

CONTENTS

CHAPTER 1: THE ENVIRONMENTAL ISOTOPES.....	1
Environmental Isotopes in Hydrogeology.....	2
Elements, nuclides, and isotopes.....	2
Nucleosynthesis and the birth of the solar system.....	3
Early days in isotope research.....	4
Why “environmental” isotopes?.....	5
Isotopes, ratios, deltas (δ) and permils (‰).....	6
Stable Isotopes: Standards and Measurement.....	7
Oxygen-18 and deuterium in waters.....	8
Carbonate, organic carbon and hydrocarbon.....	9
Sulphate and sulphide.....	11
Nitrate and reduced nitrogen.....	11
Chloride.....	12
Bromide, lithium and boron.....	12
Strontium.....	13
Isotope ratio mass spectrometry.....	13
Gas source mass spectrometry.....	13
Solid source mass spectrometry.....	15
δ -Value corrections and conversions.....	15
Radioisotopes.....	16
Tritium.....	16
Carbon-14.....	18
Chlorine-36 and iodine-129.....	19
Argon-39.....	20
Krypton.....	20
Uranium series isotopes.....	20
Isotope Fractionation.....	21
Physicochemical fractionation.....	21
Diffusive fractionation.....	24
Isotopic equilibrium.....	25
The example of ^{18}O fractionation between water and vapour.....	26
Temperature effect on fractionation.....	27
Kinetic (nonequilibrium) fractionation.....	29
Isotope Fractionation (α), Enrichment (ϵ) and Separation (Δ).....	31
The example of water-vapour reaction.....	31
Problems.....	33
CHAPTER 2: TRACING THE HYDROLOGICAL CYCLE.....	35
Craig’s Meteoric Relationship in Global Fresh Waters.....	36
Partitioning of Isotopes Through the Hydrological Cycle.....	37
Isotopic composition of ocean waters.....	37

The atmosphere and vapour mass formation.....	39
Isotopic equilibrium in water-vapour exchange	39
Humidity and kinetic (nonequilibrium) evaporation	41
Deuterium excess "d" in meteoric waters.....	43
Atmospheric mixing and global atmospheric water vapour.....	46
Condensation, Precipitation and the Meteoric Water Line.....	46
Rainout and Rayleigh distillation	47
Slope of the meteoric water line	49
Local meteoric water lines.....	51
A Closer Look at Rayleigh Distillation	55
Effects of Extreme Evaporation	57
Evaporation in Lakes	57
Evaporation of brines.....	59
Problems	60

CHAPTER 3: PRECIPITATION 63

The T- $\delta^{18}\text{O}$ Correlation in Precipitation	64
$\delta^{18}\text{O}$ on the global scale	64
Latitude effect	66
Continental effects	67
Local effects on T- $\delta^{18}\text{O}$	70
Altitude effect	70
Seasonal effects.....	71
Condensation of coastal fog.....	73
Kinetic effects of secondary evaporation.....	74
Ice Cores and Paleotemperature	75
Problems	77

CHAPTER 4: GROUNDWATER 79

Recharge in Temperate Climates	80
Attenuation of seasonal variations.....	80
Comparing shallow groundwaters with precipitation.....	83
Recharge by snowmelt	85
Recharge in Arid Regions.....	86
Evaporative enrichment in alluvial groundwaters.....	87
Recharge by direct infiltration.....	88
Soil profiles and recharge rates	89
Estimating recharge with ^{36}Cl and chloride	92
Water loss by evaporation vs. transpiration	94
Recharge from River-Connected Aquifers.....	96
Time series monitoring in a river-connected aquifer.....	96
The Swiss tritium tracer "experiment"	96
Water balance with ^{14}C	98
Recharge from the Nile River.....	98
Recharge by desert dams.....	99
Hydrograph Separation in Catchment Studies.....	99
Example of the Big Otter Creek Basin, Ontario.....	102

An example from Australia.....	104
Groundwater Mixing.....	104
Binary and ternary groundwater mixing.....	105
Mixing of groundwaters in regional flow systems.....	105
Groundwater mixing in karst systems.....	107
Problems.....	108

CHAPTER 5: TRACING THE CARBON CYCLE.....111

Evolution of Carbon in Groundwaters.....	112
Carbonate Geochemistry.....	112
Activity, concentration and mineral solubility relationships.....	112
Atmospheric and soil CO ₂	115
Dissolution of soil CO ₂ and carbonate speciation.....	115
pH buffering and mineral weathering.....	117
Carbon-13 in the Carbonate System.....	119
Vegetation and soil CO ₂	119
¹³ C fractionation in CO ₂ – DIC reactions.....	120
Evolution of δ ¹³ C _{DIC} during carbonate dissolution.....	122
Incongruent dissolution of dolomite.....	123
Dissolved Organic Carbon.....	124
DOC and redox evolution.....	126
Methane in Groundwaters.....	127
Biogenic methane.....	127
Thermocatalytic methane.....	131
Abiogenic and mantle methane.....	131
¹⁴ C and sources of carbon.....	132
Isotopic composition of carbonates.....	132
δ ¹⁸ O in secondary calcite and paleotemperatures.....	133
Problems.....	134

CHAPTER 6: GROUNDWATER QUALITY137

Sulphate, Sulphide and the Sulphur Cycle.....	138
Marine sulphate.....	139
Oxidation of sulphide and terrestrial sulphate.....	142
Atmospheric sulphate.....	144
Sulphate reduction.....	144
Sulphate-water ¹⁸ O exchange.....	147
Nitrogen cycling in rural watersheds.....	148
The geochemistry of nitrate.....	149
Isotopic composition of nitrate.....	150
Nitrate contamination in shallow groundwaters.....	151
The "Fuhrberger Feld" Study.....	152
Denitrification and ¹⁵ N.....	153
Sulphate reduction at depth.....	154
Source of chloride salinity.....	155
Ionic ratio indicators.....	155
Chlorine isotopes — δ ³⁷ Cl.....	155

Landfill Leachates	157
Degradation of Chloro-organics and hydrocarbon	159
Sensitivity of Groundwater to Contamination	160
Temporal monitoring with stable isotopes	161
Aquitards — impermeable or leaky barriers?	161
Diffusion across aquitards	163
Summary of Isotopes in Contaminant Hydrogeology	165
Contamination in agricultural watersheds	166
Sanitary landfills	167
Fuel and solvent contaminated sites	167
Siting hazardous waste facilities	168
Problems	168

CHAPTER 7: IDENTIFYING AND DATING MODERN GROUNDWATERS..... 171

The “Age” of Groundwater	172
“Modern” groundwater	172
The tools for dating groundwater	172
Stable Isotopes	173
Tritium in Precipitation	174
Cosmogenic tritium	174
Thermonuclear (bomb) tritium	175
Nuclear reactor tritium	178
Geogenic production of ^3H	179
Dating Groundwaters with Tritium	179
Velocity of the 1963 “bomb peak”	180
Radioactive decay	181
Input function for ^3H in groundwater	183
Time series analysis	184
Qualitative interpretation of ^3H data	184
Tritium in alluvial groundwaters — an example from Oman	185
Deep groundwaters - mixing in fractured rock	186
Groundwater Dating with ^3H - ^3He	186
Helium–tritium systematics	187
Applications of the ^3H - ^3He method	188
Chlorofluorocarbons (CFCs)	188
Thermonuclear ^{36}Cl	189
Detecting Modern Groundwaters with ^{85}Kr	191
Submodern groundwater	192
Argon-39	192
Silica-32	194
Problems	195

CHAPTER 8: AGE DATING OLD GROUNDWATERS..... 197

Stable Isotopes and Paleogroundwaters	198
Groundwater Dating with Radiocarbon	200
Decay of ^{14}C as a measure of time	201
Production of ^{14}C in the atmosphere	202

Natural variations in atmospheric ^{14}C	203
Anthropogenic impacts on atmospheric ^{14}C	204
The ^{14}C pathway to groundwater in the recharge environment.....	205
Correction for Carbonate Dissolution.....	206
Statistical correction (STAT model).....	207
Alkalinity correction (ALK model).....	208
Chemical mass-balance correction (CMB model).....	209
$\delta^{13}\text{C}$ mixing ($\delta^{13}\text{C}$ model).....	210
The effect of dolomite dissolution.....	212
Matrix exchange (Fontes-Garnier model).....	212
Which model do I use?.....	213
Case study of the Triassic sandstone aquifer, U.K.	215
Some Additional Complications to ^{14}C Dating.....	217
Matrix diffusion of ^{14}C	217
Sulphate reduction.....	218
Incorporation of geogenic CO_2	220
Methanogenesis.....	220
Dilution factors for multiple processes.....	222
Revisiting the groundwaters in southern Oman.....	222
Modelling ^{14}C ages with NETPATH.....	224
^{14}C Dating with Dissolved Organic Carbon (DOC).....	225
The initial ^{14}C activity in fulvic acid ($a_0^{14}\text{C}_{\text{FA}}$).....	225
Advantages and disadvantages of DOC.....	226
Case studies for ^{14}C dating with DOC and DIC.....	227
The Milk River aquifer.....	227
The Gorleben study, Germany.....	229
Chlorine-36 and Very Old Groundwater.....	231
Units of expression for ^{36}Cl data.....	231
Cosmogenic production of ^{36}Cl	232
Subsurface production of ^{36}Cl	234
Example of the Great Artesian Basin, Australia.....	235
Summary of ^{36}Cl in groundwater dating.....	237
The Uranium Decay Series.....	238
$^{234}\text{U}/^{238}\text{U}$ disequilibrium.....	238
Dating with ^{226}Ra and ^{222}Rn	240
^4He and old groundwater.....	241
Problems.....	243

CHAPTER 9: WATER - ROCK INTERACTION.....245

Mechanisms of Isotope Exchange.....	246
High Temperature Systems.....	247
Magmatic water and primary silicates.....	247
The ^{18}O shift in geothermal waters.....	250
Andesitic volcanism and geothermal waters.....	252
Subsurface steam separation.....	253
Geothermometry.....	253
Low Temperature Water-Rock Interaction.....	255
Hydration of primary silicate minerals.....	255
The example of shield brines.....	256

Low-temperature exchange in sedimentary formations.....	258
Hyperfiltration of isotopes.....	260
Strontium Isotopes in Water and Rock.....	260
Isotope Exchange in Gas - Water Reactions.....	262
Deuterium shift — exchange with H ₂ S.....	262
¹⁸ O exchange between H ₂ O and CO ₂	263
High pH Groundwaters — The Effect of Cement Reactions.....	264
Problems.....	265

CHAPTER 10: FIELD METHODS FOR SAMPLING..... 267

Groundwater.....	271
Sample sites.....	271
Getting water from the well.....	272
Deuterium and oxygen-18.....	273
Tritium.....	273
Carbon-13 in DIC.....	274
Radiocarbon in DIC.....	275
Carbon-13 and ¹⁴ C in DOC.....	279
Sulphur-34 and ¹⁸ O in aqueous sulphur compounds.....	279
Nitrate and organic nitrogen.....	280
Chloride.....	281
Uranium series nuclides.....	281
Water in the Unsaturated Zone.....	282
Precipitation.....	282
Rain samples for ¹⁸ O, ² H and ³ H.....	282
Snow and ice ¹⁸ O, ² H and tritium.....	283
Gases.....	283
Soil CO ₂	283
Gas in groundwater.....	284
Geochemistry.....	285
Field measurements.....	285
Major anions (Cl ⁻ , SO ₄ ⁻ , NO ₃ ⁻ , F ⁻ , Br ⁻).....	289
Major, minor and trace metals.....	289
Dissolved organic carbon (DOC).....	290

REFERENCES..... 291

SUBJECT INDEX..... 312