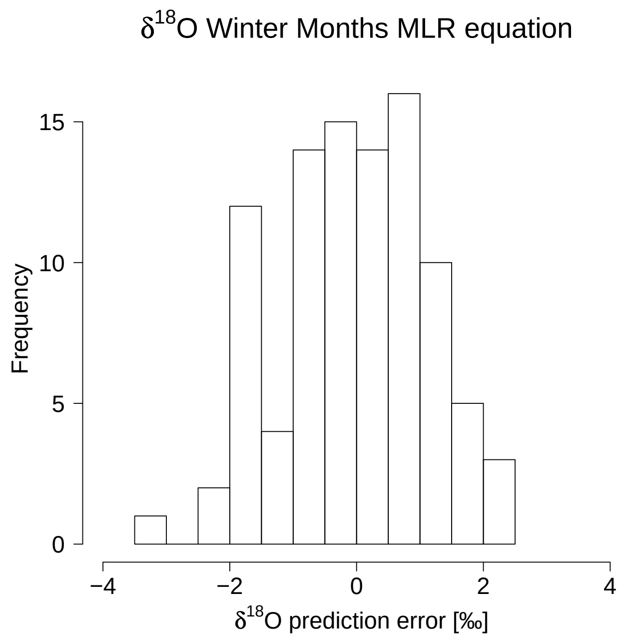


Figure 4.2.3.: Frequency distribution for the estimation error of $\delta^{18}O$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein and Salzburg (Austria) with the MLR equation for the winter months. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).

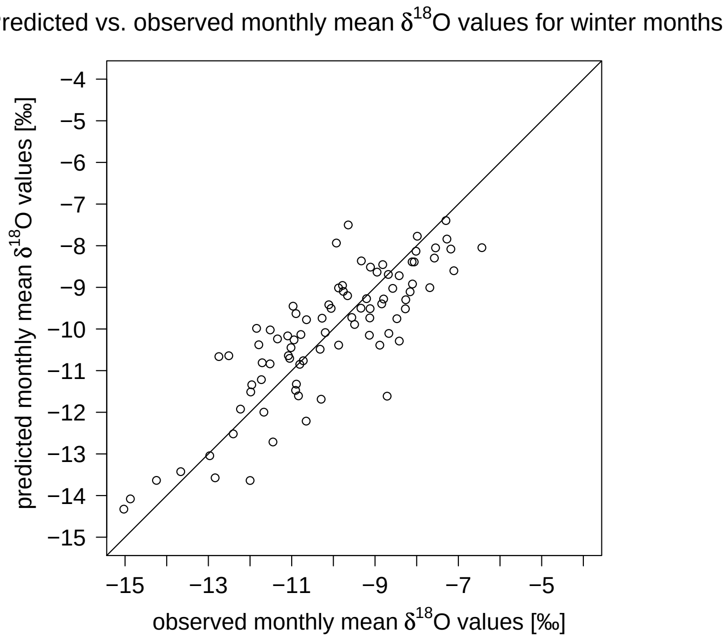


Figure 4.2.4.: Predicted versus observed monthly mean $\delta^{18}O$ values of German GNIP and DWD stations for the winter months. Predicted values were calculated with the MLR equation 4.2.3.

perature. While the inclusion of longitude to this group of parameters leads to a minor increase and the inclusion of longitude to a slightly higher increase of the adjusted R^2, the addition of both paramters, longitude and precipitation, to the basic 4 results in a decrease of the overall measure of quality.
This leads to:

$$\overline{\delta^2 H}_{month} = -0.8003 * La^2 + 86.740 * La + 0.035280 * A + 6.7480 * \overline{T}_{month} + 0.002694 * \overline{P}_{month} - 2435.00 \tag{4.2.4}$$

The corresponding SEP_{cv} is 7.78 ‰ (table 4.2.6), the SEP_{DWD} 9.79 ‰ (table 4.2.9). Figure A.0.8 (in the appendix) shows the frequency distribution for the estimation error for full cross validation.
In figure A.0.13 monthly mean $\delta^2 H$ values predicted for the German GNIP and DWD stations for the winter months, using equation 4.2.4, are plotted against the observed values.

4.2.2.2. Spring Months MLR equations

$\delta^{18}O$ values:
For the $\delta^{18}O$ MLR equations based on the spring months the comparison of different combinations of parameters in the MLR equations (table A.0.1) shows that latitude squared, latitude, longitude and temperature are the most important parameters, just as for the *All Months MLR equations*. Adding altitude to these basic parameters leads to a slight decrease of the adjusted R^2. By including precipitation, however, the adjusted R^2 can be improved. The best result is achieved when both, precipitation and altitude, are added to the basic 4 parameters:

$$\overline{\delta^{18}O}_{month} = -0.1117 * La^2 + 11.780 * La - 0.1359 * Lo - 0.0006893 * A + 0.3004 * \overline{T}_{month} + 0.01049 * \overline{P}_{month} - 320.00 \tag{4.2.5}$$

The SEP_{cv} is 0.98 ‰ (table 4.2.5), the SEP_{DWD} is 1.35 ‰ (table 4.2.8). The frequency distribution for the estimation error for full cross validation is shown in figure A.0.9.
Monthly mean $\delta^{18}O$ values predicted for the German GNIP and DWD stations for the spring months, using equation 4.2.5, are plotted against the observed values in figure A.0.14.

$\delta^2 H$ values:
The most important parameters for the MLRs on the spring months are the same for the $\delta^2 H$ values as for the $\delta^{18}O$ ones. But the best adjusted R^2 is obtained if precipitation is added to the parameters latitude squared, latitude, longitude and temperature (equation 4.2.6). The inclusion of altitude does not

increase the adjusted R^2.

$$\overline{\delta^2 H}_{month} = -0.8425 * La^2 + 89.770 * La - 1.2050 * Lo + 2.4190 * \overline{T}_{month} + 0.09967 * \overline{P}_{month} - 2459.00 \tag{4.2.6}$$

The corresponding SEP_{cv} is 7.58 ‰ (table 4.2.6), the SEP_{DWD} is 8.80 ‰ (table 4.2.9). Figure A.0.9 shows the frequency distribution for the estimation error for full cross validation.
In figure A.0.14 monthly mean $\delta^2 H$ values predicted for the German GNIP and DWD stations for the spring months, using equation 4.2.6, are plotted against the observed values.

4.2.2.3. Summer Months MLR equations

As can be seen in the tables A.0.2 and 4.2.2 the most important MLR parameters for the prediction of monthly mean $\delta^{18}O$ and $\delta^2 H$ values for the summer months are longitude, altitude, temperature and precipitation. Adding latitude and the squared latitude to these 4 parameters leads to further improvement of the adjusted R^2:

$$\overline{\delta^{18} O}_{month} = -0.04910 * La^2 + 4.638 * La - 0.06254 * Lo - 0.003699 * A - 0.26140 * \overline{T}_{month} - 0.008429 * \overline{P}_{month} - 108.30 \tag{4.2.7}$$

with a SEP_{cv} of 0.66 ‰ (table 4.2.5) and a SEP_{DWD} of 0.71 ‰ (table 4.2.8). The frequency distribution for the estimation error for full cross validation is shown in figure A.0.10 in the appendix.
Monthly mean $\delta^{18}O$ values predicted for the German GNIP and DWD stations for the summer months, using equation 4.2.7, are plotted against the observed values in figure A.0.15.

$$\overline{\delta^2 H}_{month} = -0.32922 * La^2 + 31.30882 * La - 0.49481 * Lo - 0.022550 * A - 1.75749 * \overline{T}_{month} - 0.059750 * \overline{P}_{month} - 737.19 \tag{4.2.8}$$

with a SEP_{cv} of 4.90 ‰ (table 4.2.6) and a SEP_{DWD} of 5.39 ‰ (table 4.2.9). Figure A.0.10 shows the frequency distribution for the estimation error for full cross validation.
In figure A.0.15 monthly mean $\delta^2 H$ values predicted for the German GNIP and DWD stations for the summer months, using equation 4.2.8, are plotted against the observed values.

4.2.2.4. Autumn Months MLR equations

$\delta^{18}O$ values:

Comparing MLRs with different sets of parameters (table A.0.2) it can be concluded that latitude squared, latitude, longitude and temperature are the most important parameters for the MLRs on monthly mean $\delta^{18}O$ values of the autumn months. Adding altitude to these parameters increases the adjusted R^2. Further improvement is obtained by adding precipitation to the basic 4 parameters and leaving out altitude:

$$\overline{\delta^{18}O}_{month} = -0.08574 * La^2 + 8.948 * La - 0.2869 * Lo + 0.2699 * \overline{T}_{month} - 0.0072 * \overline{P}_{month} - 241.50 \quad (4.2.9)$$

The SEP_{cv} for this set of parameters is 0.95 ‰ (table 4.2.5), the SEP_{DWD} is 0.99 ‰ (table 4.2.8). The frequency distribution for the estimation error for full cross validation is shown in figure A.0.11.
Monthly mean $\delta^{18}O$ values predicted for the German GNIP and DWD stations for the autumn months, using equation 4.2.9, are plotted against the observed values in figure A.0.16.

δ^2H values:
As for the $\delta^{18}O$ values the most important regression parameters for MLR equations of monthly mean δ^2H of precipitation for the autumn months are latitude squared, latitude, longitude and temperature. But in contrast to the $\delta^{18}O$ MLRs the adjusted R^2 cannot be improved by adding altitude and precipitation to these parameters. So the best equation is:

$$\overline{\delta^2H}_{month} = -0.70150*La^2+73.9115*La-2.0574*Lo+2.0206*\overline{T}_{month}-2006.32 \quad (4.2.10)$$

with a SEP_{cv} of 7.97 ‰ (table 4.2.6) and a SEP_{DWD} of 8.35 ‰ (table 4.2.9). The frequency distribution for the estimation error for full cross validation is shown in figure A.0.11.
In figure A.0.16 monthly mean δ^2H values predicted for the German GNIP and DWD stations for the autumn months, using equation 4.2.10, are plotted against the observed values.

4.2.2.5. All seasons

Taking the monthly mean values calculated with the *Seasonal MLR equations*, mean annual values of $\delta^{18}O$ and δ^2H of precipitation can be calculated. For $\delta^{18}O$ a SEP_{cv} of 0.52 ‰ (table 4.2.5) and a SEP_{DWD} of 0.60 ‰ (table 4.2.8) are obtained. For δ^2H the SEP_{cv} is 3.60 ‰ (table 4.2.6) and the SEP_{DWD} 3.48 ‰ (table 4.2.9).

4.2.3. Annual Mean MLR equations

Based on precipitation weighted annual means of all stations listed in table 2.1.1, except for Reutte and Scharnitz, MLRs with different parameter combinations were performed. The MLRs with the 4 highest adjusted R^2 values for $\delta^{18}O$ and δ^2H respectively are listed in table A.0.2 in the appendix.

In order to see how annual mean $\delta^{18}O$ or δ^2H values of precipitation are correlated with the different regression parameters scatterplots were produced (figures A.0.4 and A.0.5 in the appendix) and the R^2 was calculated for all pairs (table 4.2.3). The highest linear correlations are obtained with the geographic parameters, especially with altitude, while the correlation with the annual mean temperature is very low. Linear correlations with the squared latitude and latitude are distinctively higher for δ^2H than for $\delta^{18}O$.

Table 4.2.3.: R^2 values of all pairs of amount-weighted annual mean $\delta^{18}O$ or δ^2H values of precipitation with each of the regression parameters (La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; $\overline{T}_{year}$: amount-weighted annual mean temperature; $\overline{P}_{year}$: mean annual amount of precipitation). Data are taken from all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria).

Annual mean	La^2	La	Lo	A	$\overline{T}_{year}$	$\overline{P}_{year}$
$\overline{\delta^{18}O}_{year}$	0.2582	0.2636	0.2944	0.5799	0.1390	0.1886
$\overline{\delta^2H}_{year}$	0.3966	0.4035	0.3145	0.5323	0.0515	0.1739

In accordance with the correlations shown in table 4.2.3 the best MLR equation (the highest adjusted R^2) for both, $\delta^{18}O$ and δ^2H, is obtained using the regression parameters latitude squared , latitude, longitude and altitude. Adding precipitation or temperature or both to this set of parameters leads to a decrease in the adjusted R^2. Thus only geographic parameters are needed to set up the MLR equations for annual mean $\delta^{18}O$ and δ^2H values. This allows the inclusion of the two Austrian stations Reutte and Scharnitz (missing temperature values) to the set of stations used to perform the regression. Based on these 34 stations the following MLR equations were obtained:

$$\overline{\delta^{18}O}_{year} = -0.07975 * La^2 + 8.164 * La - 0.1519 * Lo - 0.002589 * A - 214.80 \tag{4.2.11}$$

with an adjusted R^2 of 0.8815 (instead of 0.8352 when Reutte and Scharnitz are left out). The SEP_{cv} is 0.43 ‰ (table 4.2.5), the SEP_{DWD} is 0.61 ‰ (table 4.2.8). The frequency distribution for the estimation error for full cross validation is shown in figure A.0.12.
Annual mean $\delta^{18}O$ values predicted for the German GNIP and DWD stations using equation 4.2.11 are plotted against the observed values in figure A.0.17.

$$\overline{\delta^2H}_{year} = -0.58950 * La^2 + 61.110 * La - 1.2750 * Lo - 0.015080 * A - 1623.00 \tag{4.2.12}$$

with an adjusted R^2 of 0.9014 (instead of 0.8714 when Reutte and Scharnitz are left out). The SEP_{cv} is 3.05 ‰ (table 4.2.6) and the SEP_{DWD} 3.35 ‰ (table 4.2.9). Figure A.0.12 shows the frequency distribution for the estimation error for full cross validation.
In figure A.0.17 annual mean δ^2H values predicted for the German GNIP and DWD stations using equation 4.2.12 are plotted against the observed values.

These two MLR equations were used to produce the maps shown in the figures 4.2.11 and 4.2.12.

4.2.4. Comparison of all MLR methods

4.2.4.1. Importance of regression parameters

Looking at the coefficients of determination in tables 4.2.1, 4.2.2 and 4.2.3 as well as at the regression equations with different sets of parameters shown in tables A.0.1 and A.0.2 one can find the most important parameters for each of the differnt regression methods. However, as the parameters are multicollinear it is not possible to simply take the importance of parameters for the regressions as a measure for the importance of the corresponding isotope effects.

Table 4.2.4.: Most important regression parameters for the different MLR methods on $\delta^{18}O$ and δ^2H values of precipitation (La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; $\overline{T}_{month}$: monthly mean temperature; $\overline{P}_{month}$: mean monthly amount of precipitation).

MLR method	Months	most important Parameters
All Months	all	La^2, La, Lo, $\overline{T}_{month}$
Seasonal	D,J,F	La^2, La, A, $\overline{T}_{month}$
	M,A,M	La^2, La, Lo, $\overline{T}_{month}$
	J,J,A	La^2, Lo, A, $\overline{T}_{month}$, $\overline{P}_{month}$
	S,O,N	La^2, La, Lo, $\overline{T}_{month}$
Annual Mean		La^2, La, Lo, A

All Months MLR equations

When using monthly means of all months the most important regression parameters for the MLRs on $\delta^{18}O$ and δ^2H values of precipitation in Germany are latitude squared, latitude, longitude and temperature, with temperature being the most important one of all. This can be easily explained by the fact that temperature is needed to account for the seasonal change of isotope values through the year.

Seasonal MLR equations

To account for changes in the influence of the parameters on the monthly mean isotope ratios of precipitation a separate regression equation was set up for the months within each single season.

For the MLRs on the winter months (Dec - Feb) latitude squared, latitude, altitude and temperature have got the strongest influence on the predicted isotope values. So, in contrast to the *All Months MLR equations*, a change in longitude does not have a major effect while altitude seems to be of some importance during winter.

Just as for the MLR equations based on all months the most important variables for MLRs on the spring months (Mar - May) are latitude squared, latitude, longitude and temperature. Altitude does only play a minor role for the prediction of the monthly mean $\delta^{18}O$ and $\delta^{2}H$ values.

For the MLRs on the summer months (Jun - Aug) all regression parameters available (latitude squared, latitude, longitude, altitude, temperature and precipitation) are needed to obtain a good result. The *Summer Months MLR equations* for $\delta^{18}O$ and $\delta^{2}H$ are the only seasonal equations that need the amount of precipitation as a variable to work properly. This is most likely due to the enhanced evaporation of the raindrops during summer (see amount effect in section 3.1.3). The use of latitude or latitude squared as regression parameters is less important for the summer months than for the other seasons. This could be caused by a weak continental effect during summer, most likely caused by increased transpiration (see continental effect in section 3.1.3). Temperature is of lower importance during the summer months, too, which might be due to the generally low variablity of monthly mean temperatures from June to August.

Latitude squared, latitude, longitude and temperature are needed to perform a good MLR on the autumn months (Sep - Nov), just as for the regressions on all months and on spring months. Thus a change in longitude during spring and autumn seems to have a greater effect on the $\delta^{18}O$ and $\delta^{2}H$ values in precipitation than during summer and winter.

Annual Mean MLR equations

When performing MLRs on annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation only geographic parameters (latitude squared, latitude, longitude and altitude) are needed to obtain the best results. This is most likely caused by multicollinearity between geographic paramters and the mean annual amount of precipitation or annual mean temperature, and by the generally low correlation between the annual mean isotope ratios in precipitation and the annual mean temperature in Germany (table 4.2.3).

4.2.4.2. Quality of the predicted values

Seasonal MLR equations

As mentioned above the quality of the prediction of monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany is improved by setting up a separate regression equation for each season instead of performing one MLR on all months. So, concerning the prediction of monthly mean values, only the performance of the *Seasonal MLR equations* will be discussed in the following.

Looking at the standard error of prediction for full cross validation (SEP_{cv}) (tables 4.2.5 and 4.2.6) one can see that for both, $\delta^{18}O$ and $\delta^{2}H$, the deviation between predicted and observed monthly mean values is in general lower for the summer months than for the rest of the year. This is most likely due to the lower variability of isotope values during summer compared to the other seasons, which can be seen in the plots of the predicted versus the observed values (figures A.0.13 to A.0.16). But even the highest SEP_{cv} of the seasonal equations (1.14 ‰ for the $\delta^{18}O$ *Winter Months MLR equations* and 7.97 ‰ for the $\delta^{2}H$ *Autumn Months MLR equations*) is lower than the SEP_{cv} of the *All Months MLR equations* (1.19 ‰ and 8.86 ‰ for monthly mean $\delta^{18}O$ and $\delta^{2}H$ respectively).

Table 4.2.5.: Standard error of prediction for full cross validation for different $\delta^{18}O$ regression equations (in [‰ VSMOW]). (n: number of stations; m: number of monthly means; La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; T: temperature; P: precipitation)

MLR method	Months	n	m	Parameters	SEP_{cv} (monthly)	SEP_{cv} (annual)
All Months	all	32	384	La^2, La, Lo, T, P	1.19	0.51
Seasonal	D,J,F	32	96	La^2, La, Lo, A, T, P	1.14	
	M,A,M	32	96	La^2, La, Lo, A, T, P	0.98	
	J,J,A	32	96	La^2, La, Lo, A, T, P	0.66	
	S,O,N	32	96	La^2, La, Lo, T, P	0.95	
	all	32				0.52
Annual Mean		34		La^2, La, Lo, A		0.43

Table 4.2.6.: Standard error of prediction for full cross validation for different $\delta^{2}H$ regression equations (in [‰ VSMOW]). (n: number of stations; m: number of monthly means; La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; T: temperature; P: precipitation)

MLR method	Months	n	m	Parameters	SEP_{cv} (monthly)	SEP_{cv} (annual)
All Months	all	32	384	La^2, La, Lo, T	8.86	3.51
Seasonal	D,J,F	32	96	La^2, La, A, T, P	7.78	
	M,A,M	32	96	La^2, La, Lo, T, P	7.58	
	J,J,A	32	96	La^2, La, Lo, A, T, P	4.90	
	S,O,N	32	96	La^2, La, Lo, T	7.97	
	all	32				3.60
Annual Mean		34		La^2, La, Lo, A		3.05

Figures A.0.8 to A.0.11 show the frequency distributions of the estimation errors of the δ values (predicted - observed δ values), obtained for full cross validation of the *Seasonal MLR equations*. Stations where predicted and observed isotope ratios differ clearly (producing estimation errors lying at the ends of the frequency distributions) are listed in table 4.2.7. It can be seen that the observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ values at Artern are strongly

Table 4.2.7.: Stations with high deviations between observed and predicted $\delta^{18}O$ and $\delta^{2}H$ values for full cross validation on different MLR equations.

	$\delta^{18}O$			$\delta^{2}H$		
MLR method	Station	predicted - observed $\delta^{18}O$ [‰]	Month	Station	predicted - observed $\delta^{2}H$ [‰]	Month
Winter Months	Artern	+ 2.38 ‰; + 2.34 ‰	Dec; Feb	Emmerich	+ 16.61 ‰	Dec
	Emmerich	+ 2.33 ‰	Feb	Artern	+ 15.20 ‰; + 15.19 ‰	Dec; Feb
				Zinnwald	+ 14.76 ‰	Feb
	Zinnwald	- 3.47 ‰	Jan	Zinnwald	- 28.04 ‰	Jan
	Regensburg	- 2.22 ‰	Feb	Schleswig	- 16.36 ‰	Dec
	Braunschweig	- 2.04 ‰	Feb	Weil am Rhein	- 14.56 ‰	Dec
Spring Months	Neubrandenburg	+ 2.80 ‰	Apr	Neubrandenburg	+ 20.60 ‰	Apr
	Karlsruhe	+ 2.45 ‰	May	Emmerich	+ 18.53 ‰	Apr
	Dresden	+ 2.16 ‰	Apr	Karlsruhe	+ 16.25 ‰	May
	Regensburg	- 2.56 ‰	Mar	Berlin	- 17.86 ‰; - 15.06 ‰	Mar; May
	Berlin	- 2.16 ‰	Mar			
Summer Months	Fuerstenzell	+ 1.56 ‰	Jun	Fürstenzell	+ 10.47 ‰	Jun
				Neubrandenburg	+ 9.20 ‰	Aug
	Garmisch	- 1.74 ‰; - 1.56 ‰	Jun; Jul	Garmisch	- 12.01 ‰; - 9.69 ‰	Jun; Jul
	Koblenz	- 1.50 ‰	Jun	Stuttgart	- 9.85 ‰	Jun
				Koblenz	- 9.60 ‰	Jun
Autumn Months	Garmisch	+ 2.48 ‰	Nov	Garmisch	+ 22.01 ‰	Nov
	Artern	+ 1.83 ‰	Sep	Koblenz	+ 14.70 ‰	Sep
	Konstanz	+ 1.83 ‰	Sep	Artern	+ 14.47 ‰	Sep
	Regensburg	- 2.29 ‰	Oct	Regensburg	- 17.07 ‰	Oct
	Weil am Rhein	- 2.02 ‰	Oct	Weil am Rhein	- 14.50 ‰	Oct
	Schleswig	- 1.83 ‰	Oct	Schleswig	- 14.33 ‰	Oct
Annual Mean	Emmerich	+ 0.92 ‰		Emmerich	+ 5.87 ‰	
	Artern	+ 0.67 ‰		Artern	+ 5.76 ‰	
	Regensburg	- 0.83 ‰		Scharnitz (AUT)	- 5.01 ‰	
	Berlin	- 0.74 ‰		Cuxhaven	- 4.33 ‰	

overestimated by the *Seasonal MLR equations* for December, February and September (i.e. the predicted δ values are higher (isotopically more enriched) than the observed values). As Artern is situated at the lee side (south-east) of the mountain Harz (Müller-Westermeier et al., 1999), isotope values should be strongly affected by the raining out of air masses coming from the north-east and forced to rise and precipitate when hitting the Harz. According to the Rayleigh distillation equation (3.1.5) this leads to a decrease of the δ values in the air mass and could therefore explain the overestimation of the isotope ratios by the MLR equations. Looking at the prediction errors for Zinnwald one can see that monthly mean $\delta^{18}O$ and $\delta^{2}H$ values are significantly underestimated for January while the $\delta^{2}H$ value for February is clearly overestimated by the MLRs. But as the mean istope values for Zinnwald are derived from only two years of observation (2001-2002) the means might differ clearly from the long term values. At Garmisch-Partenkirchen observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ are strongly underestimated for June and July and clearly overestimated for November. This might be due to the pronounced change of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation at Garmisch-Partenkirchen through the year, which can be seen in figures 4.1.5 and 4.1.6.

Looking at the standard error of prediction when regression equations are based on German GNIP stations alone and tested for the DWD stations (SEP_{DWD}) (tables 4.2.8 and 4.2.9) one can see that for both, monthly mean $\delta^{18}O$ and $\delta^{2}H$ values, the SEP_{DWD} is higher than the SEP_{cv} for all seasons, especially for the winter months. This is to be expected as the number of stations used to set up the MLR equations is reduced from 28 for the calculation of the SEP_{cv} to 12 for the SEP_{DWD}. In addition the German GNIP stations are not equally distributed throughout Germany, with almost no stations in the north-eastern part (see map 2.1.1).

Annual MLR equations

Annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation can be predicted by calculating the average of the monthly mean values predicted by the *All Months MLR equations* or the *Seasonal MLR equations*, or by setting up MLR equations on the annual means (*Annual Mean MLR equations*). As can be seen in tables 4.2.5 and 4.2.6 the lowest standard error of prediction for full cross validation (SEP_{cv}) is obtained for both, $\delta^{18}O$ and $\delta^{2}H$, when using the *Annual Mean MLR equation*. Therefore only the performance of the *Annual Mean MLR equation* will be discussed in the following.

Figure A.0.12 shows the frequency distributions of the estimation error (difference between predicted and observed values) obtained for full cross validation of the *Annual Mean MLR equations*. Stations where predicted and observed isotope ratios differ clearly are listed in table 4.2.7. At Emmerich and Artern observed annual mean $\delta^{18}O$ and $\delta^{2}H$ values are strongly overestimated by the MLRs. As discussed above overestimations of the isotope ratios observed at Artern might be caused by the raining out of air masses coming from the north-west and forced to rise when hitting the Harz before coming to Artern.

When regression equations are based on German GNIP stations alone and tested for the DWD stations (tables 4.2.8 and 4.2.9) the standard errors of prediction (SEP_{DWD}) for the mean annual $\delta^{18}O$ values are higher than the SEP_{cv} values for all three ways of predicting annual mean values. This can be easily explained by the lower number of stations available for the calculation of the SEP_{DWD}. For the mean annual $\delta^{2}H$ values calculated from the predicted monthly means of the *Seasonal MLR equations* and the *All Months MLR equations* the SEP_{DWD} is lower than the SEP_{cv}. However, this is not true for the *Annual Mean MLR equation*, which was chosen as the most suitable MLR method before.

Table 4.2.8.: Standard error of prediction for different $\delta^{18}O$ regression equations (in [‰ VSMOW]). The regression equations are based on German GNIP stations and tested with observations at DWD stations. (n GNIP/DWD: number of GNIP/DWD stations; m: number of monthly means; La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; T: temperature; P: precipitation)

MLR method	Months	n_{GNIP}	m	n_{DWD}	Parameters	SEP_{DWD} (monthly)	SEP_{DWD} (annual)
All Months	all	17	204	12	La^2, La, Lo, T, P	1.35	0.59
Seasonal	D,J,F	17	51	12	La^2, La, Lo, A, T, P	1.63	
	M,A,M	17	51	12	La^2, La, Lo, A, T, P	1.35	
	J,J,A	17	51	12	La^2, La, Lo, A, T, P	0.71	
	S,O,N	17	51	12	La^2, La, Lo, T, P	0.99	
	all	17	204	12			0.60
Annual Mean		17		12	La^2, La, Lo, A		0.61

Table 4.2.9.: Standard error of prediction for different $\delta^{2}H$ regression equations (in [‰ VSMOW]). The regression equations are based on German GNIP stations and tested with observations at DWD stations. ($n_{GNIP/DWD}$: number of GNIP/DWD stations; m: number of monthly means; La^2: latitude squared; La: latitude; Lo: longitude; A: altitude; T: temperature; P: precipitation)

MLR method	Months	n_{GNIP}	m	n_{DWD}	Parameters	SEP_{DWD} (monthly)	SEP_{DWD} (annual)
All Months	all	17	204	12	La^2, La, Lo, T	9.60	3.28
Seasonal	D,J,F	17	51	12	La^2, La, A, T, P	9.79	
	M,A,M	17	51	12	La^2, La, Lo, T, P	8.80	
	J,J,A	17	51	12	La^2, La, Lo, A, T, P	5.39	
	S,O,N	17	51	12	La^2, La, Lo, T	8.35	
	all	17		12			3.48
Annual Mean		17		12	La^2, La, Lo, A		3.35

4.2.5. Maps

When looking at the maps of monhly mean $\delta^{18}O$ and δ^2H values of precipitation in Germany (figures 4.2.5 to 4.2.10) one can see that there is a clear decrease in isotope ratios from the north-west to the south-east of Germany during all seasons, except for the summer. This spatial shift can be explained by the continental effect, with air masses coming from the west/north-west (North Sea) and moving (south)-eastwards (Müller-Westermeier et al. (1999), pp. 13-15), and by an increase in altitude towards the Alps in the south(-east). German low mountain ranges (Harz, Rothaargebirge (station Kahler Asten), Thüringer Wald, Rhön (station Wasserkuppe), Erzgebirge, Bayerischer Wald, Schwarzwald and Schwäbische Alb) can be identified by low δ values, caused by the altitude effect (compare to DEM in figure 2.2.1).

As the legends are the same for all months it is easy to see that differences between the months are most pronounced from April to May and August to September for both, $\delta^{18}O$ and δ^2H values. From November to January and from June to August the spatial distribution of monthly isotope ratios seems to be fairly stable for the respective three months. This is most likely due to the general change of weather conditions with approximately constant conditions in winter and summer and distinct changes in spring and autumn (see maps of monthly mean temperature values in figures A.0.1 - A.0.3 in the appendix). When comparing maps of February and March of both, $\delta^{18}O$ and δ^2H, it can be seen that δ values in the north of Germany are sightly higher for February than for March which is in contradiction to what would be expected from theory (seasonal effect). One possible explanation is that this effect is caused by the change from the *Winter Months MLR equation* to the *Spring Months MLR equation*, but as differences in the isotope ratios between February and March in the dataset are generally low, with slight increases as well as decreases in the δ values for different stations, this change in the predicted values might also be due to actual variations in the observed data. Although altitude is an important parameter in the *Winter Months MLR equations* the maps of monthly mean δ^2H values (and $\delta^{18}O$ values) for December and January show very little influence of topography, which might be caused by multicollinearity of altitude with temperature values. For the summer months the isotope maps do show only little spatial variation, except for changes with altitude. Obviously there is no significant continental effect, which could be explained by increased transpiration (see continental effect, section 3.1.3).

The maps of annual mean $\delta^{18}O$ and δ^2H values of precipitation (figures 4.2.11 and 4.2.11) do show a distinct continental and altitude effect.

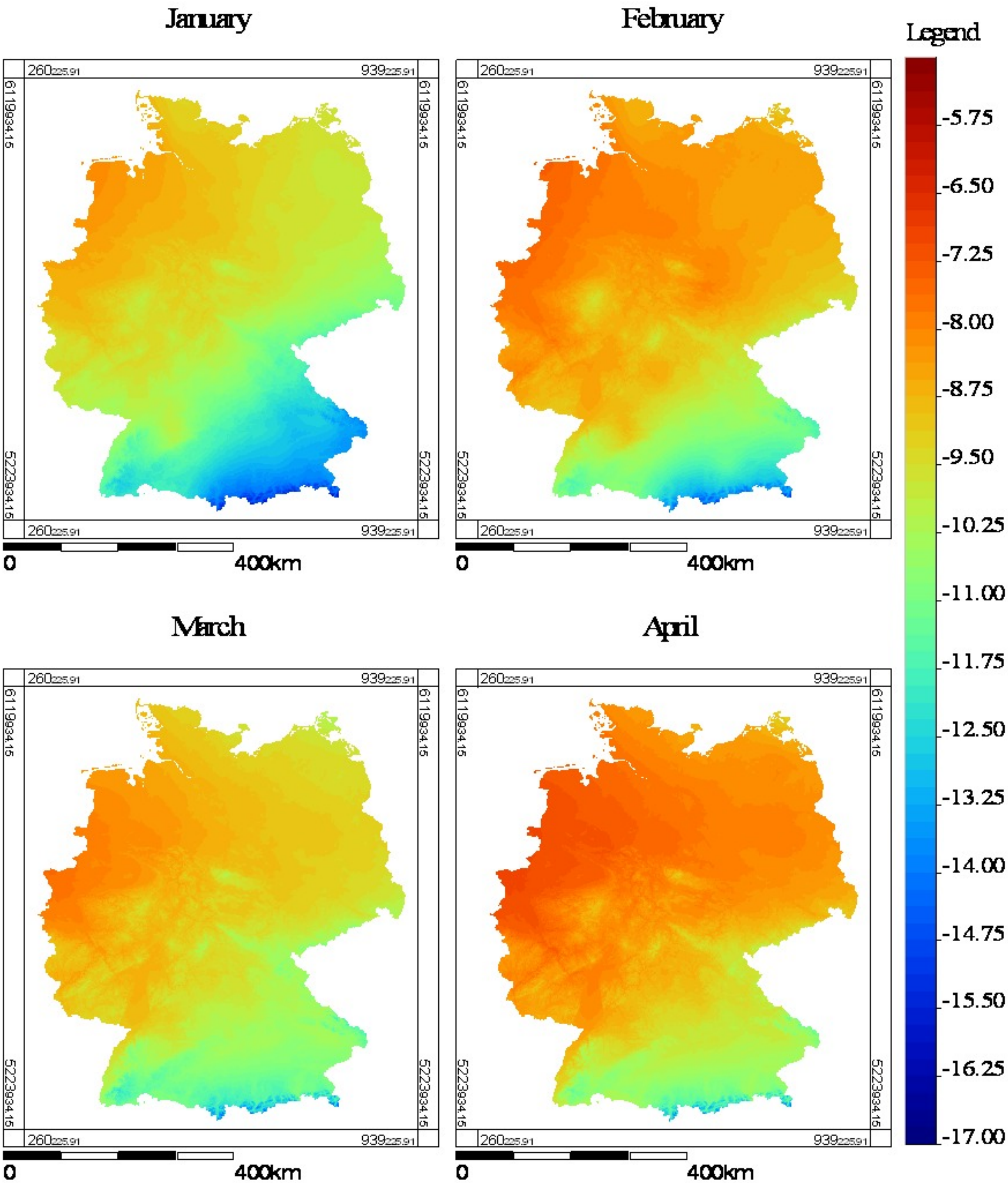


Figure 4.2.5.: Maps of monthly mean $\delta^{18}O$ values of precipitation in Germany, from January to April. Values were calculated with the *Winter Months multiple linear regression (MLR) equation* (January, February) and the *Spring Months MLR equation* (March, April). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of $\delta^{18}O$ values in [‰ VSMOW].

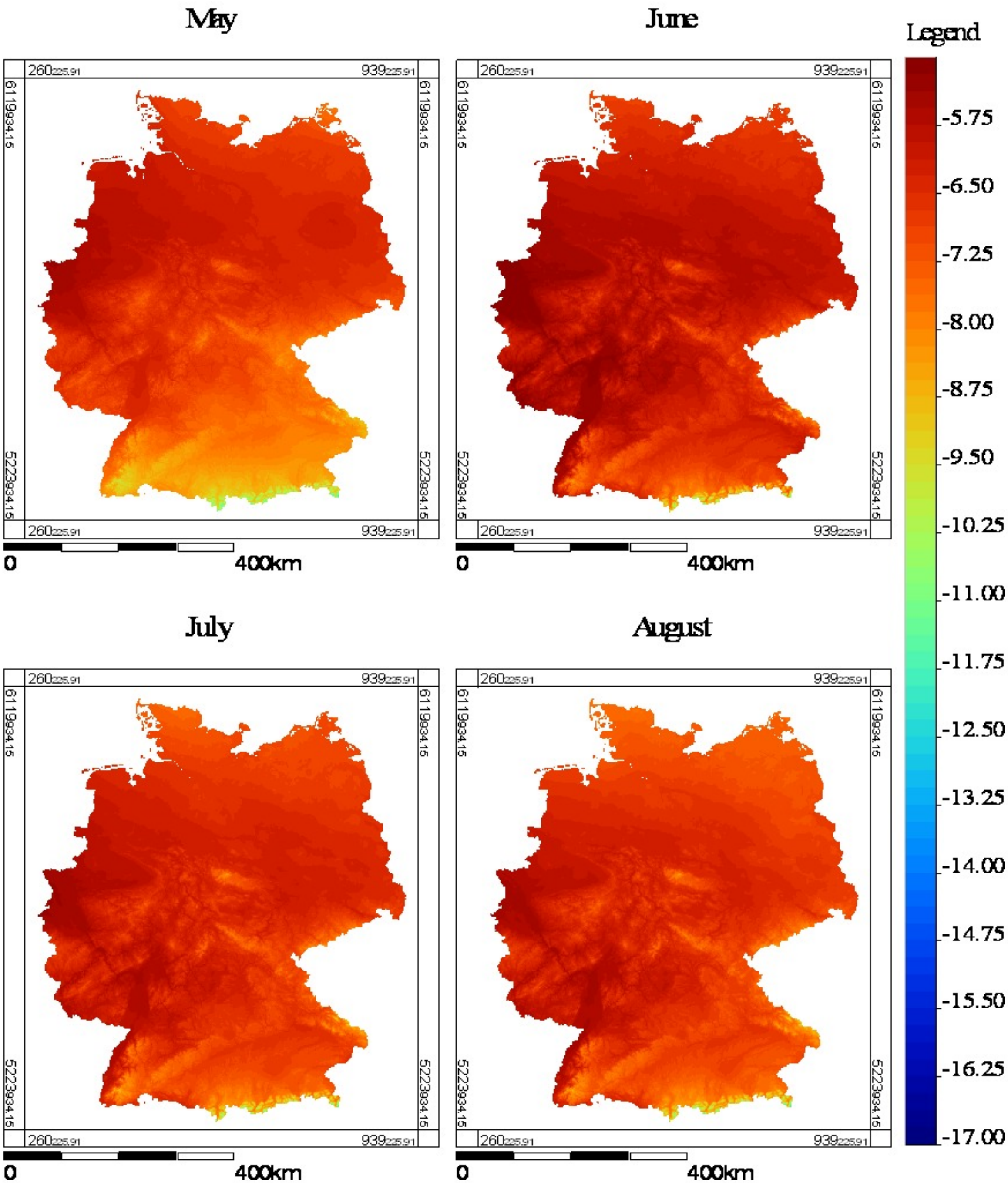


Figure 4.2.6.: Maps of monthly mean $\delta^{18}O$ values of precipitation in Germany, from May to August. Values were calculated with the *Spring Months MLR equation* (May) and the *Summer Months MLR equation* (June - August). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of $\delta^{18}O$ values in [‰ VSMOW].

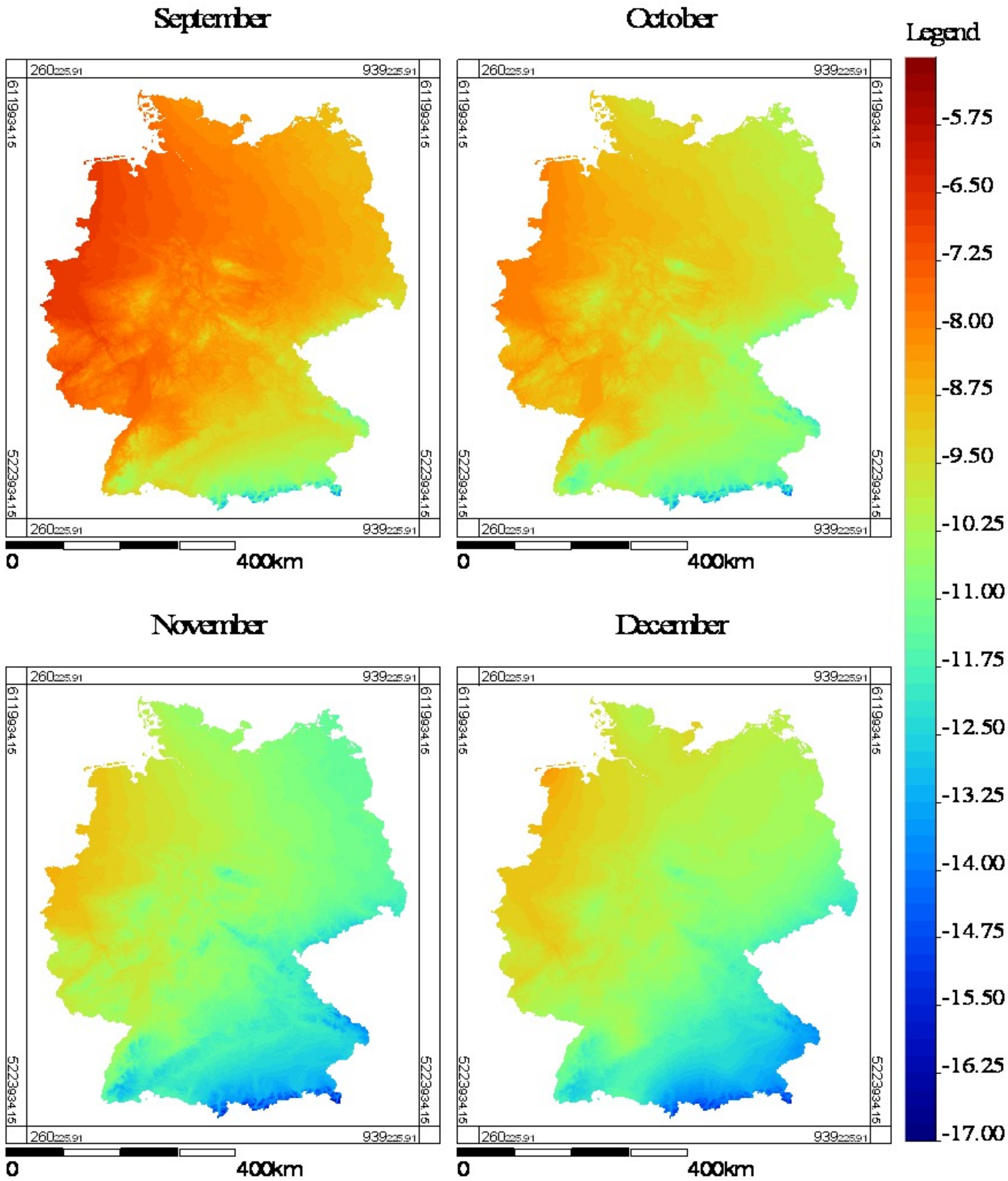


Figure 4.2.7.: Maps of monthly mean $\delta^{18}O$ values of precipitation in Germany, from September to December. Values were claculated with the *Autumn Months MLR equation* (September - November) and the *Winter Months MLR equation* (December). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of $\delta^{18}O$ values in [‰ VSMOW].

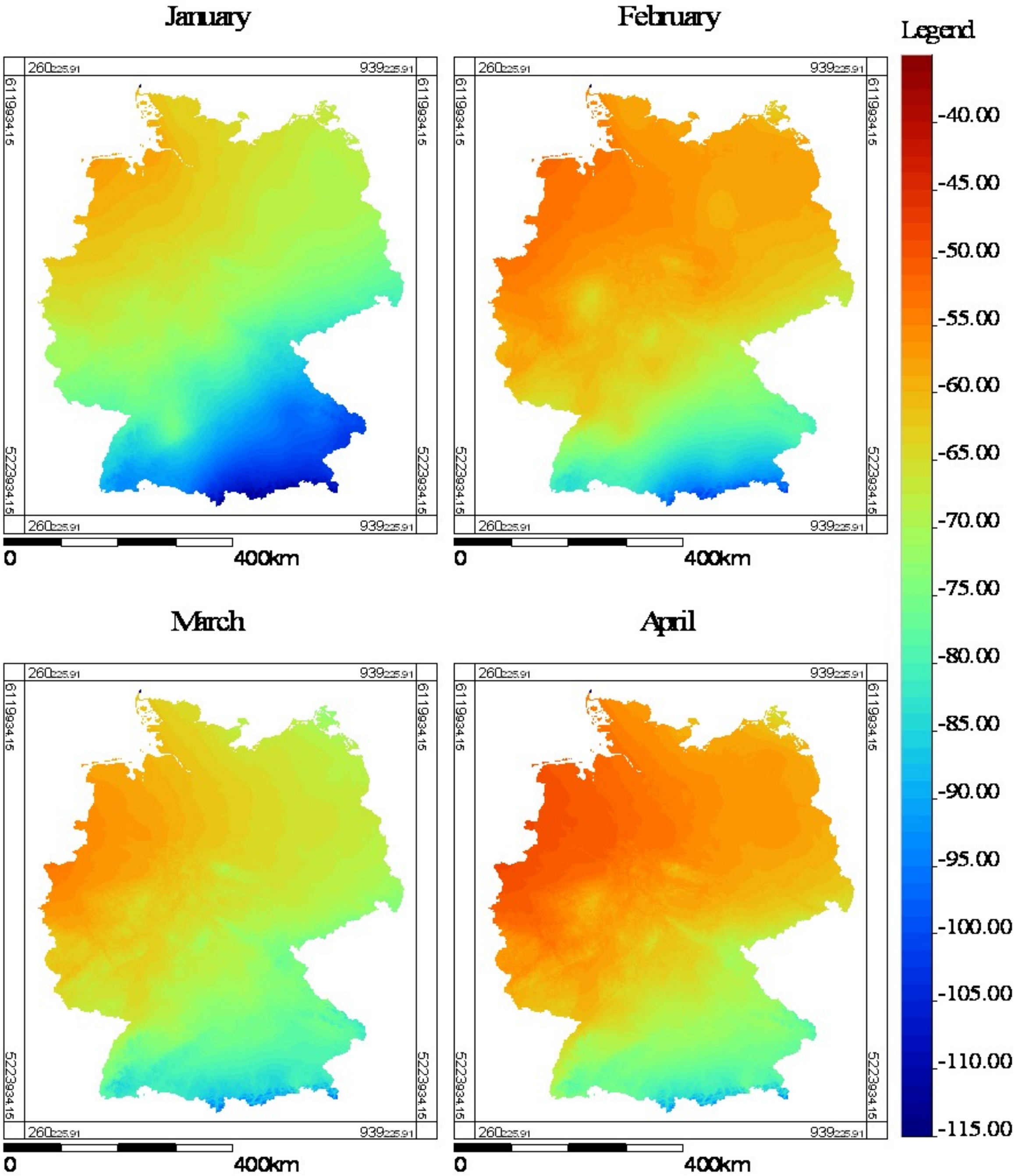


Figure 4.2.8.: Maps of monthly mean δ^2H values of precipitation in Germany, from January to April. Values were calculated with the *Winter Months MLR equation* (January, February) and the *Spring Months MLR equation* (March, April). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of δ^2H values in [‰ VSMOW].

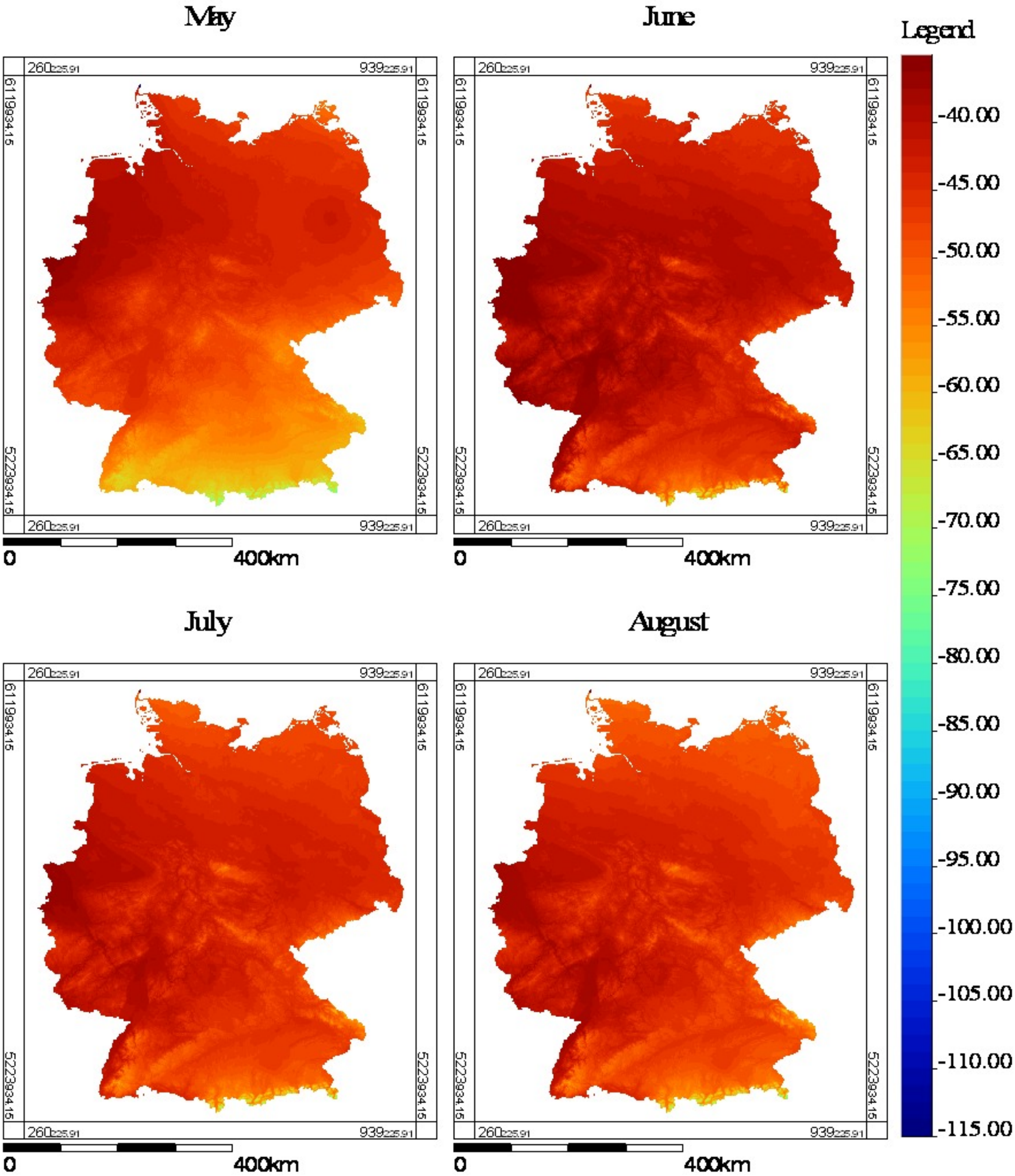


Figure 4.2.9.: Maps of monthly mean $\delta^2 H$ values of precipitation in Germany, from May to August. Values were calculated with the *Spring Months MLR equation* (May) and the *Summer Months MLR equation* (June - August). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of $\delta^2 H$ values in [‰ VSMOW].

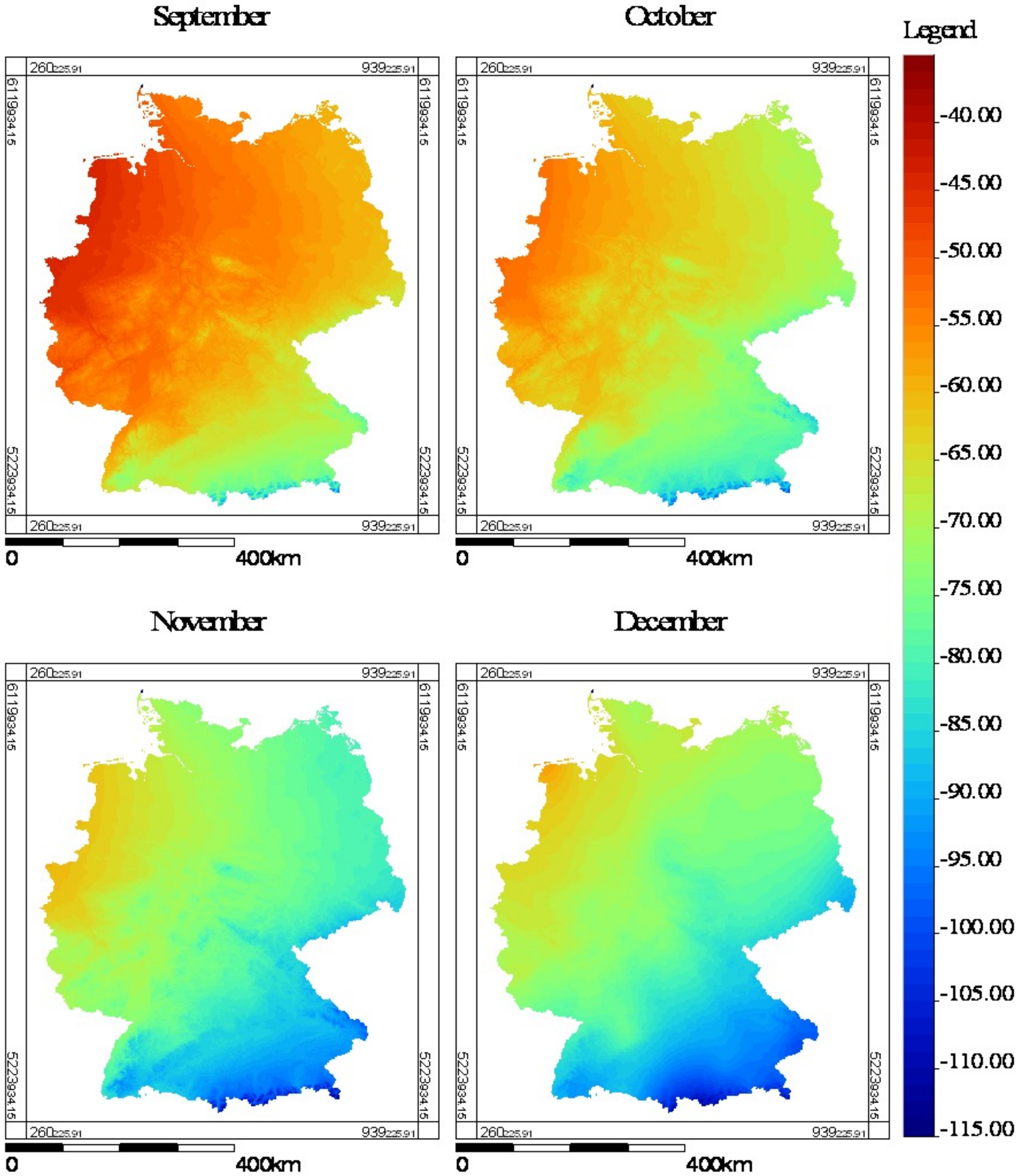


Figure 4.2.10.: Maps of monthly mean δ^2H values of precipitation in Germany, from September to December. Values were calculated with the *Autumn Months MLR equation* (September - November) and the *Winter months MLR equation* (December). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of δ^2H values in [‰ VSMOW].

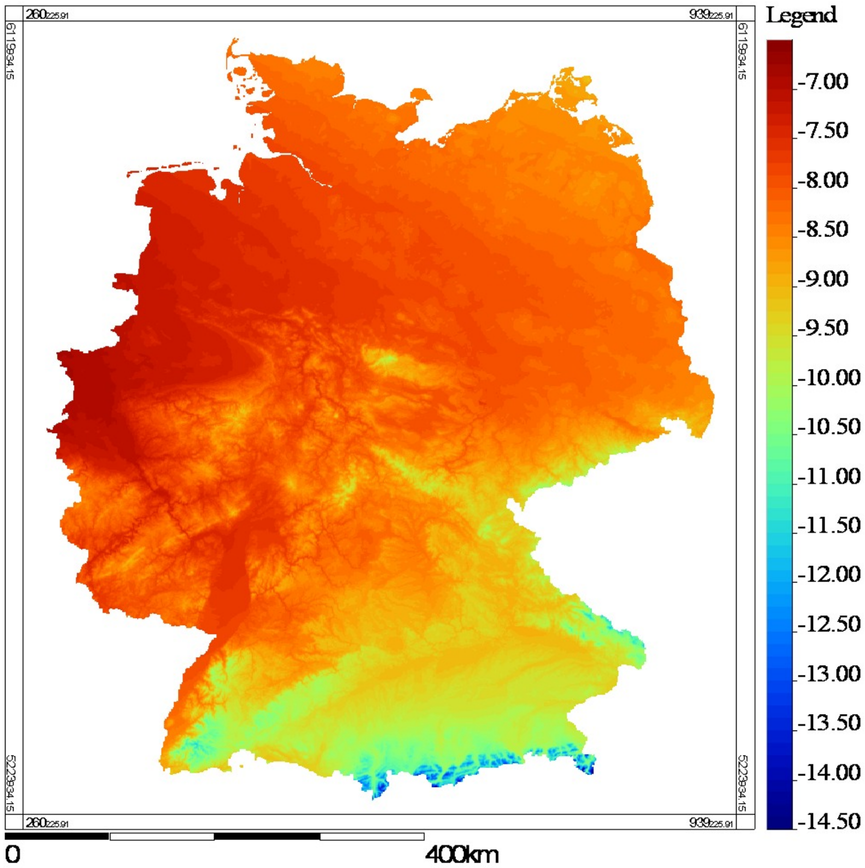


Figure 4.2.11.: Map of annual mean $\delta^{18}O$ values of precipitation in Germany. Values were calculated with the *Annual Mean MLR equation*. The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of $\delta^{18}O$ values in [‰ VSMOW].

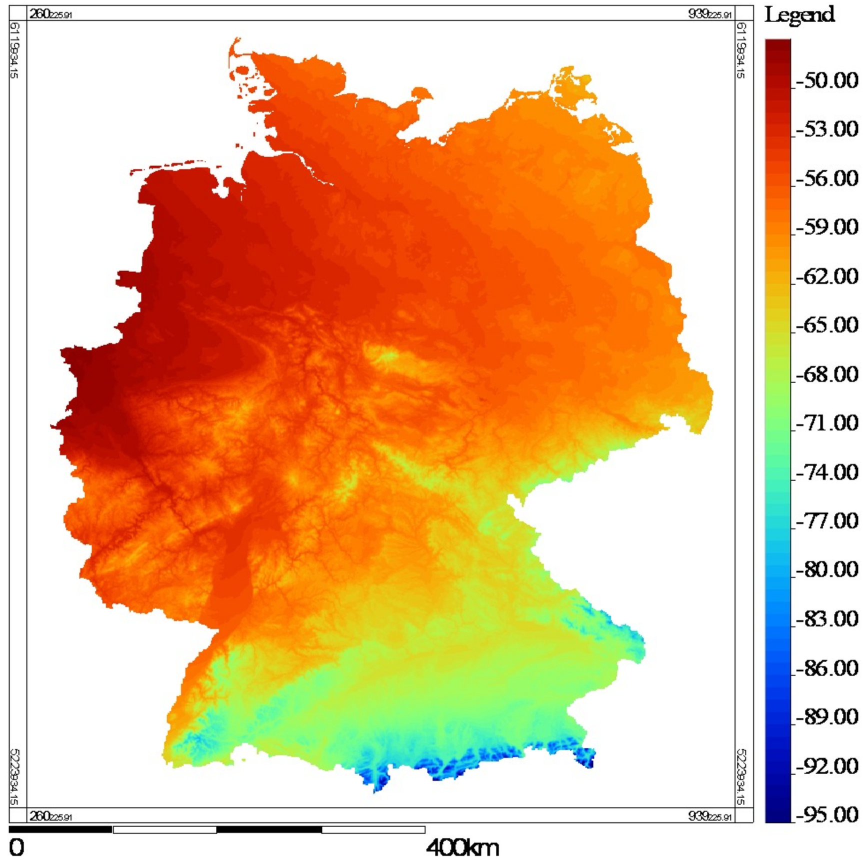


Figure 4.2.12.: Map of annual mean δ^2H values of precipitation in Germany. Values were calculated with the *Annual Mean MLR equation*. The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of δ^2H values in [‰ VSMOW].

4.3. Conclusions

To get a summary of the spatial and temporal distribution of the whole dataset boxplots of different groups of the data were created. From the boxplots of monthly $\delta^{18}O$ and $\delta^{2}H$ values of precipitation for all stations used within this study it could be seen that the δ values tend to decrease from the north of Germany towards the south, while the seasonal variation seems to increase in the same direction. This impression is confirmed when comparing seasonal variations of monthly $\delta^{18}O$ and $\delta^{2}H$ values at Norderney and Garmisch-Partenkirchen as typical examples for a maritime and a continental station. For the continental stations local temperature seems to control the variation of δ values through the year.

To predict monthly and annual amount-weighted mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany multiple linear regressions (MLRs) with different combinations and numbers of the chosen parameters (latitude squared, latitude, longitude, altitude, temperature and precipitation) were performed. The equations with the highest adjusted R^2 were considered to be the most suitable ones and are presented again in table 4.3.1.
As the influence of the different parameters on the isotope ratios of precipitation changes through the year the standard error of prediction of monthly mean δ values (calculated for full cross validation) could be reduced by setting up a separate regression equation for each single season instead of using one equation for all months. Temperature and latitude (as well as the squared latitude) are important parameters for the monthly MLR equations of winter, spring and autumn months. For the summer months, however, altitude and the amount of precipitation seem to dominate the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation. The average deviations between observed and predicted monthly mean $\delta^{18}O$ values of precipitation in Germany (standard errors of prediction for full cross validation) are between 0.66 ‰ for the summer months and 1.14 ‰ for the winter months. The standard errors for $\delta^{2}H$ range from 4.90 ‰ for the summer months to 7.97 ‰ for the autumn months.
For the prediction of amount-weighted annual mean isotope ratios the best results were obtained when the MLR equations were set up on observed annual mean δ values, using only geographic parameters for the regression. This resulted in standard errors of prediction for full cross validation of 0.43 ‰ for annual mean $\delta^{18}O$ values and 3.05 ‰ for $\delta^{2}H$. Calculating annual mean $\delta^{18}O$ and $\delta^{2}H$ values from the predicted monthly means leads to higher standard errors of prediction.

Using the most suitable MLR equations for each season, maps of monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany were created for every month. The same was done for the annual mean isotope ratios calculated with the respective regression equations.

Table 4.3.1.: MLR equations for the prediction of monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany set up in this study (equations 4.2.1 - 4.2.12). Results are in [‰ VSMOW]. ($\overline{\delta^{18}O}_{month/year}$: precipitation weighted mean monthly/annual $\delta^{18}O$ value of precipitation [‰ VSMOW]; $\overline{\delta^{2}H}_{month/year}$: precipitation weighted mean monthly/annual $\delta^{2}H$ value of precipitation [‰ VSMOW]; La^2: latitude squared [°^{2}]; La: latitude [°]; Lo: longitude [°]; A: altitude [m asl]; $\overline{T}_{month/year}$: precipitation weighted monthly/annual mean temperature [°C]; $\overline{P}_{month/year}$: mean monthly/annual amount of precipitation [mm].)

MLR Method	Months	MLR equation
All Months	all	$\overline{\delta^{18}O}_{month}$ = -0.08229*La^2 + 8.6270*La - 0.2034*Lo + 0.2685*$\overline{T}_{month}$ - 0.006326*$\overline{P}_{month}$ - 234.10
		$\overline{\delta^{2}H}_{month}$ = -0.68020*La^2 + 71.7846*La - 1.5049*Lo + 2.0246*$\overline{T}_{month}$ - 1953.38
Winter Months	D,J,F	$\overline{\delta^{18}O}_{month}$ = -0.1042*La^2 + 11.200*La - 0.08608*Lo + 0.004141*A + 0.7915*$\overline{T}_{month}$ - 0.010380*$\overline{P}_{month}$ - 311.00
		$\overline{\delta^{2}H}_{month}$ = -0.8003*La^2 + 86.740*La + 0.035280*A + 6.7480*$\overline{T}_{month}$ + 0.002694*$\overline{P}_{month}$ - 2435.00
Spring Months	M,A,M	$\overline{\delta^{18}O}_{month}$ = -0.1117*La^2 + 11.780*La - 0.1359*Lo - 0.0006893*A + 0.3004*$\overline{T}_{month}$ + 0.01049*$\overline{P}_{month}$ - 320.00
		$\overline{\delta^{2}H}_{month}$ = -0.8425*La^2 + 89.770*La - 1.2050*Lo + 2.4190*$\overline{T}_{month}$ + 0.09967*$\overline{P}_{month}$ - 2459.00
Summer Months	J,J,A	$\overline{\delta^{18}O}_{month}$ = -0.04910*La^2 + 4.638*La - 0.06254*Lo - 0.003699*A - 0.26140*$\overline{T}_{month}$ - 0.008429*$\overline{P}_{month}$ - 108.30
		$\overline{\delta^{2}H}_{month}$ = -0.32922*La^2 + 31.30882*La - 0.49481*Lo - 0.022550*A - 1.75749*$\overline{T}_{month}$ - 0.059750*$\overline{P}_{month}$ - 737.19
Autumn Months	S,O,N	$\overline{\delta^{18}O}_{month}$ = -0.08574*La^2 + 8.948*La - 0.2869*Lo + 0.2699*$\overline{T}_{month}$ - 0.0072*$\overline{P}_{month}$ - 241.50
		$\overline{\delta^{2}H}_{month}$ = -0.70150*La^2 + 73.9115*La - 2.0574*Lo + 2.0206*$\overline{T}_{month}$ - 2006.32
Annual Mean		$\overline{\delta^{18}O}_{year}$ = -0.07975*La^2 + 8.164*La - 0.1519*Lo - 0.002589*A - 214.80
		$\overline{\delta^{2}H}_{year}$ = -0.58950*La^2 + 61.110*La - 1.2750*Lo - 0.015080*A - 1623.00

5. Discussion

The objective of this work was to evaluate regionalization methods determining the spatio-temporal distribution of the isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of precipitation in Germany (expressed with $\delta^{18}O$ and $\delta^{2}H$ in [‰]). Using the most suitable methods the spatial distribution of monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values should be calculated and presented in maps for Germany. These goals were achieved by setting up multiple linear regression (MLR) equations on monthly and annual amount-weighted mean values of $\delta^{18}O$ and $\delta^{2}H$ of precipitation from 17 German GNIP (Global Network of Isotopes in Precipitation) stations, 12 DWD (German Weather Service) stations and 4 stations of the Austrian Network of Isotopes in Precipitation (ANIP) (all provided by Willibald Stichler, GSF, Neuherberg), as well as from the GNIP station in Groningen, Netherlands (IAEA/WMO, 2004).

MLR equations were chosen to predict isotope ratios of precipitation in Germany as they allow to combine different parameters representing the different effects on the isotopic composition and can be performed within the given period. Latitude, longitude, altitude, temperature and precipitation have been used as regression parameters as they stand for known isotope effects describing the isotopic depletion of precipitation when the rainout of vapour masses proceeds (Rayleigh distillation). The amount of precipitation can also be used as an indicator for the degree of evaporation of falling raindrops, leading to an isotopic enrichment of precipitation. As done by Bowen and Wilkinson (2002) the squared latitude was added to this set of parameters to improve predictions. Although there is a clear physical effect of the regression parameters on the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation, multicollinearity of the parameters prevents the corresponding coefficients in the regression equations from getting the meaning of a physical gradient. So the MLR equations cannot be seen as physical models and must not be used for places outside of Germany.

As the influence of the different parameters on the isotope ratios of precipitation changes through the year the quality of the prediction of monthly mean values of $\delta^{18}O$ and $\delta^{2}H$ could be significantly improved by setting up a separate regression equation for each season instead of using one equation for all months. Average deviations between observed and predicted monthly means of $\delta^{18}O$ (standard errors of prediction for full cross validation, including all stations available (equation 3.2.4)) range from 0.66 ‰ for the summer months to 1.14 ‰ for the winter months, standard errors for $\delta^{2}H$ are between 4.90 ‰ for the summer months and 7.97 ‰ for the autumn months. The low uncertainties for the summer months are most likely due to a generally lower spatial and temporal variability of the monthly mean isotope ratios during this time of the year. When comparing these uncertainties of the predicted monthly mean δ values with their spatial variability throughout Germany (shown in

the maps in figures 4.2.5 to 4.2.10) one can see that the regression equations allow the differentiation of regions within Germany for all months. Beyond that, monthly mean δ values for the summer months can well be distinguished from isotope ratios predicted for the winter months.
For the prediction of amount-weighted annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation standard errors of prediction for full cross validation of 0.43 ‰ and 3.05 ‰ are obtained for $\delta^{18}O$ and $\delta^{2}H$ respectively. Considering the spatial variation of the predicted annual mean values of $\delta^{18}O$ from about -7 ‰ in the north-west of Germany to about -11.5 ‰ in the south-east (not including places within the higher parts of the Alps), shown in the map in figure 4.2.11, clear spatial differentiations can be derived from the predicted values. The same is true for the predicted annual mean values of $\delta^{2}H$, showing a spatial variation from approximately -50 ‰ in the north-west to about -75 ‰ in the sout-east (see figure 4.2.12).

When looking at the frequency distribution of the estimation errors for full cross validation (predicted - observed δ values, shown in figures A.0.8 to A.0.11) it can be seen that predicted δ values closely match the observed ones for a clear majority of stations and months. However, there are a few stations showing higher deviations between observed and predicted monthly and annual mean isotope ratios (see table 4.2.7).
Highest over- and underestimations of observed annual mean $\delta^{18}O$ values are obtained for Emmerich (+0.92 ‰) and Regensburg (-0.83 ‰). Worst predictions of annual means of $\delta^{2}H$ were found for Emmerich (+5.87 ‰) and Cuxhaven (-4.33 ‰). Thus, even for places with bad predictions, clear differentiations can be made between annual mean values predicted for the north-west and the south-east of Germany.
The highest deviations between observed and predicted monthly mean $\delta^{18}O$ values are obtained for Neubrandenburg in April, where the observed value is overestimated by 2.80 ‰ and for Regensburg in March, where the predicted value is 2.56 ‰ lower than the observed one. For $\delta^{2}H$ the highest deviations between measured and predicted monthly means were observed at Garmisch-Partenkirchen (overestimation of the measured value by 22.01 ‰ for November) and at Berlin (underestimation by 17.86 ‰ for March). Stronger underestimations for $\delta^{18}O$ as well as for $\delta^{2}H$ are obtained for Zinnwald in January, but as data from Zinnwald are only based on measurements from January 2001 to December 2002 these deviations are most likely caused by the short period of the data record. So, for a few places in Germany the prediction of the mean δ values seems to be difficult for certain months. This might be due to local conditions that are not represented by the regression parameters used in this study.

The quality of prediction of the regression equations might be further improved by adding the relative humidity to the set of parameters to take into account the isotopic enrichment of precipitation by subcloud evaporation, as done by LIEBMINGER ET AL. (2006b). The North Atlantic Oscillation (NAO) index could help to incorporate changes in weather conditions, although DAR-

LING and TALBOT (2003) could not find a clear correlation between the annual NAO index and annual mean $\delta^{18}O$ values of precipitation for Wallingford, England, and Valentia, Ireland.
As can be seen by the comparison of the predictions based on all stations and those based on GNIP stations alone, the quality of the regressions also depends on the density and distribution of the isotope stations. To get good estimates of the long term mean values and to provide data for trend analysis it is important that long time series of the isotope ratios are recorded at as many stations as possible.
The setup of a physical model to predict $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany might lead to further improvement of the quality of prediction.

After all it can be said that the MLR equations for predicting monthly and annual mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in Germany, that were set up in this study, present the basis for a possible future transformation from the isotope ratios of precipitation to the isotopic concentrations in local groundwater.

A. Appendix

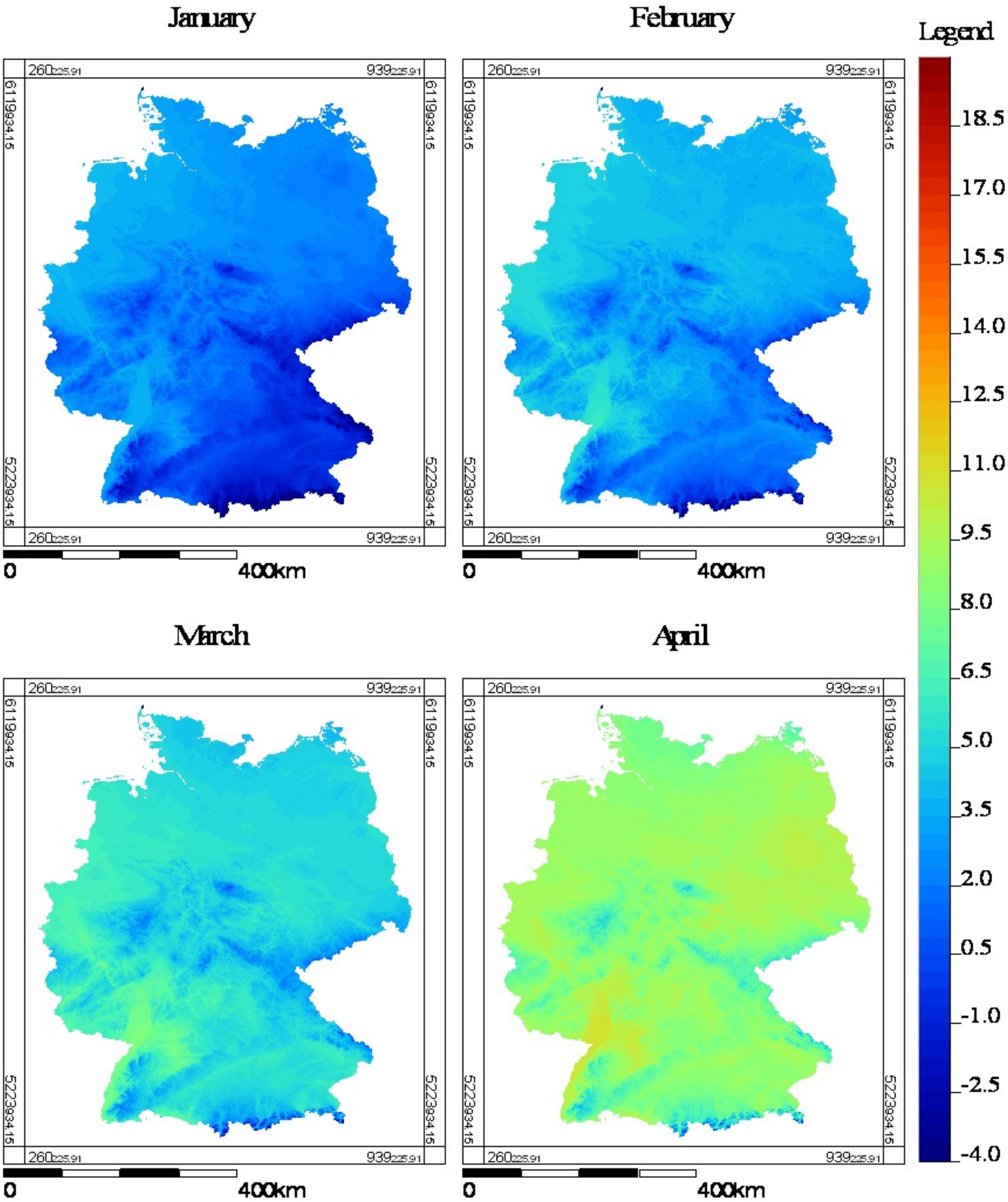


Figure A.0.1.: Maps of monthly mean temperature values from January to April, created by inverse distance weighting (IDW). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of temperature values in [°C].

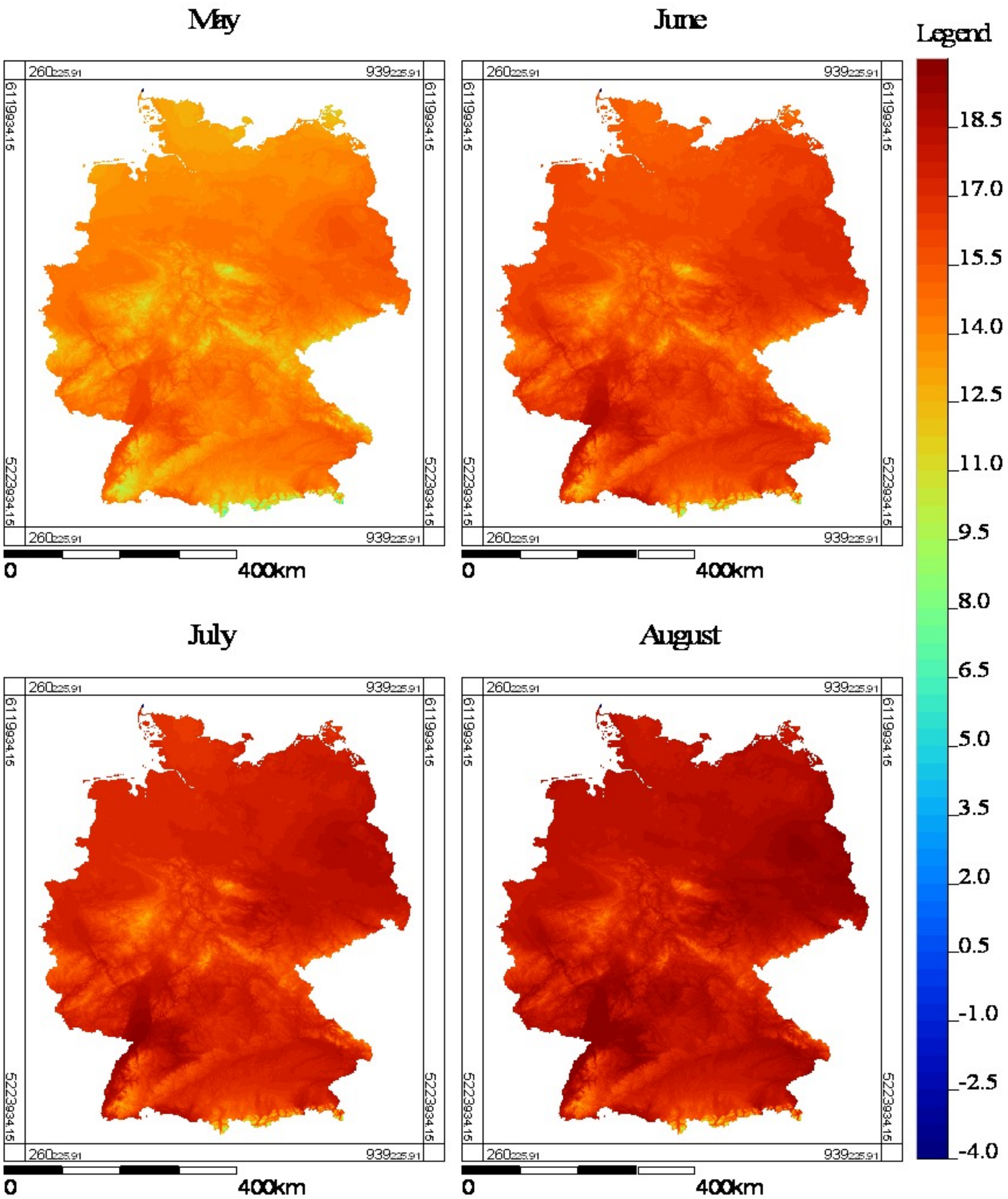


Figure A.0.2.: Maps of monthly mean temperature values from May to August, created by inverse distance weighting (IDW). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of temperature values in [°C].

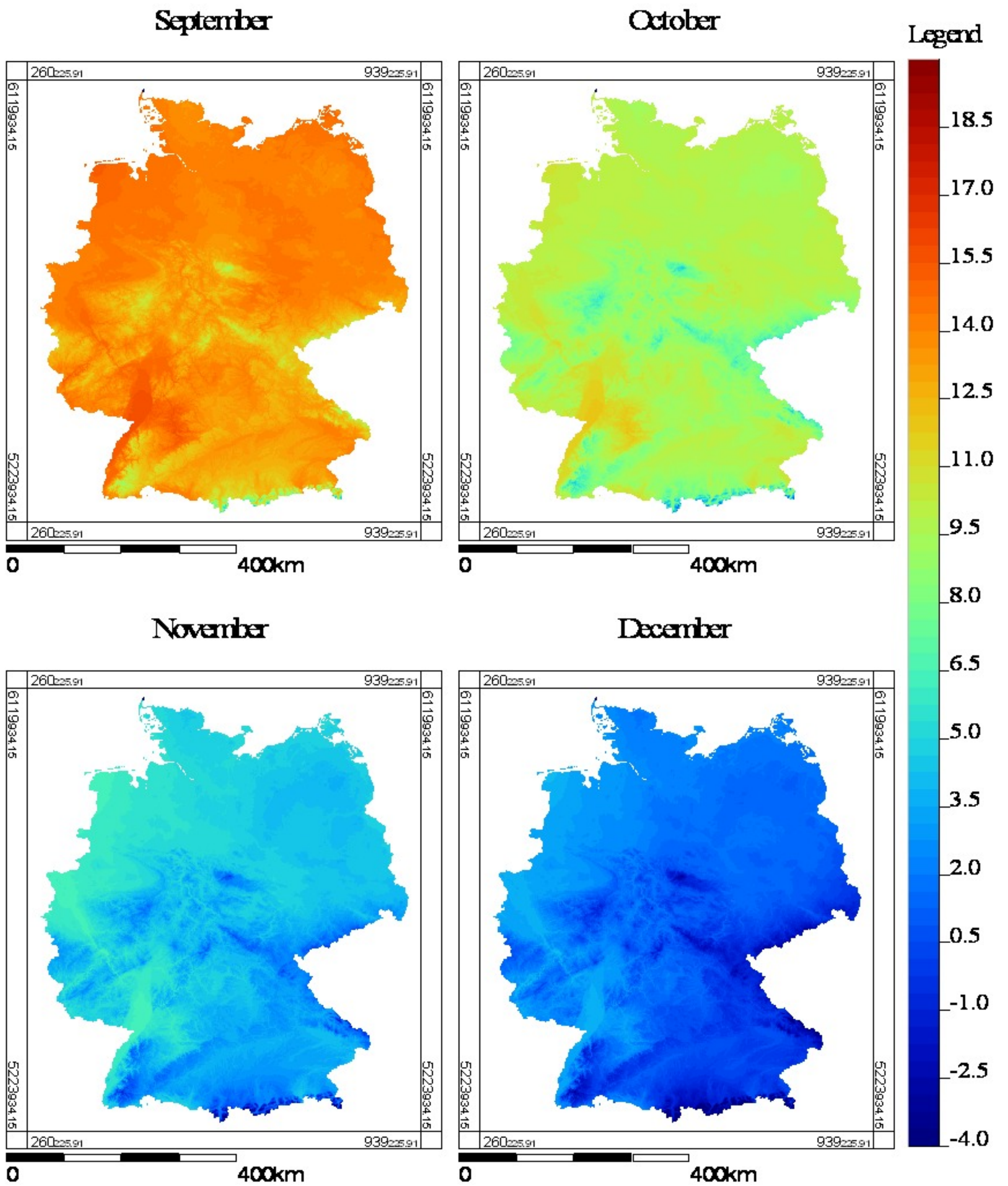


Figure A.0.3.: Maps of monthly mean temperature values of precipitation from September to December, created by inverse distance weighting (IDW). The horizontal resolution is 30 arc seconds (approximately 1km). The legend shows the range of temperature values in [°C].

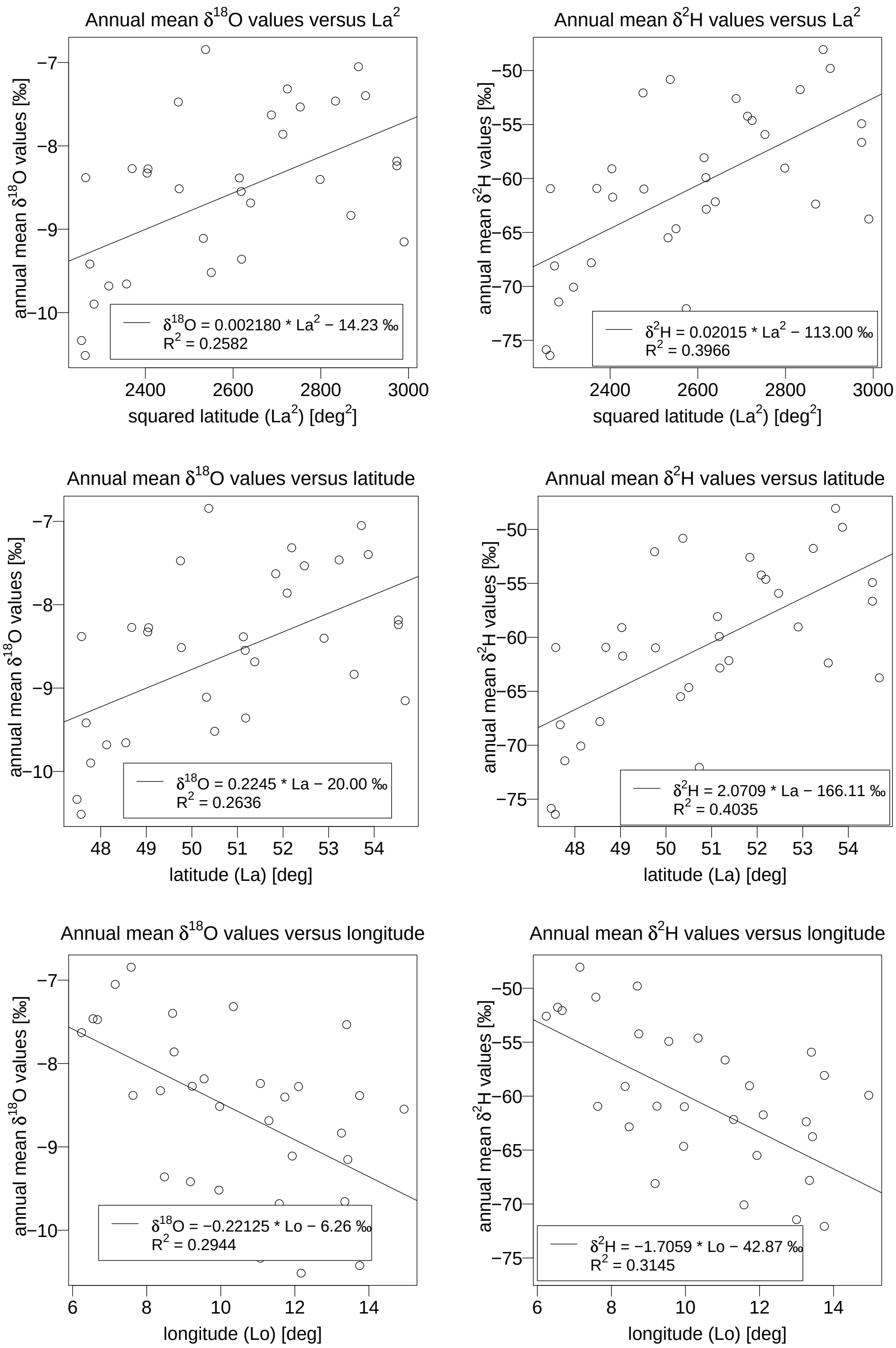


Figure A.0.4.: Scatterplots of annual mean $\delta^{18}O$ and δ^2H values versus latitude squared, latitude and longitude of all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria). The regression equations and the corresponding R^2 values are shown in the plots.

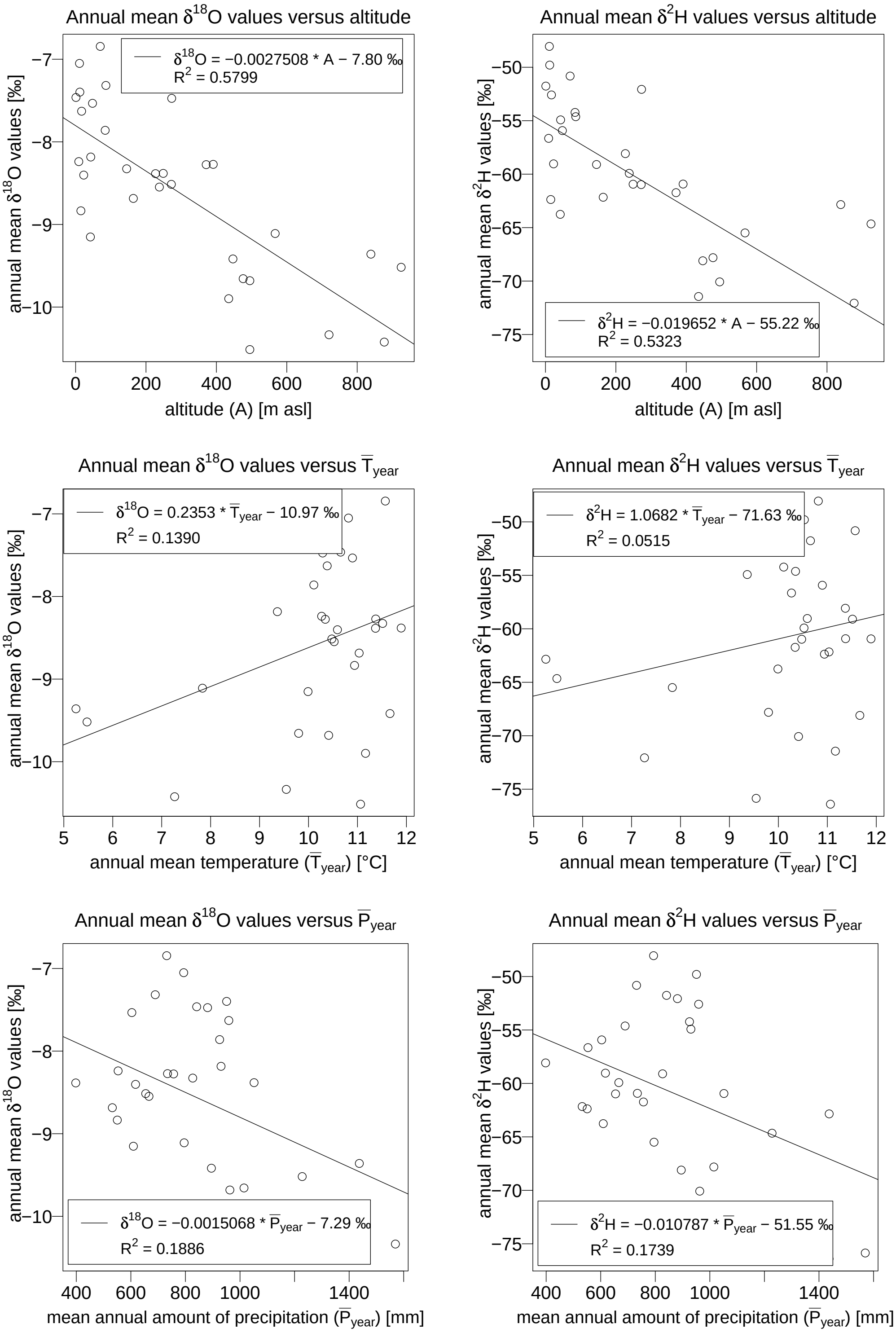


Figure A.0.5.: Scatterplots of annual mean $\delta^{18}O$ and $\delta^{2}H$ values versus altitude, monthly mean temperature and mean monthly amount of precipitation of all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria). The regression equations and the corresponding R^2 values are shown in the plots.

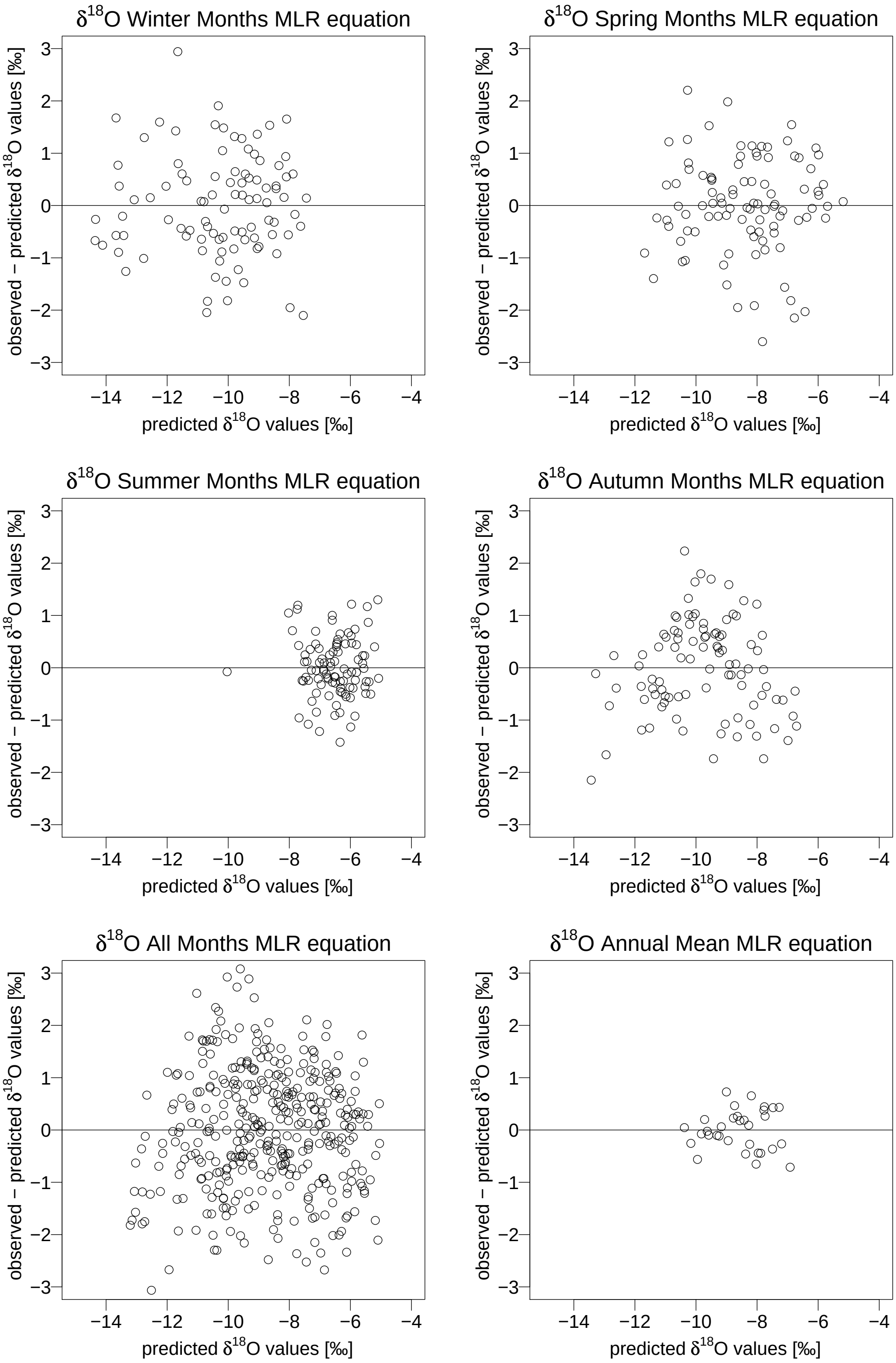


Figure A.0.6.: Residuals between the observed $\delta^{18}O$ values and the ones predicted by the different MLR equations presented in section 4.2 are plotted against the predicted values to check for heteroscedasticity. The data were taken from all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria).

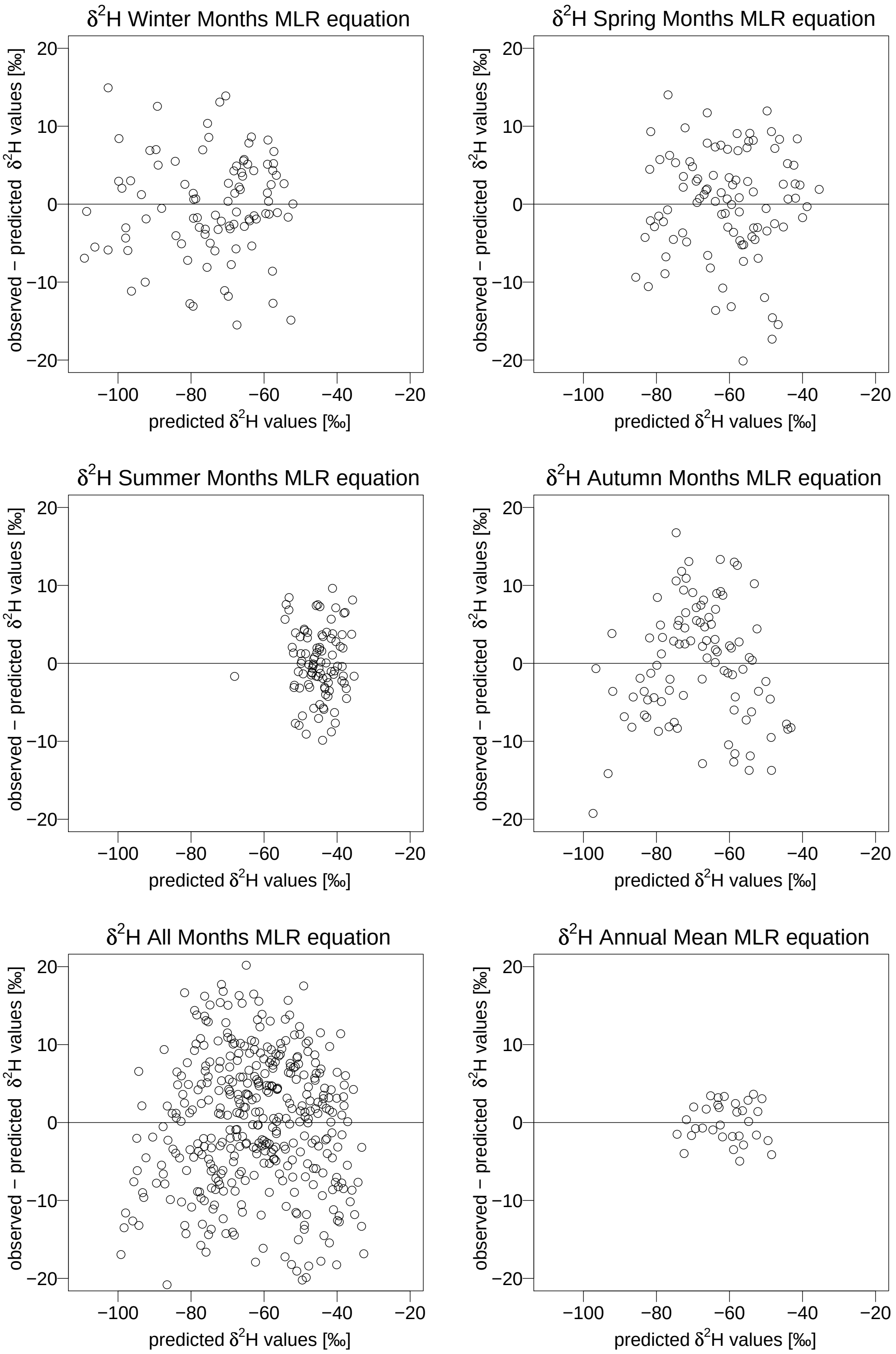


Figure A.0.7.: Residuals between the observed $\delta^2 H$ values and the ones predicted by the different MLR equations presented in section 4.2 are plotted against the predicted values to check for heteroscedasticity. The data were taken from all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria).

Table A.0.1.: Regression equations based on monthly mean values of all months, winter months and spring months for all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria). Equations are sorted by their adjusted R^2 (R$_a^2$). Results are in [‰ VSMOW]. ($\overline{\delta^{18}O}_{month}$: precipitation weighted mean monthly $\delta^{18}O$ value of precipitation [‰ VSMOW]; $\overline{\delta^{2}H}_{month}$: precipitation weighted mean monthly $\delta^{2}H$ value of precipitation [‰ VSMOW]; La^2: latitude squared [°^{2}]; La: latitude [°]; Lo: longitude [°]; A: altitude [m asl]; $\overline{T}_{month}$: precipitation weighted monthly mean temperature [°C]; $\overline{P}_{month}$: mean monthly amount of precipitation [mm].)

Method	Months	MLR equations sorted by adjusted R^2 (R$_a^2$)	R$_a^2$
$\delta^{18}O$		$\overline{\delta^{18}O}_{month}$ = -0.08229*La^2 + 8.6270*La - 0.2034*Lo + 0.2685*$\overline{T}_{month}$ - 0.006326*$\overline{P}_{month}$ - 234.10	0.7251
All	all	$\overline{\delta^{18}O}_{month}$ = -0.08373*La^2 + 8.7670*La - 0.2004*Lo - 0.000115*A + 0.2672*$\overline{T}_{month}$ - 0.005870*$\overline{P}_{month}$ - 237.60	0.7245
Months		$\overline{\delta^{18}O}_{month}$ = -0.09310*La^2 + 9.7200*La - 0.1842*Lo - 0.000574*A + 0.2578*$\overline{T}_{month}$ - 262.10	0.7213
MLR		$\overline{\delta^{18}O}_{month}$ = -0.08797*La^2 + 9.2380*La - 0.1965*Lo + 0.2619*$\overline{T}_{month}$ - 251.00	0.7193
$\delta^{2}H$		$\overline{\delta^{2}H}_{month}$ = -0.68020*La^2 + 71.7846*La - 1.5049*Lo + 2.0246*$\overline{T}_{month}$ - 1953.38	0.7444
All	all	$\overline{\delta^{2}H}_{month}$ = -0.66700*La^2 + 70.5500*La - 1.5360*Lo + 0.001474*A + 2.0350*$\overline{T}_{month}$ - 1925.00	0.7440
Months		$\overline{\delta^{2}H}_{month}$ = -0.63670*La^2 + 67.4700*La - 1.5890*Lo + 0.002957*A + 2.0650*$\overline{T}_{month}$ - 0.018970*$\overline{P}_{month}$ - 1846.00	0.7440
MLR		$\overline{\delta^{2}H}_{month}$ = -0.67370*La^2 + 71.0900*La - 1.5130*Lo + 2.0320*$\overline{T}_{month}$ - 0.007230*$\overline{P}_{month}$ - 1934.00	0.7438
$\delta^{18}O$		$\overline{\delta^{18}O}_{month}$ = -0.10420*La^2 + 11.2000*La - 0.0861*Lo + 0.004141*A + 0.7915*$\overline{T}_{month}$ - 0.010380*$\overline{P}_{month}$ - 311.00	0.7535
Winter	D,J,F	$\overline{\delta^{18}O}_{month}$ = -0.10730*La^2 + 11.5000*La + 0.004132*A + 0.8614*$\overline{T}_{month}$ - 0.005989*$\overline{P}_{month}$ - 319.60	0.7507
Months		$\overline{\delta^{18}O}_{month}$ = -0.10920*La^2 + 11.6700*La + 0.003560*A + 0.8327*$\overline{T}_{month}$ - 323.20	0.7502
MLR		$\overline{\delta^{18}O}_{month}$ = -0.10850*La^2 + 11.5900*La - 0.0370*Lo + 0.003383*A + 0.7935*$\overline{T}_{month}$ - 320.70	0.7488
$\delta^{2}H$		$\overline{\delta^{2}H}_{month}$ = -0.80030*La^2 + 86.7400*La + 0.035280*A + 6.7480*$\overline{T}_{month}$ + 0.002694*$\overline{P}_{month}$ - 2435.00	0.8125
Winter	D,J,F	$\overline{\delta^{2}H}_{month}$ = -0.79160*La^2 + 85.8400*La - 0.3930*Lo + 0.033660*A + 6.3450*$\overline{T}_{month}$ - 2407.00	0.8045
Months		$\overline{\delta^{2}H}_{month}$ = -0.79950*La^2 + 86.6600*La + 0.035540*A + 6.7610*$\overline{T}_{month}$ - 2433.00	0.8042
MLR		$\overline{\delta^{2}H}_{month}$ = -0.78230*La^2 + 84.9900*La - 0.5011*Lo + 0.035330*A + 6.3410*$\overline{T}_{month}$ - 0.022880*$\overline{P}_{month}$ - 2385.00	0.8029
$\delta^{18}O$		$\overline{\delta^{18}O}_{month}$ = -0.11170*La^2 + 11.7800*La - 0.1359*Lo - 0.000689*A + 0.3004*$\overline{T}_{month}$ + 0.010490*$\overline{P}_{month}$ - 320.00	0.7209
Spring	M,A,M	$\overline{\delta^{18}O}_{month}$ = -0.10230*La^2 + 10.8500*La - 0.1524*Lo + 0.3095*$\overline{T}_{month}$ + 0.008177*$\overline{P}_{month}$ - 297.20	0.7188
Months		$\overline{\delta^{18}O}_{month}$ = -0.09063*La^2 + 9.6015*La - 0.1615*Lo + 0.2963*$\overline{T}_{month}$ - 262.85	0.7138
MLR		$\overline{\delta^{18}O}_{month}$ = -0.09368*La^2 + 9.8860*La - 0.1547*Lo - 0.000341*A + 0.2899*$\overline{T}_{month}$ - 269.40	0.7120
$\delta^{2}H$		$\overline{\delta^{2}H}_{month}$ = -0.84250*La^2 + 89.7700*La - 1.2050*Lo + 2.4190*$\overline{T}_{month}$ + 0.099670*$\overline{P}_{month}$ - 2459.00	0.7457
Spring	M,A,M	$\overline{\delta^{2}H}_{month}$ = -0.83040*La^2 + 88.5800*La - 1.2260*Lo + 0.000884*A + 2.4310*$\overline{T}_{month}$ + 0.096710*$\overline{P}_{month}$ - 2430.00	0.7430
Months		$\overline{\delta^{2}H}_{month}$ = -0.66400*La^2 + 71.0800*La - 1.3990*Lo + 0.004093*A + 2.3350*$\overline{T}_{month}$ - 1963.00	0.7293
MLR		$\overline{\delta^{2}H}_{month}$ = -0.70060*La^2 + 74.4985*La - 1.3162*Lo + 2.2584*$\overline{T}_{month}$ - 2040.78	0.7289

Table A.0.2.: Regression equations based on monthly mean values of summer and autumn months as well as on annual means for all German stations, plus Groningen (Netherlands), Kufstein and Salzburg (Austria). Equations are sorted by their adjusted R^2 (R^2_a). ($\overline{\delta^{18}O}_{month/year}$: precipitation weighted mean monthly/annual $\delta^{18}O$ value of precipitation [‰ VSMOW]; $\overline{\delta^{2}H}_{month/year}$: precipitation weighted mean monthly/annual $\delta^{2}H$ value of precipitation [‰ VSMOW]; La^2: latitude squared [°^{2}]; La: latitude [°]; Lo: longitude [°]; A: altitude [m asl]; $\overline{T}_{month/year}$: precipitation weighted monthly/annual mean temperature [°C]; $\overline{P}_{month/year}$: mean monthly/annual amount of precipitation [mm].)

Method	Months	MLR equations sorted by adjusted R^2 (R^2_a)	R^2_a
$\delta^{18}O$	J,J,A	$\overline{\delta^{18}O}_{month}$ = -0.04910*La^2 + 4.6380*La - 0.0625*Lo - 0.003699*A - 0.2614*$\overline{T}_{month}$ - 0.008429*$\overline{P}_{month}$ - 108.30	0.6297
Summer		$\overline{\delta^{18}O}_{month}$ = -0.05204*La^2 + 4.9030*La - 0.004145*A - 0.3036*$\overline{T}_{month}$ - 0.008402*$\overline{P}_{month}$ - 113.90	0.6124
Months		$\overline{\delta^{18}O}_{month}$ = -0.00350*La^2 - 0.0692*Lo - 0.003330*A - 0.2592*$\overline{T}_{month}$ - 0.011038*$\overline{P}_{month}$ + 9.62	0.5932
MLR		$\overline{\delta^{18}O}_{month}$ = - 0.3506*La - 0.0708*Lo - 0.003257*A - 0.2541*$\overline{T}_{month}$ - 0.011214*$\overline{P}_{month}$ + 18.31	0.5868
$\delta^{2}H$	J,J,A	$\overline{\delta^{2}H}_{month}$ = -0.32922*La^2 + 31.3088*La - 0.4948*Lo - 0.022550*A - 1.7575*$\overline{T}_{month}$ - 0.059750*$\overline{P}_{month}$ - 737.19	0.5503
Summer		$\overline{\delta^{2}H}_{month}$ = -0.35250*La^2 + 33.4000*La - 0.026070*A - 2.0910*$\overline{T}_{month}$ - 0.059530*$\overline{P}_{month}$ - 781.50	0.5271
Months		$\overline{\delta^{2}H}_{month}$ = -0.02146*La^2 - 0.5404*Lo - 0.020054*A - 1.7422*$\overline{T}_{month}$ - 0.077359*$\overline{P}_{month}$ + 58.58	0.5165
MLR		$\overline{\delta^{2}H}_{month}$ = - 2.1443*La - 0.5501*Lo - 0.019580*A - 1.7085*$\overline{T}_{month}$ - 0.078420*$\overline{P}_{month}$ + 111.51	0.5109
$\delta^{18}O$	S,O,N	$\overline{\delta^{18}O}_{month}$ = -0.08574*La^2 + 8.9480*La - 0.2869*Lo + 0.2699*$\overline{T}_{month}$ - 0.007200*$\overline{P}_{month}$ - 241.50	0.7349
Autumn		$\overline{\delta^{18}O}_{month}$ = -0.09679*La^2 + 10.050*La - 0.2509*Lo - 0.000787*A + 0.2555*$\overline{T}_{month}$ - 269.70	0.7326
Months		$\overline{\delta^{18}O}_{month}$ = -0.08884*La^2 + 9.2530*La - 0.2773*Lo - 0.000259*A + 0.2654*$\overline{T}_{month}$ - 0.005624*$\overline{P}_{month}$ - 249.10	0.7323
MLR		$\overline{\delta^{18}O}_{month}$ = -0.09066*La^2 + 9.4850*La - 0.2662*Lo + 0.2677*$\overline{T}_{month}$ - 256.84	0.7277
$\delta^{2}H$	S,O,N	$\overline{\delta^{2}H}_{month}$ = -0.70150*La^2 + 73.9115*La - 2.0574*Lo + 2.0206*$\overline{T}_{month}$ - 2006.32	0.7166
Autumn		$\overline{\delta^{2}H}_{month}$ = -0.69220*La^2 + 72.8900*La - 2.0970*Lo + 2.0250*$\overline{T}_{month}$ - 0.01364*$\overline{P}_{month}$ - 1977.00	0.7140
Months		$\overline{\delta^{2}H}_{month}$ = -0.70330*La^2 + 74.0800*La - 2.0530*Lo - 0.000238*A + 2.0170*$\overline{T}_{month}$ - 2010.00	0.7134
MLR		$\overline{\delta^{2}H}_{month}$ = -0.66320*La^2 + 70.0500*La - 2.1860*Lo + 0.002423*A + 2.0670*$\overline{T}_{month}$ - 0.02837*$\overline{P}_{month}$ - 1906.00	0.7113
$\delta^{18}O$		$\overline{\delta^{18}O}_{year}$ = -0.07371*La^2 + 7.5490*La - 0.1546*Lo - 0.002444*A - 199.20	0.8352
Annual		$\overline{\delta^{18}O}_{year}$ = -0.06666*La^2 + 6.8260*La - 0.1680*Lo - 0.002275*A - 0.000285*$\overline{P}_{year}$ - 180.30	0.8321
Mean		$\overline{\delta^{18}O}_{year}$ = -0.07631*La^2 + 7.8540*La - 0.1618*Lo - 0.001981*A + 0.0678*$\overline{T}_{year}$ - 208.70	0.8300
MLR		$\overline{\delta^{18}O}_{year}$ = -0.06729*La^2 + 6.8950*La - 0.1684*Lo - 0.002210*A + 0.0089*$\overline{T}_{year}$ - 0.000274*$\overline{P}_{year}$ - 182.30	0.8254
$\delta^{2}H$		$\overline{\delta^{2}H}_{year}$ = -0.50960*La^2 + 52.9800*La - 1.3100*Lo - 0.013150*A - 1417.00	0.8714
Annual		$\overline{\delta^{2}H}_{year}$ = -0.47820*La^2 + 49.7500*La - 1.3700*Lo - 0.012390*A - 0.001272*$\overline{P}_{year}$ - 1333.00	0.8676
Mean		$\overline{\delta^{2}H}_{year}$ = -0.52130*La^2 + 54.3500*La - 1.3430*Lo - 0.011050*A + 0.3072*$\overline{T}_{year}$ - 1460.00	0.8668
MLR		$\overline{\delta^{2}H}_{year}$ = -0.48140*La^2 + 50.1100*La - 1.3720*Lo - 0.012110*A + 0.0463*$\overline{T}_{year}$ - 0.001212*$\overline{P}_{year}$ - 1343.00	0.8623

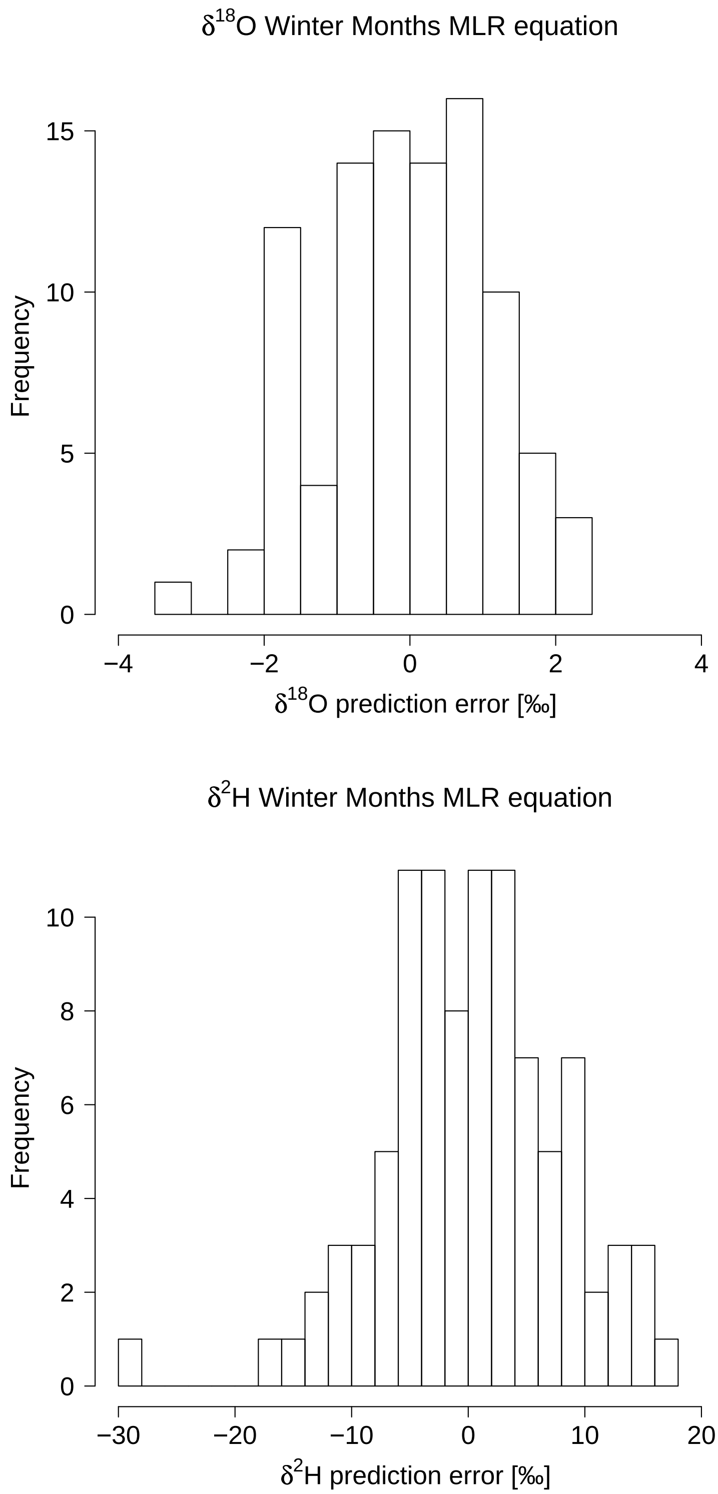


Figure A.0.8.: Frequency distribution for the estimation error of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein and Salzburg (Austria) using the respective MLR equations for the winter months. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).

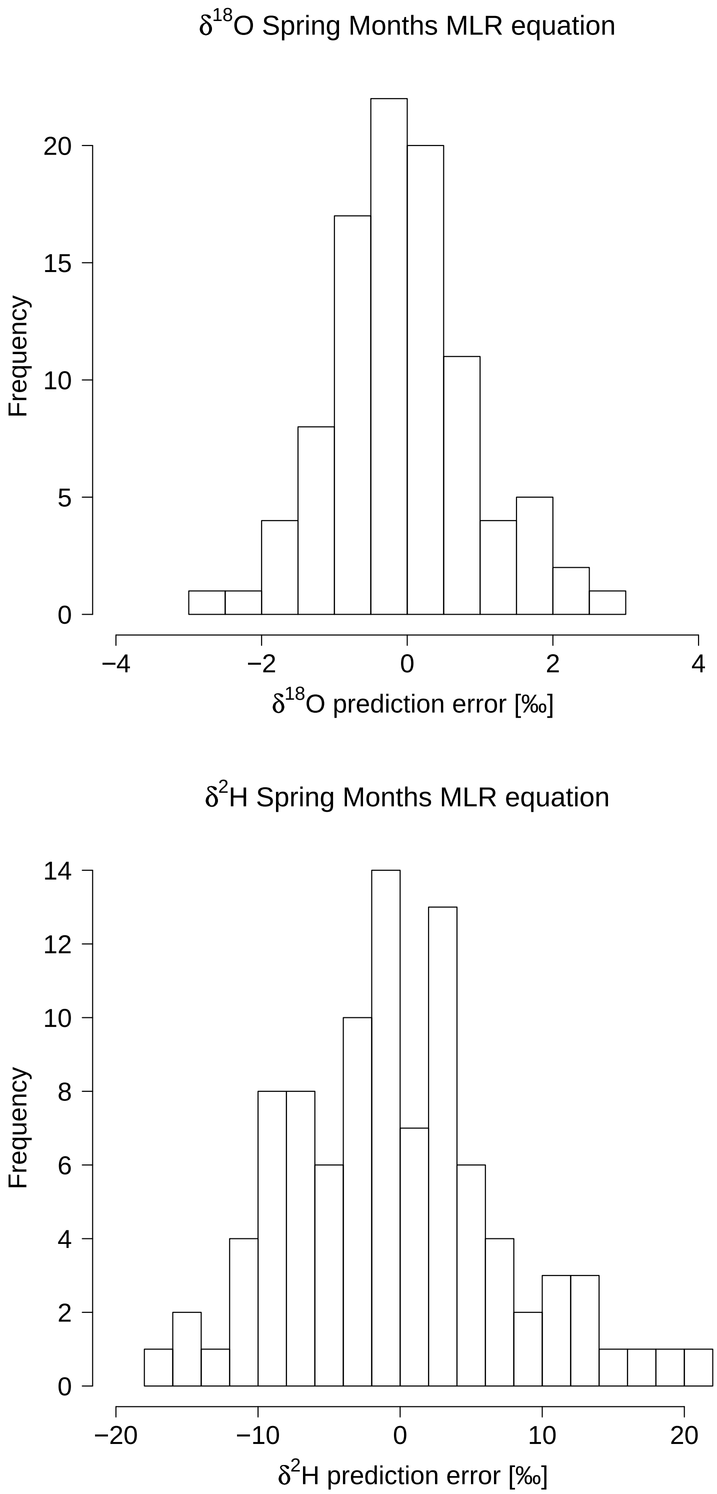


Figure A.0.9.: Frequency distribution for the estimation error of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein and Salzburg (Austria) using the respective MLR equations for the spring months. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).

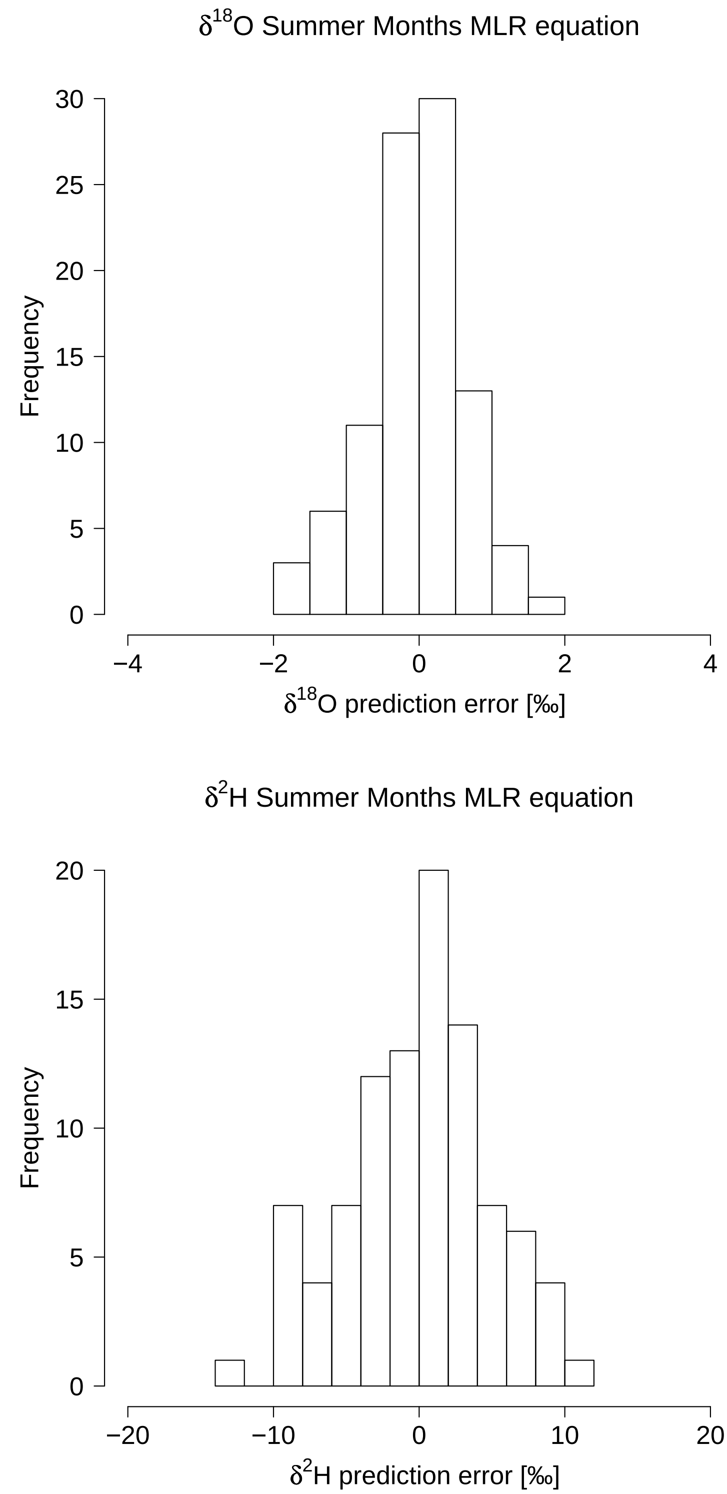


Figure A.0.10.: Frequency distribution for the estimation error of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein and Salzburg (Austria) using the respective MLR equations for the summer months. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).

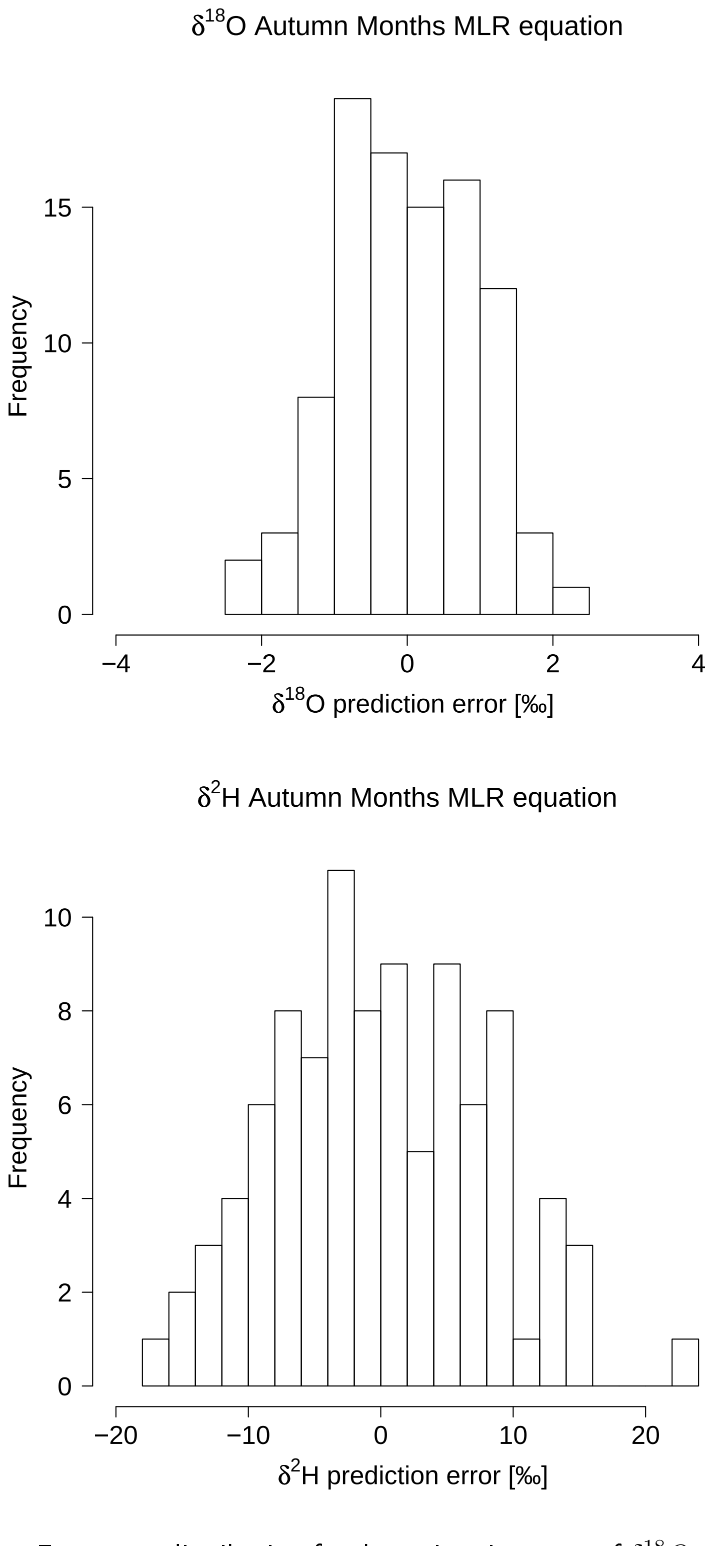
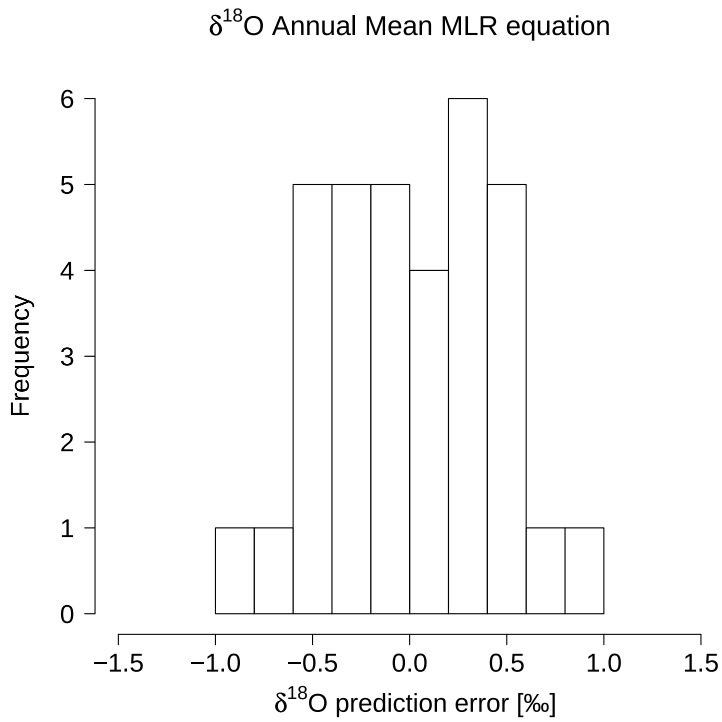


Figure A.0.11.: Frequency distribution for the estimation error of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein and Salzburg (Austria) using the respective MLR equations for the autumn months. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).



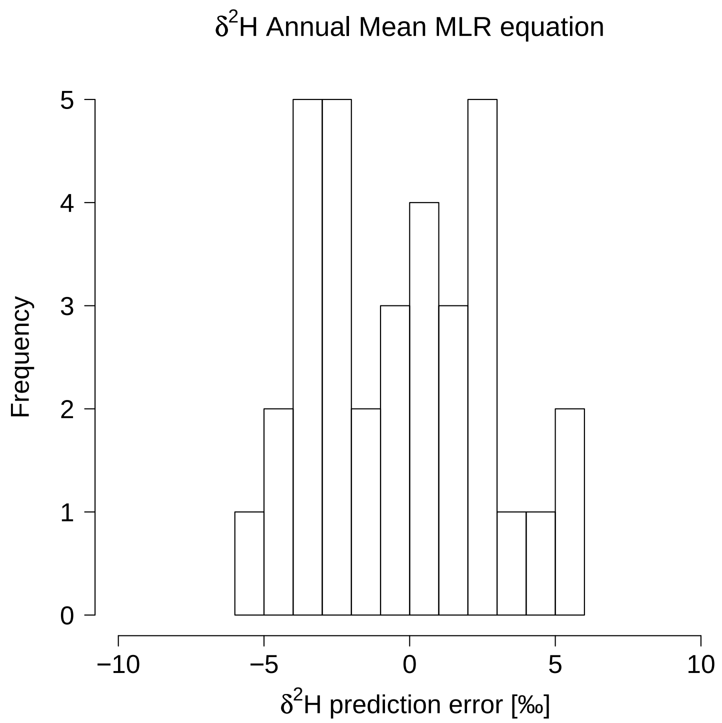
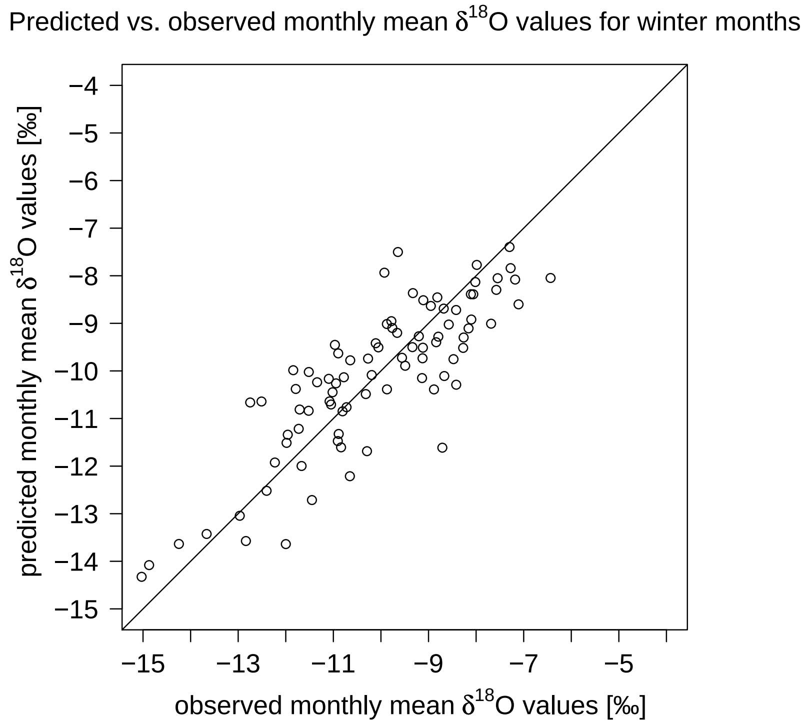


Figure A.0.12.: Frequency distribution for the estimation error of annual mean δ^2H and $\delta^{18}O$ values of precipitation calculated for all German stations plus Groningen (Netherlands), Kufstein, Reutte, Salzburg and Scharnitz (Austria) using the respective Annual MLR equations. The estimation errors equal the difference between the value observed at a certain station and the one predicted by the MLR equation based on the rest of the stations (predicted - observed).



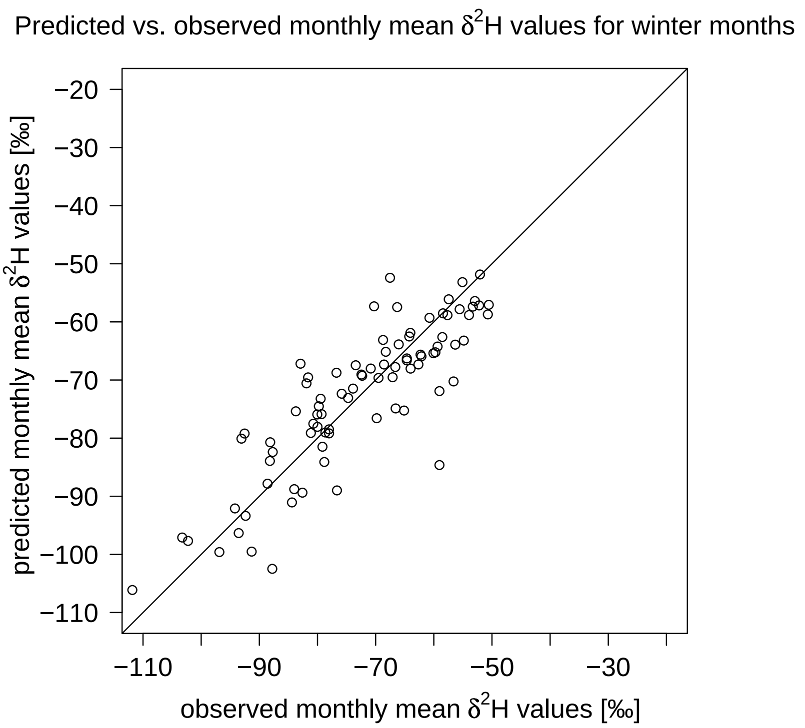
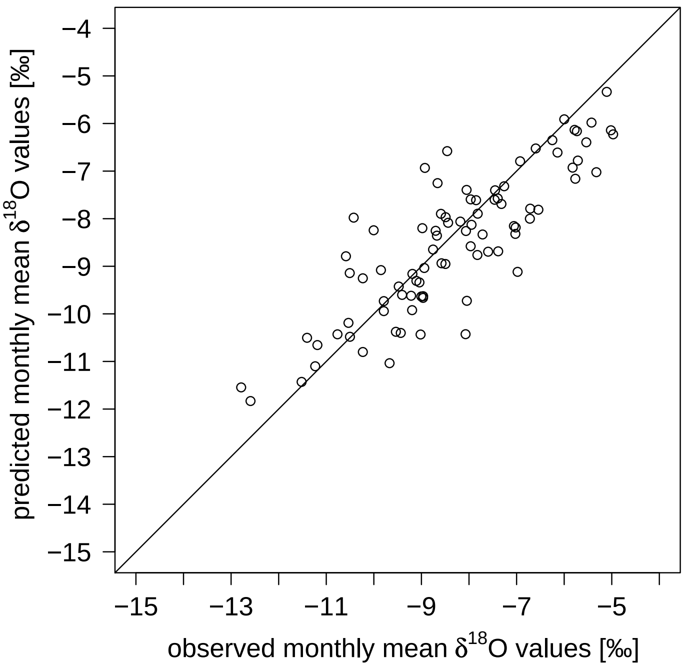


Figure A.0.13.: Predicted versus observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ values at German GNIP and DWD stations for winter months. Predicted values were calculated with the MLR equations 4.2.3 and 4.2.4 respectively.

Predicted vs. observed monthly mean δ18O values for spring months



Predicted vs. observed monthly mean δ2H values for spring months

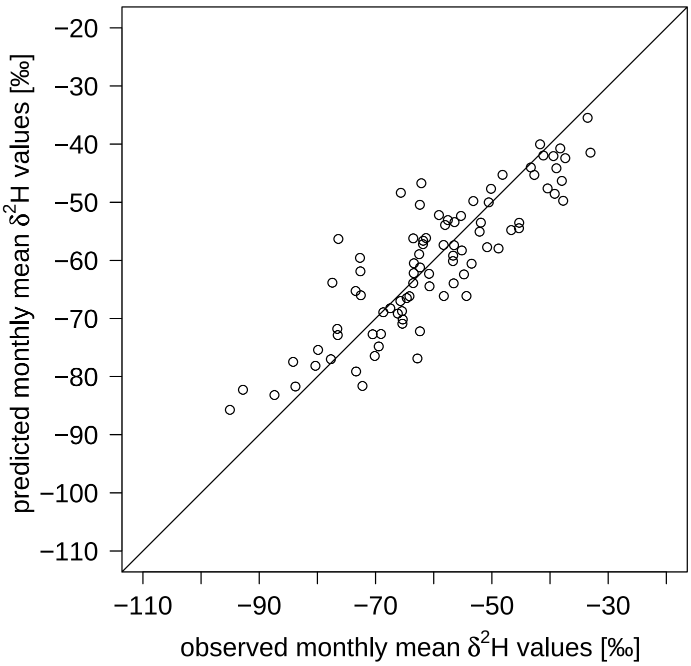
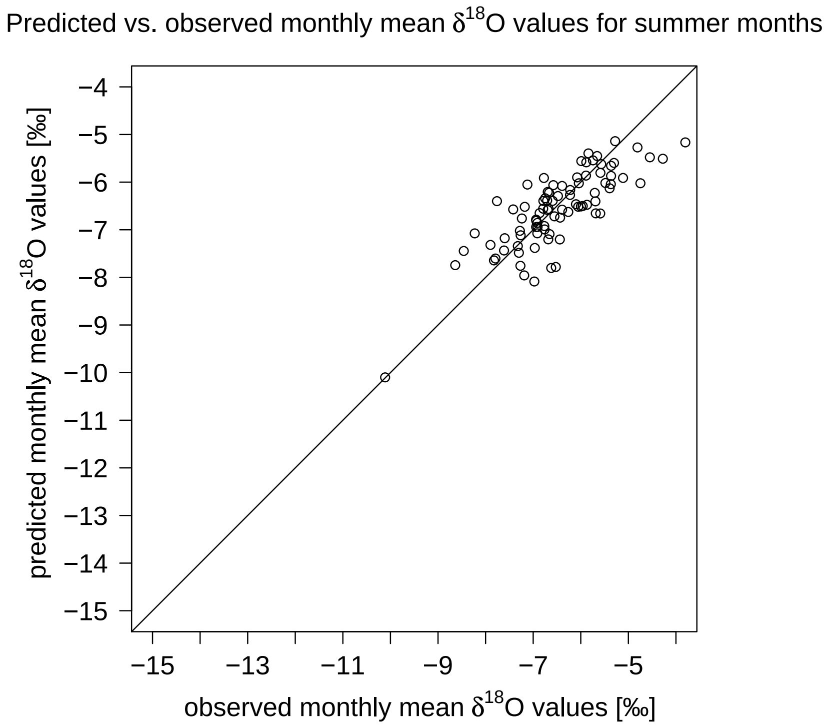


Figure A.0.14.: Predicted versus observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of German GNIP and DWD stations for spring months. Predicted values were calculated with the MLR equations 4.2.5 and 4.2.6 respectively.



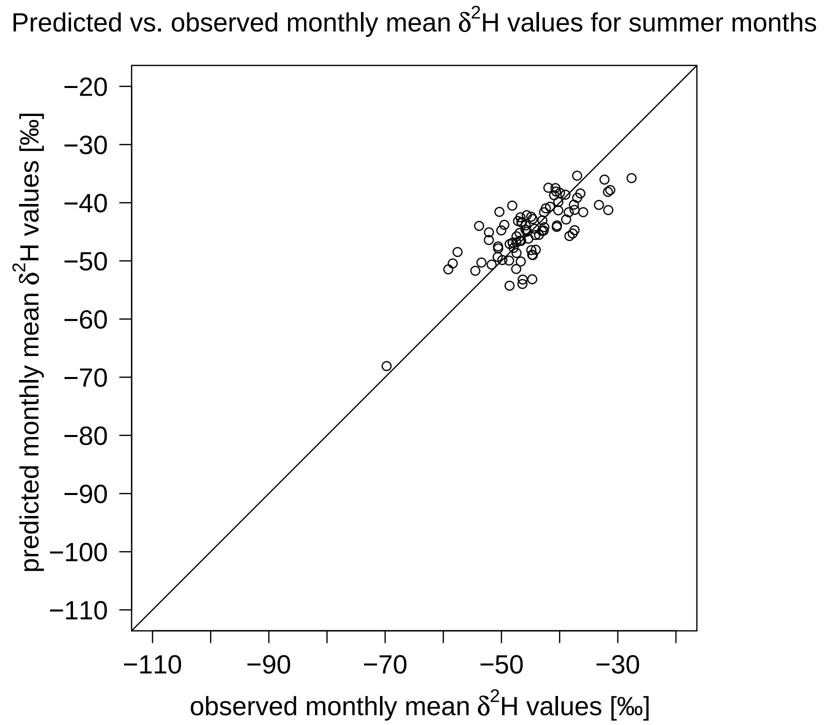
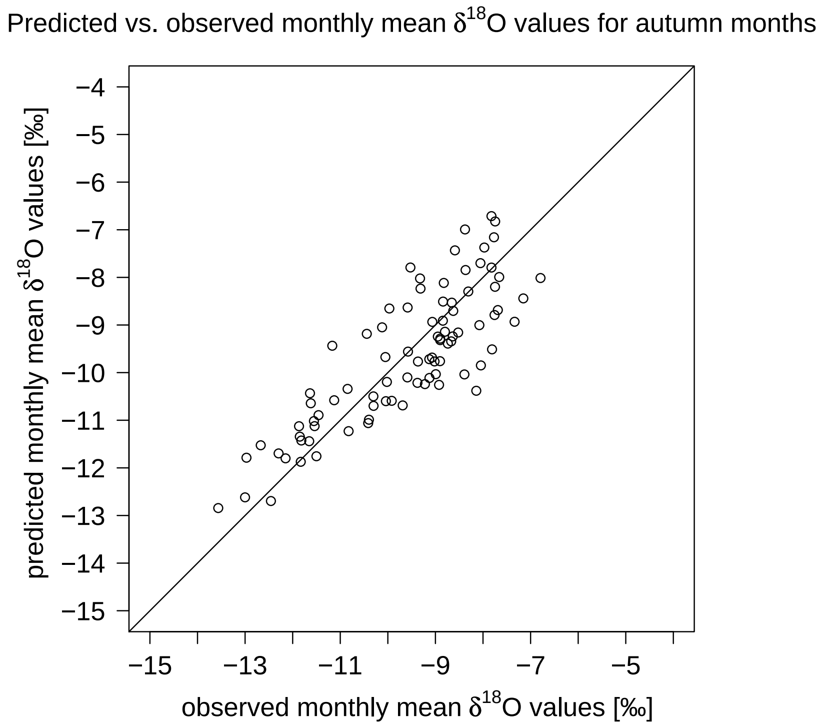


Figure A.0.15.: Predicted versus observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ values of German GNIP and DWD stations for summer months. Predicted values were calculated with the MLR equations 4.2.7 and 4.2.8 respectively.



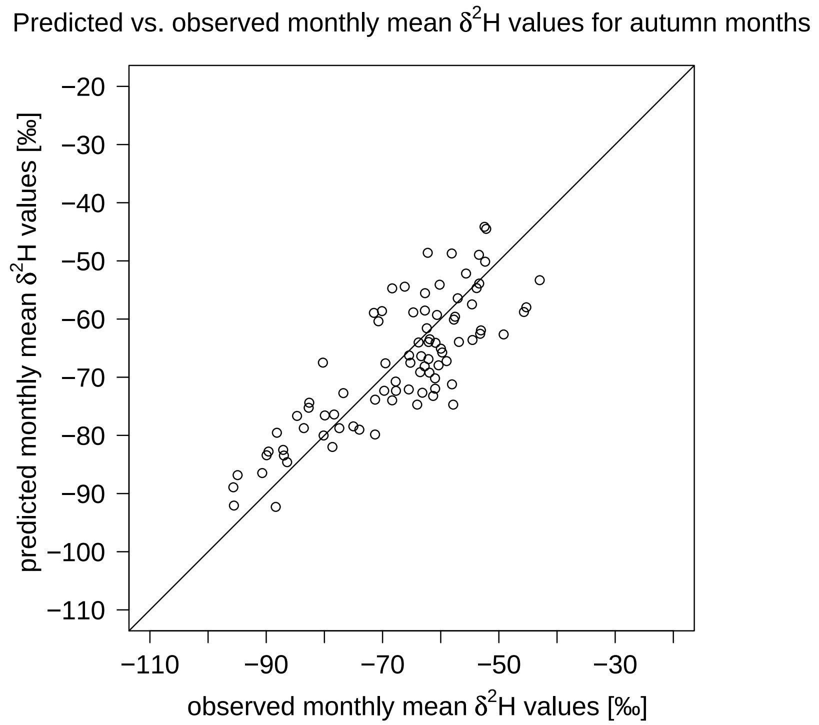
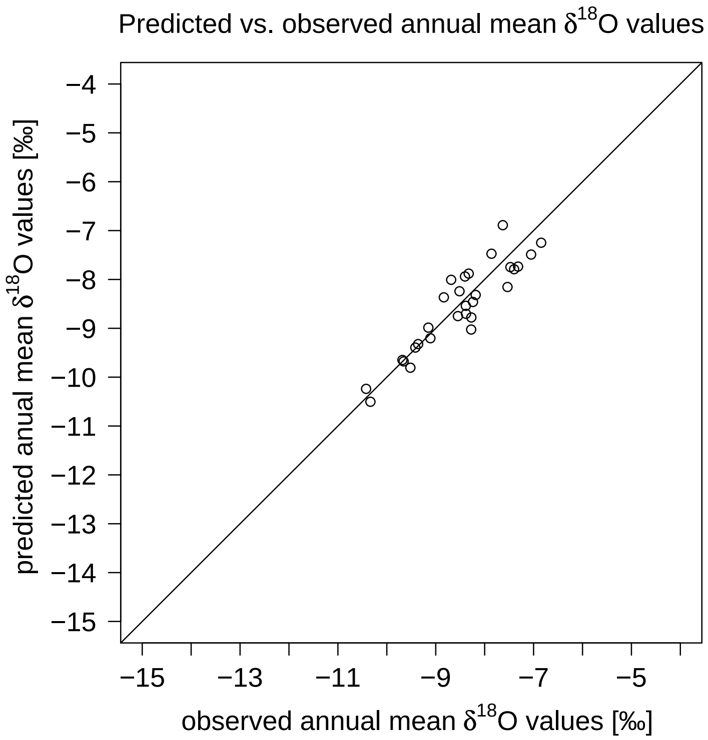


Figure A.0.16.: Predicted versus observed monthly mean $\delta^{18}O$ and $\delta^{2}H$ values at German GNIP and DWD stations for autumn months. Predicted values were calculated with the MLR equations 4.2.9 and 4.2.10 respectively.



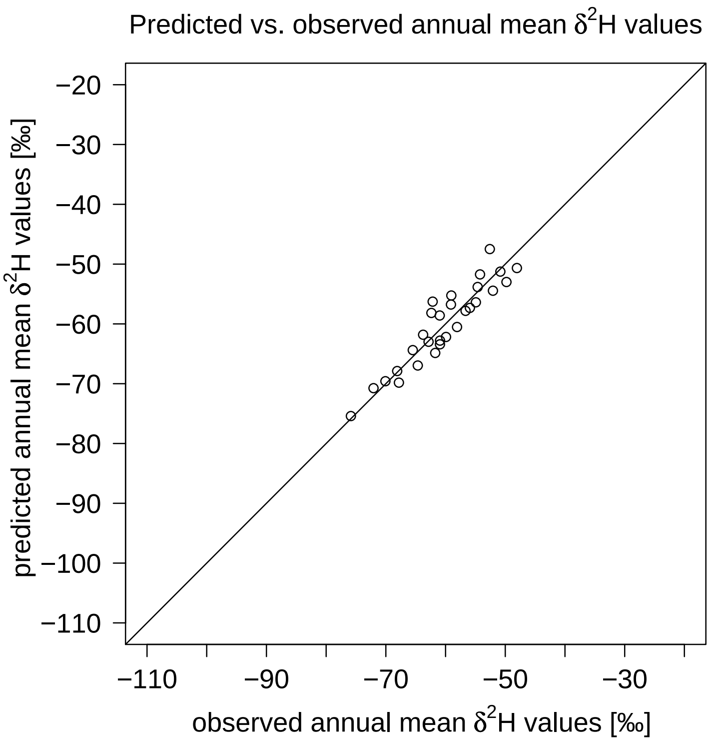


Figure A.0.17.: Predicted versus observed annual mean $\delta^{18}O$ and $\delta^{2}H$ values of German GNIP and DWD stations. Predicted values were calculated with the MLR equations 4.2.11 and 4.2.12 respectively.

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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