

ISOTOPE EXPERIMENTS

12.0 INTRODUCTION

In this chapter the basic concepts of isotopic fractionation during evaporation are reviewed. Isotopic content of atmospheric water vapour δ_A and isotopic content of lake evaporate δ_E are introduced and their importance in isotopic balances of water bodies is discussed. Evaporation pan experiments are described to experimentally determine limiting steady state isotopic enrichment and location specific values of δ_A and δ_E . The application of pan derived exchange parameters to the water balance of an adjacent wetland is discussed. Field data directly measuring δ_A and δ_E is introduced. The time course of deuterium in East and West Lakes are constructed with accompanying δ_A and δ_E for integration with the mass balance.

Isotopic balances rely on knowing the isotopic composition of atmospheric water vapour δ_A and vapour evaporating from the lake surface δ_E . Generally these are estimated from published averages. At Perry Lakes a series of experiments were conducted to determine δ_E independently using data unique to the local area. These experiments build on earlier work by Craig *et al* 1963, Gat 1970, Welhan & Fritz 1977, Allison *et al* 1979 and Allison & Leaney (1982) but are more rigorous in terms of their duration and methodology. Experiments were also devised to measure δ_E directly. A routine air vapour sampling program was also conducted to directly measure δ_A . Due to the large number and complexity of the equations presented, separate notation is provided at the end of this chapter, page 12-56.

12.1 CONCEPTS OF ISOTOPIC FRACTIONATION

12.1.1 Natural Environmental Isotopes

Fractionation is any process (physical, chemical, biological) which separates isotopes of an element (Toran 1982, Clark & Fritz 1997). The Perry Lakes study deals almost solely with deuterium. Initial co-analysis of ^{18}O was abandoned due to cost considerations. Depletion or enrichment of deuterium (designated ^2H) relative to H is reflected by different 'delta' (designated δ) values (Gonfiantini 1981). Absolute measurement of isotopic

values is analytically difficult. Therefore relative ratios are measured instead such that the δ value represents the relative difference in units of permil (‰) of $^2\text{H}:\text{H}$ relative to a standard ('VSMOW' - Vienna Standard Mean Ocean Water) maintained by the International Atomic Energy Agency (IAEA). Substituting ^2H in equation (6.10)

$$\delta ^2\text{H}_{\text{sample}} = \left(\frac{^2\text{H}:\text{H}_{\text{sample}}}{^2\text{H}:\text{H}_{\text{VSMOW}}} - 1 \right) \cdot 1000\text{‰} \quad (12.1)$$

In natural waters and evaporation pan experiments at Perry Lakes, deuterium values ranged from about -15.0‰ to +100.0‰ signifying waters with 15‰ (1.5%) less than the standard to waters with 100‰ (10%) more than the standard. The equivalent ^{18}O was about -3.4‰ to +21.1‰. All samples were analysed on CSIRO Floreat Laboratories mass spectrometer (VG Isogas Ltd SIRA 9). Measurement precision¹ is approximately 1‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$.

Molecules with different masses have different thermodynamic properties and thus different rates of diffusion, evaporation, condensation, freezing and melting. Different meteorological processes thus result in varying degrees of fractionation. Fractionation results from both chemical and physical reactions. It includes kinetic fractionation, essentially a unidirectional movement (controlled by the relative velocity and vibrational frequency of molecules) and equilibrium chemical reactions where isotopes are continuously exchanged (Gat 1981b, Toran 1982). At Perry Lakes, fractionation (represented by different δ values of ^2H and ^{18}O) is evident in all components of the water balance.

Rainfall, Stormwater, Groundwater

Rainfall originates in atmospheric vapour masses fractionated during evaporation and subsequently mixed prior to condensation. Rain drops are also subject to evaporation as they fall. Thus rain water in individual rain events will display widely differing degrees of fractionation. At Perry Lakes, rainfall collected between April 1996 and January 1998 ranged from -71.0‰ to +34.4‰ deuterium. As an air mass travels the loss of vapour as precipitation results in 'rainout', a process whereby condensation preferentially partitions ^2H and ^{18}O in the cloud droplets through Rayleigh distillation (Dansgaard 1953 & 1954, Epstein & Mayeda 1953). Rain drops subsequently formed from the droplets are

¹ Instrument precision (internal reproducibility) is 2x std deviation of 10 delta values derived from a series of 12 alternate sample-reference ratio measurements of one gas sample and is typically 0.3‰. The commonly cited precision of 1.0‰ represents the average spread obtained by simply analysing the same sample multiple times. Deviation from the true value is controlled by instrument precision, chemical purity, vacuum stability during gas transfer, leakage, time between water reduction and analysis and human error (V. Gailitis, mass spectrometer technician, CSIRO pers com).

isotopically enriched, but fall from a diminishing vapour mass which is continuously undergoing isotopic depletion (Clark & Fritz 1997).

The minimum -71.0‰ occurred April 10-11 1997 under conditions of bush fire smoke which possibly seeded precipitation from vapour already strongly isotopically depleted. A major frontal system September 5-6 1997 dropped 39.3mm which averaged -54.8‰ . The maximum $+34.4\text{‰}$ occurred 6-7 March 1997 under conditions of low humidity, high evaporation and scattered thunder storms and virga. It reflects evaporation and isotopic enrichment of the rain as it fell. Stormwater channelled into storm drains will broadly reflect the isotopic content of the parent rainfall but is likely to undergo further isotopic enrichment through evaporation during surface flow on roads and gutters. Rain entering the soil profile and ultimately recharging the unconfined aquifer is subjected to little further evaporation. The groundwater derived from it therefore represents a volume weighted average of the isotopic content of rain over many (possibly thousands) of years.

Meteoric Water Line

The stable isotope composition of rainfall provides a baseline against which surface and groundwaters can be compared. At Perry Lakes monthly composites of rainwater have been collected since 1983. These monthly data, as amount weighted ^2H and ^{18}O , define the Perth Meteoric Water Line (MWL). Surface water in wetlands undergoing evaporation are subject to isotopic fractionation, becoming enriched in ^2H and ^{18}O . The extent depends on climate (rainfall, evaporation, temperature and humidity). Water in these wetlands or groundwater originating from them will plot in fields removed from the MWL in $\delta^2\text{H} - \delta^{18}\text{O}$ space. This water represents evaporated lake and groundwater and defines a 'low slope' evaporation line below the MWL. The 'low slope' results from ^{18}O being proportionally more enriched than deuterium in residual lake water (Dinçer 1968). Figure 12.1a shows the Perth MWL plus a low slope evaporation line defined by water undergoing evaporation (Run 1 of pan experiments described later in this chapter). Atmospheric vapour and lake evaporate collected at Perry Lakes, as would be expected, also plot on the MWL. Water in adjacent East and West Lakes was evaporating under similar meteorological conditions and also falls on the same low slope evaporation line (Figure 12.1b). West Lake during late summer evaporates to a small pond and displays significant isotopic enrichment compared to East Lake which was being maintained with periodic groundwater 'top ups'.

Feed stock for the evaporation pans was groundwater collected from CSIRO irrigation bore #2 (Figure 1.1b). This is unevaporated groundwater derived directly from rainwater and plots in a unevaporated groundwater field ('UGF' in Figure 1.1) on or close to the MWL.

12.1.2 Application to Identifying Differing Wetland Water Balance Regimes

Dinçer (1968) and Townley *et al* (1993a) summarise the non-equilibrium evaporation processes which apply unique isotopic signatures to surface waters:

- proportionally greater enrichment of ^{18}O relative to ^2H
- general enrichment of surface waters relative to groundwater in the lake capture zone or unevaporated groundwater

This results in ^2H and ^{18}O becoming enriched along 'evaporation lines' which are displaced from the local meteoric water line through the differing effects of rainfall, evaporation, temperature and humidity. These waters thus acquire a distinguishable isotopic composition (Gat 1981c). Figure 12.1e demonstrates how pans evaporating at constant volume but different humidity define unique evaporation lines. It has been suggested (Turner pers com) that significant information on the hydrology of lakes on the Swan Coastal Plain may be determined from analysis of the range of seasonal isotopic variations and slope of the ^2H and ^{18}O relation for a given lake. Thus the data collected for Perry Lakes may provide clues on the water balances of similar nearby lakes. This concept remains to be developed.

12.1.3 Isotopic Water Balance of Lakes

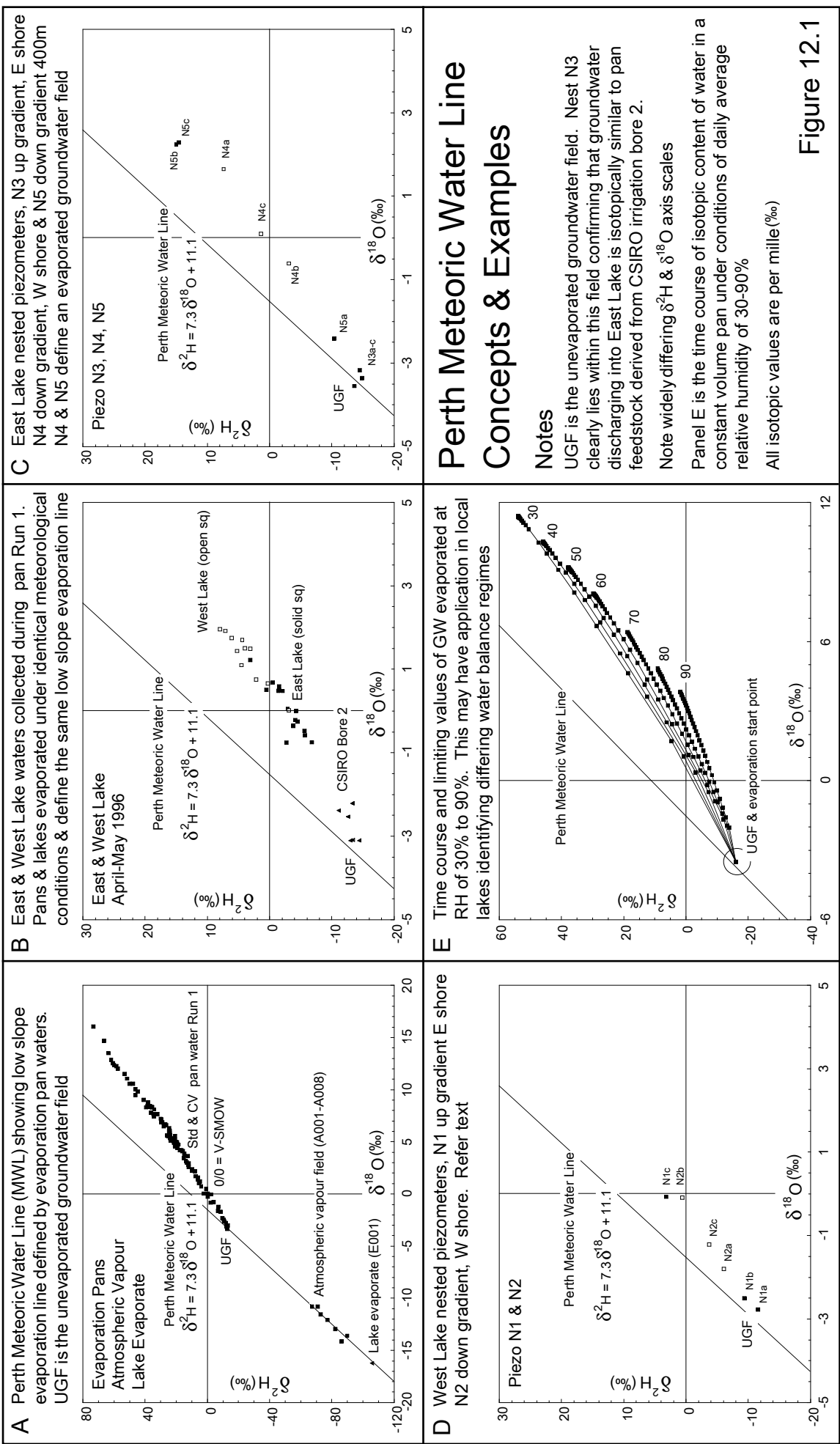
The use of isotopic water balances was introduced in Chapter 4 and demonstrated in Chapter 6. Concepts and approaches applied in isotopic water balances are reviewed by Gat *et al* (1968) and Dinçer (1968). Townley *et al* (1993a p61) introduce general steady solutions for the isotopic water balance of a lake where

$$I(1 + \delta_I) - O(1 + \delta_L) + P(1 + \delta_P) - E(1 + \delta_E) = 0 \quad (12.2)$$

and where $(1 + \delta_E)$ is unknown

$$I(1 + \delta_I) - O(1 + \delta_L) + P(1 + \delta_P) - E \frac{\alpha^* (1 - \delta_L) - h(1 - \delta_A)}{1 - h + \Delta\epsilon} = 0 \quad (12.3)$$

The critical parameters are δ_E the isotopic composition of evaporating water from the lake surface and δ_A the isotopic composition of atmospheric water vapour. The substitution for δ_E in equation 12.2 derives from equation 23 of Craig & Gordon (1965), various forms of which appear elsewhere in this chapter (equations 12.6, 12.6a and 12.32).



Atmospheric vapour δ_A is easily sampled and measured directly, however, doing so on a continuous basis is logistically impractical. In water balance studies, uncertainties of up to 50% can result from uncertainties in estimating δ_E (Zimmerman & Ehhalt 1970). Measuring δ_E directly is logistically very difficult since it requires selectively sampling evaporating moisture in the presence of ambient moisture (Zuber 1983). Techniques were developed at Perry Lakes for experimental direct sampling of δ_E under dead calm wind conditions and are described later in this chapter. Evaporation pans, (and also some lakes and ponds) can provide estimates of these crucial isotopic exchange parameters under the varying climatic and seasonal conditions unique to the wetland under study. This approach formed the basis of the 'pan experiments' conducted at East Lake from 1996 to 1998.

12.2 ISOTOPIC EXCHANGE PARAMETERS FROM EVAPORATION PANS

12.2.1 Historical Background

Lakes evaporating to dryness under high ($\gg 50\%$) relative humidity approach a limiting or steady state isotopic enrichment (Craig & Gordon 1965, Fontes & Gonfiantini 1967, Gat & Levy 1978). Gat (1981d) noted that this limiting value which he designated δ^* is independent of the initial isotopic composition, being fixed solely by ambient parameters h and δ_A and approximated as

$$\delta^* \approx \delta_A + \frac{\varepsilon}{h} \quad (\text{Gat 1981d Eqn 9.3}) \quad (12.4)$$

Similarly Gat (1981) shows how in a 'terminal lake' where inflow is approximately matched by evaporation, steady state (designated δ_L^{ss}), can be defined as

$$\delta_L^{ss} \approx h\delta_A + (1-h)\delta_{in} + \varepsilon \quad (\text{Gat 1981d Eqn 9.11a}) \quad (12.5)$$

and drawing on the work of Craig & Gordon (1965) introduces the concept of defining δ_A in terms of δ_E where

$$\delta_E = \frac{\alpha^* \delta_L (1 + E\rho_L) - h\delta_A - \varepsilon}{(1-h) + \Delta\varepsilon + \alpha^* E\rho_L^*} \quad (\text{Gat 1981d Eqn 9.9}) \quad (12.6)$$

which can be approximated by

$$\delta_E = \frac{\delta_L - h\delta_A - \varepsilon}{1-h} \quad (\text{Gat 1981d Eqn 9.10}) \quad (12.6a)$$

Working directly with natural systems to determine isotopic exchange parameters is extremely difficult. Large evaporation pans however are convenient analogues of natural systems:

Natural System	Analogue
Desiccating Lake	Pan evaporating to dryness
Terminal Lake	Pan evaporating at constant volume
Lake with inflow and outflow	Leaky pan evaporating at constant volume

Welhan & Fritz (1977) suggested using measurements of the isotopic time course of pans evaporating towards dryness as models of desiccating lakes and showed how they could be used as an indirect measure of the ambient parameters h and δ_A . Allison *et al* (1979) examined the extreme practical difficulties imposed on such measurements by natural variation in meteorological conditions. They were able to demonstrate however that where a pan evaporated to at least half its original volume, under stable humidity conditions, useable estimates of δ_E could be obtained and applied to an adjacent lake.

The ultimate goal of all these experimental techniques was to determine a value of δ_E which represented the sum effect of the varying exchange and evaporative processes occurring over time. Allison & Leaney (1982) showed how such 'flux weighted' exchange parameters, useable over weeks or months could be determined using pans evaporated at constant volume (analogues of terminal lakes) and how they could be applied to the water balance studies of adjacent lakes.

12.2.2 Pans Evaporated to Dryness

Early pan experiments using both ^2H and ^{18}O (Craig *et al* 1963, Gat 1970, Gonfiantini 1965 cited Welhan & Fritz 1977) confirmed that waters in pans evaporating to dryness reach different isotopic steady states under differing evaporation conditions. Welhan & Fritz (1977) present a method which relates the difficult to measure isotopic content of evaporating water δ_E of a water body such as a lake directly to parameters which describe the isotopic behaviour of a corresponding isolated water body with no inflow such as an evaporation pan. They develop the following equations:

$$\delta_s = \frac{h\delta_A + \varepsilon}{h - \varepsilon} \quad (\text{Welhan \& Fritz 1977 Eqn 4}) \quad (12.7)$$

and

$$\frac{\delta - \delta_s}{\delta^0 - \delta_s} = f^m \quad (\text{Welhan \& Fritz 1977 Eqn 5}) \quad (12.8)$$

where

$$m = \frac{h - \varepsilon}{l - h + \Delta\varepsilon + \alpha^* E \rho_L^*} \quad (\text{Welhan \& Fritz 1977 Eqn 6}) \quad (12.9)$$

Equation 12.8 describes the isotopic behaviour of water evaporating under constant climatic conditions, while m in 12.9 is predominantly dependant on h . Dividing 12.6 by 12.7 and noting that

$$\frac{\alpha^* (1 + E \rho_L^*)}{h - \varepsilon} = \frac{m + l}{m} \quad (\text{Welhan \& Fritz 1977 Eqn 7}) \quad (12.10)$$

yields

$$m = \frac{\delta_E - \delta}{\delta - \delta_S} \quad (\text{Welhan \& Fritz 1977 Eqn 8}) \quad (12.11)$$

Therefore for water evaporating in a pan with no flow, the exponent m describes the relationship between δ and δ_E at any instant.

Application to an Adjacent Lake

Welhan & Fritz (1977) then argue that at any instant a well mixed epilimnion of a lake may be thought of as a closed water body with $f = 1$ and $\delta^0 = \delta_{\text{lake}}$ where δ_S and m may be defined by equations 12.7 and 12.9. It follows that for the lake surface an equation taking the form of 12.11 may be written relating the isotopic content of the lake waters to $\delta_{E(\text{lake})}$, $\delta_{S(\text{lake})}$ and $m_{(\text{lake})}$.

Welhan & Fritz (1977) then expand equation 12.9 such that

$$m = \frac{h - \varepsilon^* - \Delta\varepsilon}{l - h + \Delta\varepsilon + \alpha^* E \rho_L^*} \quad (\text{Welhan \& Fritz 1977 Eqn 10}) \quad (12.12)$$

and note that since $\Delta\varepsilon \ll h$ and $\alpha^* E \rho_L^* \approx 0$ then m is mainly a function of temperature as saturation absolute humidity approximately doubles for each 10° rise in temperature. It follows that the difference between m_{pan} and m_{lake} is principally a function of the difference between pan and lake surface temperatures. Similarly from equation 12.7, $\delta_{S(\text{lake})}$ and $\delta_{S(\text{pan})}$ are also related by temperature. Welhan & Fritz (1977) note that δ_S is very sensitive to $\Delta\varepsilon$. Their critical assumption is that $\Delta\varepsilon$ is similar for the lake and the pan. Subject to these assumptions they find that

$$\delta_{S(lake)} \approx \delta_{S(pan)} \text{ and } m_{lake} \approx m_{pan} \quad (\text{Welhan \& Fritz 1977 Eqn 11}) \quad (12.13)$$

which when substituted into equation 12.11 yields

$$m_{pan} \approx \frac{\delta_{E(lake)} - \delta_{lake}}{\delta_{lake} - \delta_{S(pan)}} \quad (\text{Welhan \& Fritz 1977 Eqn 12}) \quad (12.14)$$

This applies where the pan and lake surface are at the same temperature and is the key expression developed by Welhan & Fritz (1977) allowing δ_E of a lake to be related directly to pan parameters m and δ_S .

Allison *et al* (1979) provide realistic field methods whereby pan derived parameters can be measured. Welhan & Fritz (1977) in their experiments conducted in Canada were hampered by limited data from short evaporation runs resulting from the use of unsheltered pans. Their experiments typically proceeded for 2-3 days ($f < 0.8$) before rain fell in the pans. They noted that the method was probably better suited to more arid climates where the pans could be monitored for longer time periods under conditions of low or nil precipitation. An additional problem with their original approach is that δ_E is largely a function of relative humidity, δ_A and the isotope fractionation factor for the isotope of interest (Craig & Gordon 1965). Therefore such short term pan experiments are unlikely to provide a value of δ_E which is representative of the varying exchange and evaporative processes occurring over time.

Allison *et al* (1979) also working in Canada used a temperature compensated pan (floating in a lake) and both sheltered and unsheltered pans on shore. They reported that when plotting δ_{pan} against time, rapid changes in relative humidity produced sharp breaks in the curve and noted that while the use of sheltered pans prevents interruption of a run due to precipitation, data still had to be analysed in periods of relatively constant humidity. Even with a sheltered pan Allison *et al* (1979) obtained no run longer than 16 days ($f < 0.2$). Pans did not approach dryness and δ_S was never directly measured. Instead an approximation of equation 12.12 whereby

$$m \approx \frac{(h - \varepsilon)}{(1 - h + \Delta\varepsilon)} \quad (\text{Allison et al 1979 Eqn 4}) \quad (12.15)$$

and a graphical solution whereby

$$\ln(\delta - \delta_S) - \ln(\delta^0 - \delta_S) = m \ln f \quad (\text{Allison et al 1979 Eqn 8}) \quad (12.16)$$

were used to solve with m and δ_S chosen to produce the best straight line fit with ε and $\Delta\varepsilon$ estimated from the literature.

12.2.3 Pans Held at Constant Volume

The determination of δ_S using pans evaporated to dryness is problematic. As the volume of water remaining in the pan diminishes, small changes in meteorological conditions can produce large changes in pan isotopic composition. Where pan water contains some salt, this becomes concentrated producing additional undesirable effects. These are further explored later in this chapter (refer section 12.3). When humidity is low (as it frequently is in Perth over the summer), Allison & Leaney (1982) note that δ_S is very difficult to estimate. At relative humidity of about 50% or less (depending on isotopic exchange parameters), such that $m < 1$, isotopic steady state pan conditions are never attained.

Allison and Leaney (1982) provide equations applied to a constant feed pan which utilise the m of Welhan and Fritz (1977). Such pans overcome the problems of meteorological conditions perturbing the approach to steady state and by maintaining a constant water volume they allow 'flux weighted' estimates of δ_E to be determined which are applicable for weeks or months. They introduce the term K representing isotopic steady state in a pan evaporated at constant volume.

At some time t

$$\delta = K - (K - \delta^0) \exp\left[\frac{-(m+1)Et}{V}\right] \quad (\text{Allison \& Leaney 1982 Eqn 9}) \quad (12.17)$$

where

$$K = \frac{\delta_I}{(m+1)} + \frac{m(h\delta_A + \varepsilon)}{[(m+1)(h-\varepsilon)]} \quad (\text{Allison \& Leaney 1982 Eqn 10}) \quad (12.18)$$

Welhan (1974 cited Allison & Leaney 1982) showed that where a pan evaporating to dryness is thermally coupled to an adjacent lake, rearranging equation 12.14 yields

$$\delta_{E(lake)} = (m+1)\delta_{lake} - m\delta_{S(pan)} \quad (\text{Allison \& Leaney 1982 Eqn 11}) \quad (12.19)$$

and combining (12.7) and (12.18) yields

$$\delta_{E(lake)} = (m+1)(\delta_{lake} - K) + \delta_I \quad (\text{Allison \& Leaney 1982 Eqn 12}) \quad (12.20)$$

This is the key relationship developed by Allison & Leaney (1982) which expresses the relationship between the isotopic composition of lake evaporate and exchange parameters estimated from a nearby pan evaporating at constant volume. Simpson *et al* (1992) describes a practical demonstration of constant volume pans in a field situation where flux weighted or seasonally applicable values of pan derived δ_E and δ_S are applied to an adjacent water body, in this case a rice paddy.

12.3 PERRY LAKES PAN EXCHANGE PARAMETERS EXPERIMENT

12.3.1 Evaporation Pan Experiment Design Principles

Pans evaporated to dryness, the approach taken by Welhan & Fritz (1977) and pans operated at constant volume, the method developed by Allison & Leaney (1982) represent the two basic approaches described in the literature for estimating the isotopic composition of lake evaporate from an evaporation pan operating nearby. Neither had been field tested either for an extended period or under conditions where the pan and lake temperatures were synchronous. Perry Lakes represented an opportunity to test and compare both approaches.

Pans evaporated to dryness

At the time the isotope experiments were being designed there were no detailed meteorological data for the Perry Lakes basin, specifically average monthly relative humidity and open water evaporation. Designing and operating a pan evaporating to dryness in tandem with a constant volume pan is a juggling act. We wanted to operate the experiment over two full years with sufficient pan runs to adequately quantify seasonal changes in exchange parameters. For each run, both pans would commence operation simultaneously. The basic operating premise was that the time course of the 'standard pan' evaporated to dryness should approximately equal the time course of the constant volume pan such that the pan operated at steady state for a minimum of two weeks. This meant that the starting volume for the standard pan would be varied seasonally such that time to dryness approximated adequate operation of the constant volume pan at equilibrium.

In practice this requirement is not terribly stringent because δ_s can be deduced from a pan evaporating to dryness using equation 12.8 even at $f = 0.5$, when only half the water has evaporated (Allison *et al* 1979). This is evident in theoretical curves (Figure 12.2.a-c) developed by rearranging equation 12.8 such that

$$\delta = f^m (\delta^0 - \delta_s) + \delta_s \quad (12.21)$$

These theoretical curves predict that for Perry Lakes:

- the expected annual range of δ_s would be about 40-110‰
- time to $f = 0.1$ would vary seasonally from about 15-40 days at pan start depths ($f = 1$) of 185-85mm (the volumetric time course of a pan evaporated to dryness simply requires knowledge of local pan evaporation rates)

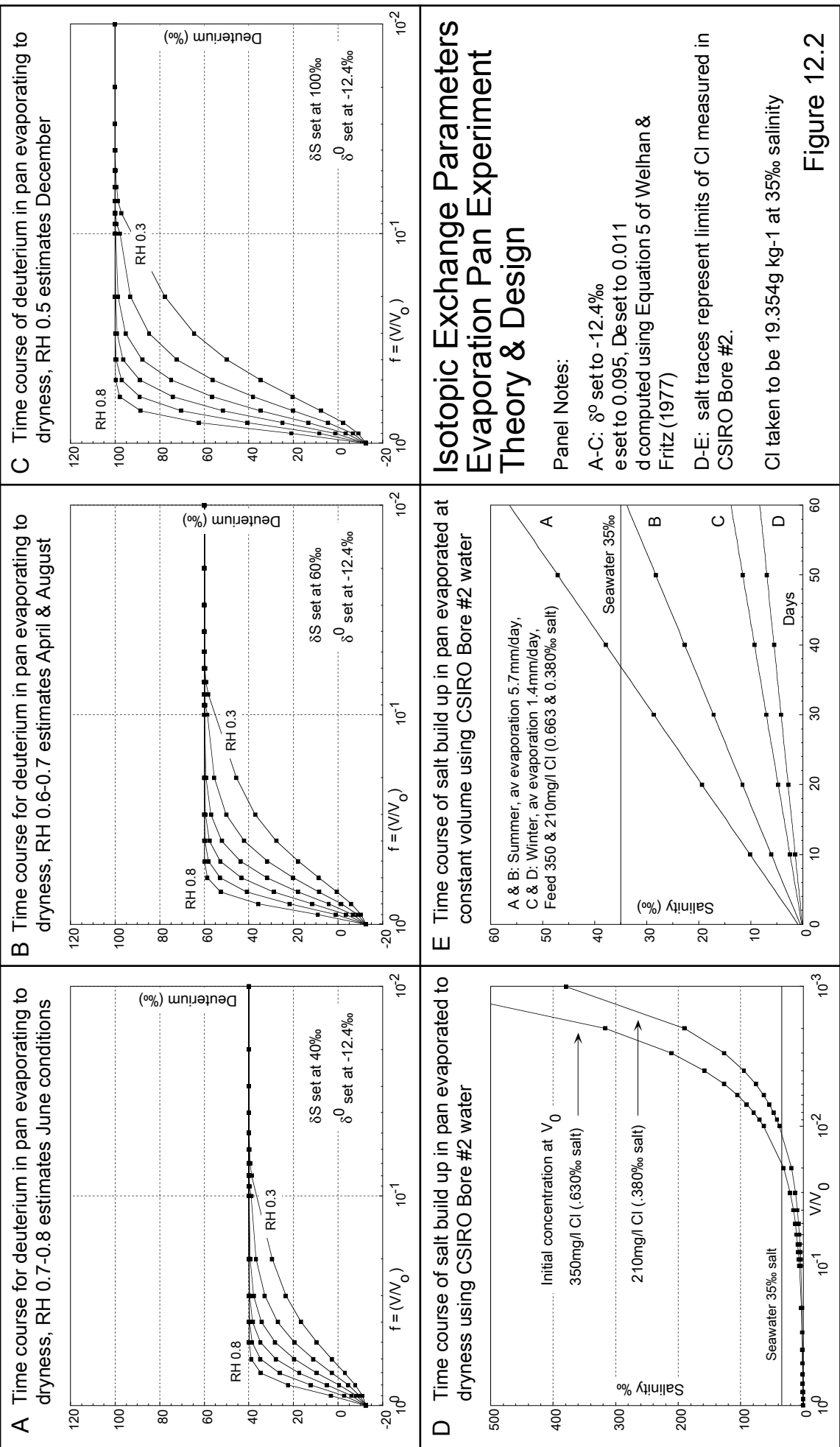


Figure 12.2

These curves also demonstrate that as average daily humidity decreases, isotopic content of water remaining at half volume ($f = 0.5$) becomes increasingly removed from steady state δ_S . Therefore in summer with lower humidity it is desirable that evaporation proceed further (approximately $f = 0.1$) to ensure accurate determination of δ_S (Table 12.1).

Table 12.1 Volume change required in standard pan to achieve $0.9\delta_S$

Relative Humidity	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f to achieve $\delta_S = 0.9$	0.05	0.10	0.25	0.37	0.48	0.59	0.68	0.80

Pans evaporating at constant volume

The isotopic concentration of a constant volume pan at any time is defined by equation 12.17. The time course and ultimate steady state (K) are functions of

- daily average relative humidity h (and associated fractionation factors integrated as m)
- evaporation rate E
- pan volume V (a function of depth where pan geometry is fixed)

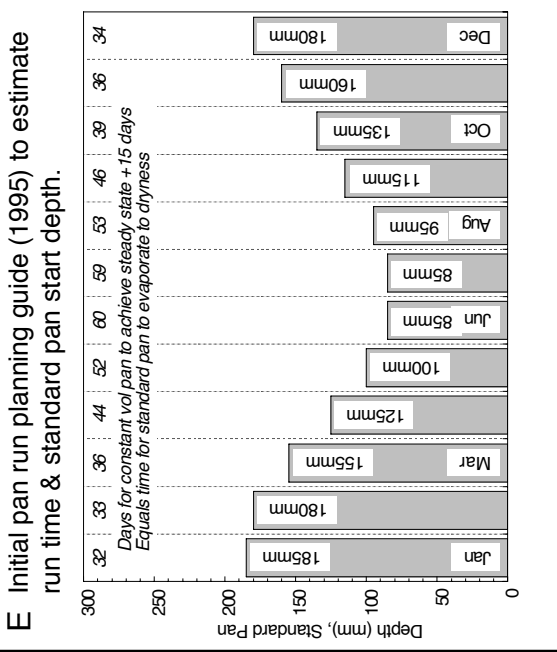
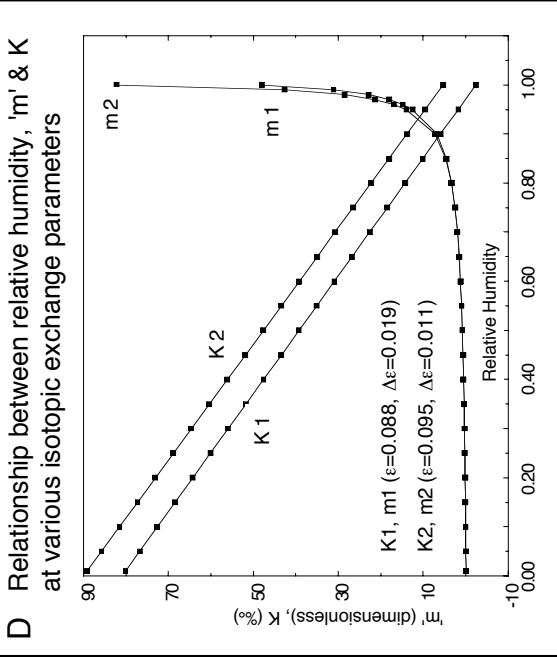
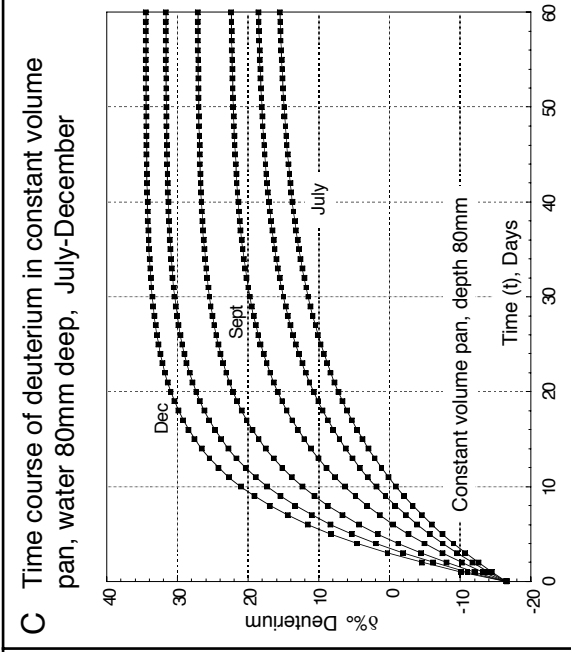
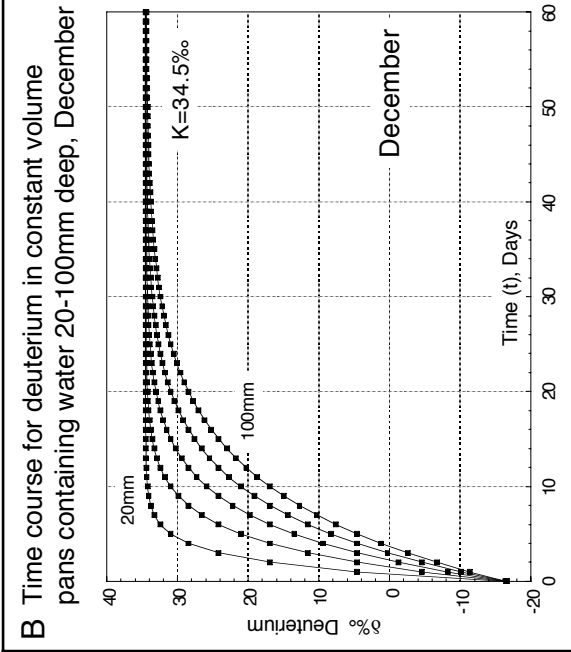
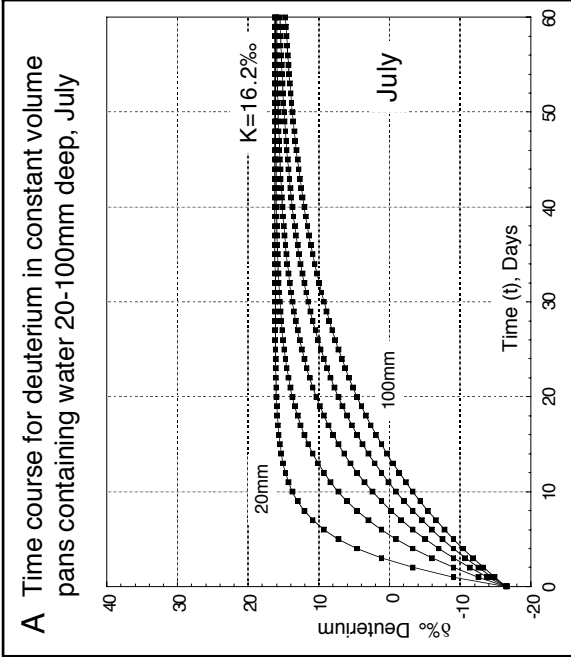
Monthly estimates of K and open water evaporation were calculated using mean monthly Fremantle 09:00 hr relative humidity which approximates daily average relative humidity and mean monthly Perth Airport Class A pan evaporation. It was anticipated that evaporation from the small experimental pans would approximate adjacent evaporation from East Lake. A suitable average pan coefficient whereby open water evaporation at Perry Lakes could be estimated from Class A pan evaporation at Perth airport was not yet available. The commonly utilised annual coefficient of 0.7 (Brutsaert 1982) was adopted. Subsequent studies indicated the coefficient for 1997 was 0.67 (refer Chapter 10). Estimates are summarised in Table 12.2.

Table 12.2 Estimated daily average humidity, E and K (deuterium) at Perry Lakes

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Av daily RH (%)	57	57	60	66	73	75	76	73	69	64	59	56
Av daily E (mm)	5.70	5.44	4.33	2.82	1.86	1.43	1.42	1.79	2.46	3.49	4.43	5.25
m	1.08	1.08	1.23	1.61	2.26	2.51	2.65	2.26	1.85	1.47	1.18	1.03
K (‰)	33.5	33.5	30.8	25.3	19.0	17.1	16.2	19.0	22.6	27.2	31.7	34.5

Fremantle humidity data mean 1852-1989, Perth evaporation data mean 1876-1992, m & K calculated using exchange parameters $\epsilon = 0.095$, $\Delta\epsilon = 0.011$, δ_I set to -16.5‰ based on groundwater deuterium analysis of sample from irrigation bore P5, δ_A set to -100‰

It was anticipated that pans would be constructed from 200 litre drum bases (area 2532cm^2). Using equation 12.18 the time course to equilibrium was modelled for each month at varying pan depths. Experimental data is summarised in Figure 12.3 a-c and predicts that for Perry Lakes:



Isotopic Exchange Parameters Evaporation Pan Experiment Theory & Design **Figure 12.3**

Panel Notes:

A-C: δ computed using eqn 12.17 (eqn 9 of Allison & Leaney 1982), δ^0 set to -16.5% , ϵ set to 0.095 , $\Delta\epsilon$ set to 0.011

D: δK computed using eqn 12.18 (eqn 10 of Allison & Leaney 1982), δ_A set to -90% , δ_l set to -12.4% m1 & m2 computed using eqn 12.15 (eqn 4 of Allison *et al* 1979)

E: At start depths indicated, standard pan achieves dryness after constant volume pan has operated a minimum 15 days at steady state ($\approx 0.9K$)

- the expected annual range of K would be about 15‰-35‰
- time to steady state could vary anywhere from 10-60 days depending on pan depth

While the equipment was subsequently constructed such that the constant volume pan depth could be varied, a standard depth for all runs was considered desirable for reasons of simplicity of operation and comparison between runs. The data suggested that a constant volume pan depth of 80-90mm would provide reasonable run lengths consistent with satisfactory standard pan start depths. Allison & Leaney (1982) recommended constant volume pan depths of greater than 50mm and less than 100mm. A bar graph (Figure 12.3e) shows time to achieve constant volume steady state vs standard pan run time to achieve dryness. In the experiments a general rule of thumb was to set standard pan start depth such that evaporation to dryness was achieved in at least double the time required to achieve steady state in the constant volume pan. In practice relative humidity was normalised to lake surface temperature. However, lacking such data in the planning phase, non normalised data was used, knowing that this would result in relative humidity and pan run times somewhat greater than required. In time, as data from the early runs became available, run times were shortened.

12.3.2 Equipment Design and Construction

In order that exchange parameters determined from evaporation pans can be applied to nearby lakes, two criteria must be met:

- the pan temperature must be maintained within a few degrees of the lake surface temperature
- the parameter m must be computed from humidity normalised to the lake surface temperature

Principal design concepts are summarised below and in Figure 12.4.

Thermal regulation

- The equipment was located in a Water Corporation sewage pumping station yard adjacent East Lake (Figure 5.1a) which provided security and 240 volt power.
- Lake water was pumped from the centre of East Lake 130m to the experiment. The feed line was weighted with bricks, and buried 100mm into the lake sediments. On shore a buried conduit of 100mm PVC beneath public walk paths carried the inlet line to the site and served as a used water return. While in the conduit the inlet was thus bathed in return water at close to lake temperature ensuring less temperature loss than burying it directly in the ground.
- In summer East Lake approaches dryness (<30cm at its deepest point). Therefore the inlet had to be located at the deepest point within a sediment trap. Shallow lakes on the Swan Coastal Plain are generally well mixed (Davis *et al* 1993). Subsequent monitoring showed that water drawn from the trap was generally within 1°C of surface water.

- The evaporating pans were constructed from 200 litre steel drum bases and hot dip galvanised. They were mounted eccentrically within two Class A evaporation pans (thermal regulation pans) via welded 30x30mm RHS steel frames. The eccentric mount pattern kept the pans close to the centre of the shelter thus minimising rain drift.
- Lake water drawn by a continuous duty 0.5hp Mono pump entered the thermal regulation pans via a flow splitter. Level was controlled by two fixed outlets with gravity return to the lake. Measured pumping rate was approximately 1900 litres hr⁻¹ resulting in a residency time within each pan of about 10 minutes. Water entered close to the base and was directed to create a circular mixing pattern ensuring circulation beneath the evaporation pans with no thermal dead spots.

Pan evaporated to dryness ('standard pan')

- Principal requirement was for accurate daily measurement of depth to compute f . An inverted point gauge (Figure 12.4f) adapted from Hunt (1925) was designed which could provide water surface level (and daily evaporation) accurate to 0.2mm. A small rain gauge (not shown) recorded any storm rain drift.

Constant volume pan

- Principal requirement was for precise and consistent level (and hence volume) control. The control system comprised a cylindrical reservoir and manometer (Figure 12.4e) coupled to an agricultural drink trough float valve (Figure 12.4g). Custom arm, float assembly and close coupled float stilling well were designed such that daily level was maintained within ± 1 mm.
- The reservoir was calibrated such that daily evaporation (accurate to better than 0.1mm) could be computed from a reservoir volume change. Due to its extreme height to width ratio 1mm of pan evaporation resulted in a 14.9mm change in manometer level.
- Output from the float valve was via a small hose to prevent evaporation. Brass counter weights on the float arm allowed precise adjustment of water level.

Feed stock water

Allison & Leaney (1982) note that where pan parameters are to be applied to an adjacent lake, choosing δ_I such that $K \approx \delta_{Lake}$ minimises the effects of errors in m . Sampling of lake and groundwater in release zones of other Swan Coastal Plain wetlands (Townley *et al* 1993b) suggested an annual deuterium range of at least 40‰ was likely. There was therefore little point in seasonally varying δ_I . Instead locally derived groundwater was used such that δ_I was similar to groundwater discharge into East Lake. Waters in piezometer nest N3 plot on the meteoric water line (MWL). Discharge to East Lake is therefore unevaporated groundwater. Water from CSIRO irrigation bore #2 plot in the same unevaporated groundwater field (Figure 12.1) and were used as pan feed stock. Feed stock details are summarised below.

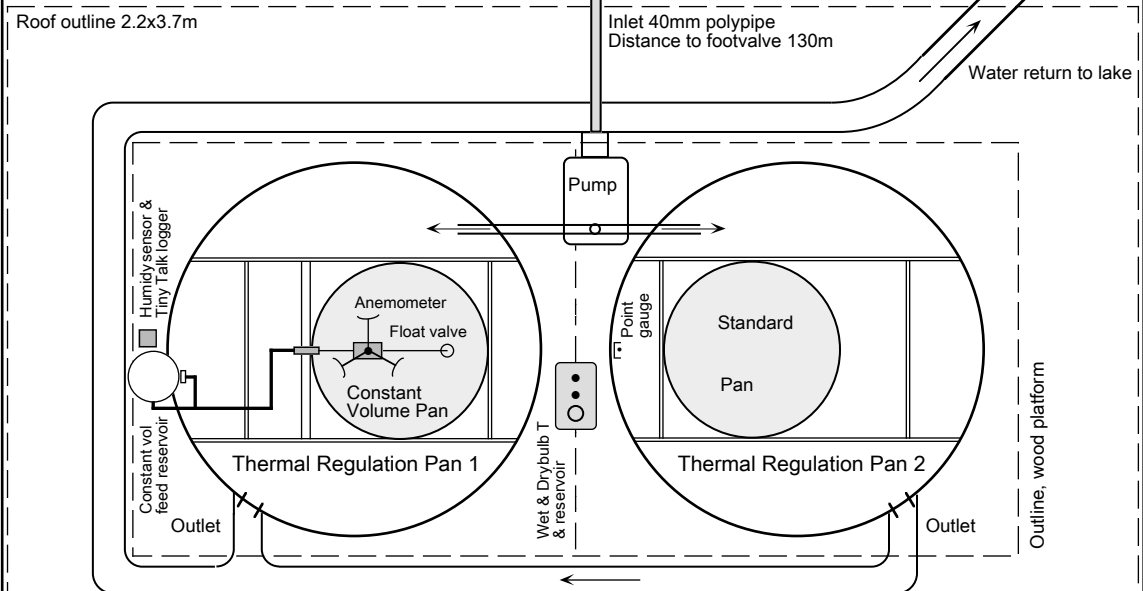
- Water was stored in tightly sealed 200 litre plastic drums. Water for immediate use was stored in a 200 litre galvanised steel drum with spigot.
- Transfer from the plastic drums to the steel drum was accomplished by pressurising the plastic drums with an air compressor, forcing water out via a sealed hose precluding exposure to the atmosphere.

Isotope Experiment Layout

Figure 12.4

Plan View

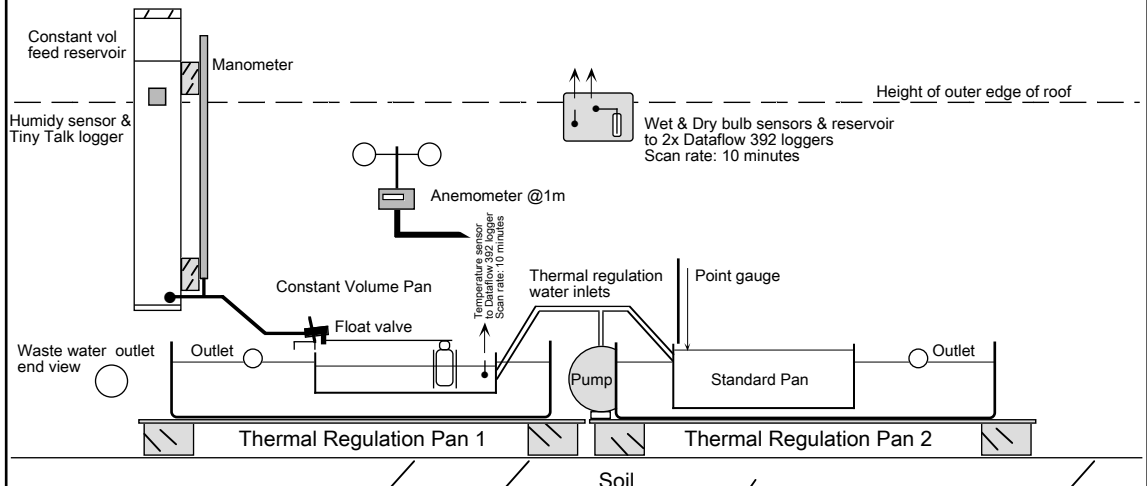
Scale: 1:25



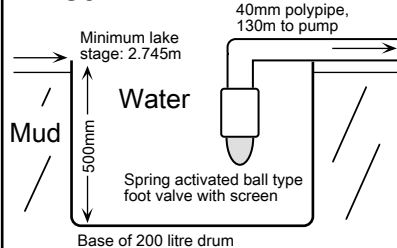
Data Loggers:
Wet & dry bulb temperature sensors & sensor in constant volume pan feed 3x Dataflow 329 loggers
Scan rate: 10 minutes

Pump: Mono CP25, 0.5hp, continuous duty
Total capacity, thermal regulation pans: 340 litres
Measured pumping rate: 1900l/hr
Thermal regulation water is replaced every 10 minutes

Side View

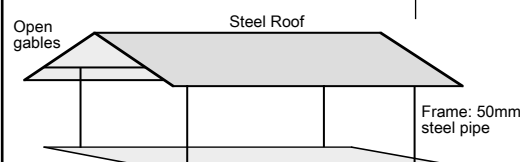


Inlet



Scale: 1:20

General Form



Site Overview

Scale: 1:100

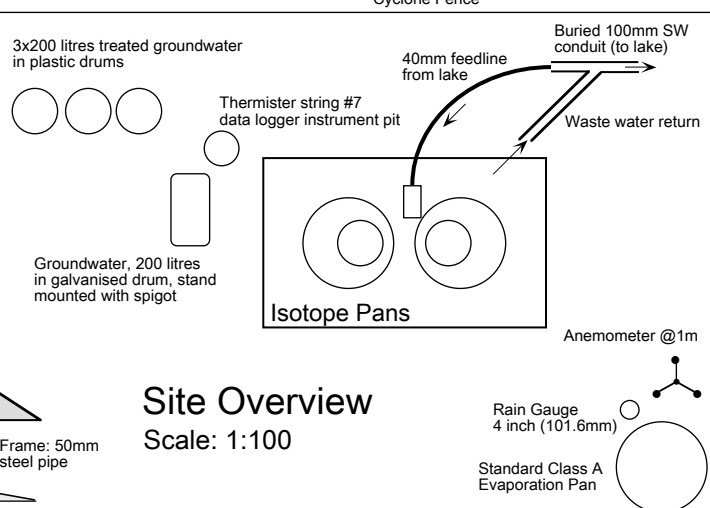
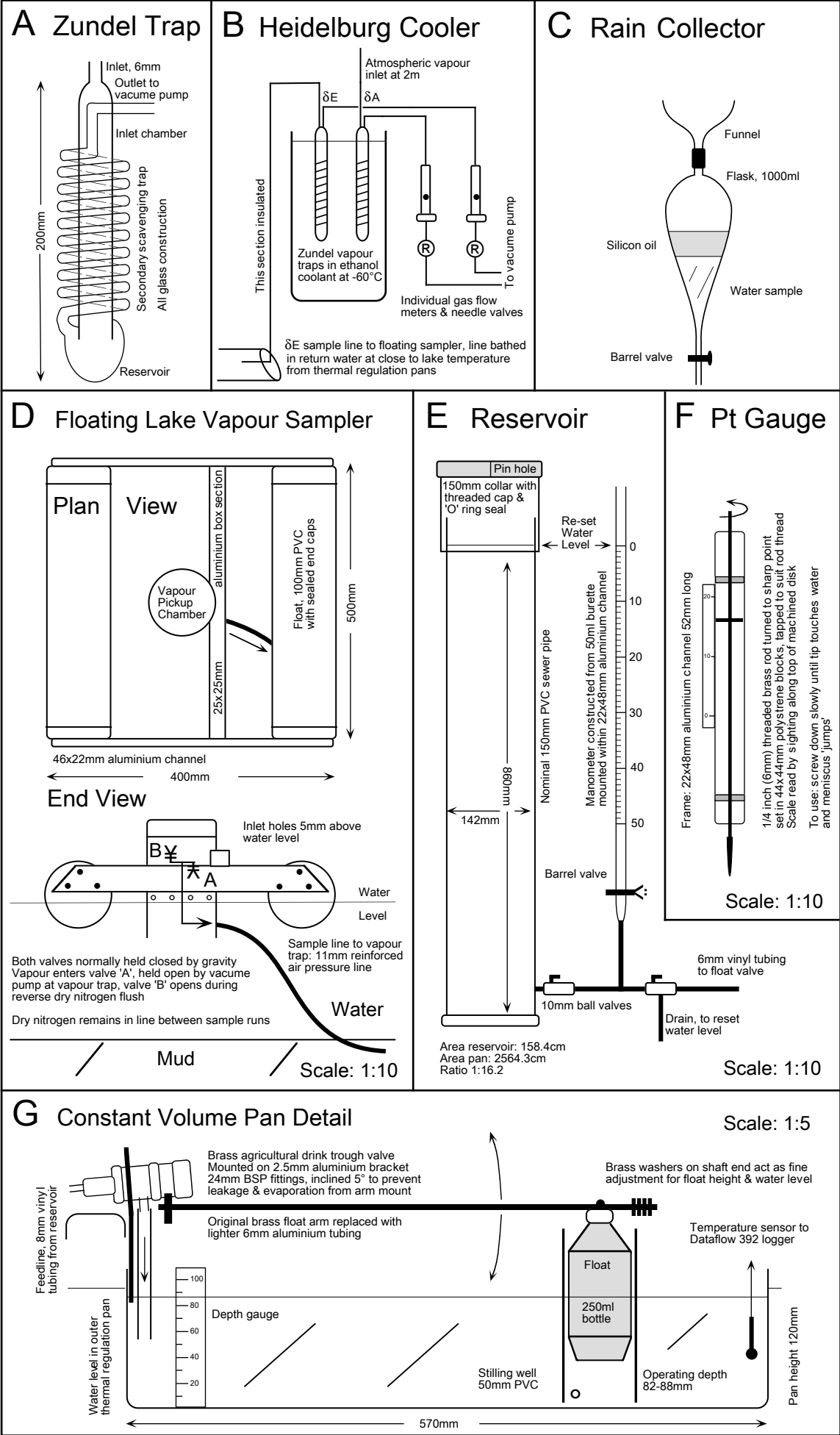


Figure 12.4



Initial tests (February 1996) suggested algae could pose a significant problem in the pans. All water was therefore treated as follows:

- Pool chlorine (calcium hypochlorite) was added to all storage drums to achieve approximately 5ppm free dissolved chlorine
- Pans were treated with pool algicide² (<1ml) as required

Instrumentation

The most critical parameter is humidity. In hindsight a ventilated wet and dry system such as the design of Alksnis *et al* (1991) would have been preferable particularly under night time high humidity low to nil wind conditions. In the event however a simpler non aspirated wet and dry bulb system (Figure 12.4) was used for the entire experiment.

- Wet bulb sensor comprised cotton wick and distilled water reservoir over Dataflow temperature sensor and adjacent 'dry bulb' sensor within mini naturally ventilated screen constructed from styrofoam sheet. Logger scan rate 10 minutes. Data was reduced using the standard Bureau of Meteorology (BOM) 'Non-ventilated wet bulb depression' chart. This was transcribed into EXCEL as a 'Lookup' chart allowing logger wet and dry bulb data to be converted directly to relative humidity.
- Back up was provided by an 'Orion' Tiny Talk relative humidity logger set to 20 minute scan rate. This instrument is rated to 98% relative humidity (*i.e.* non condensing conditions) and proved inaccurate close to dew point.
- Constant volume pan temperature was logged using a third Dataflow logger also at 10 minute scan rate. Lake surface, mid level and bottom temperatures were logged adjacent to the mid lake water inlet (refer Figures 5.1a and 9.5).
- Wind run at 1m was logged over the constant volume pan and adjacent to the pan shelter using manual readout cup anemometers. A Class A evaporation pan with bird guard and rain gauge were also operated adjacent to the shelter.

Despite the 'low tech' nature of the equipment careful design and calibration allowed very precise measurements to be made. Principal data is included as Appendix 12.1.

12.3.3 Methodology

Commencing and completing a 'pan run'

Run commencement

- Reservoir and all tubing filled, any air removed, both pans filled to operating depth via hose from feed stock reservoirs, constant volume pan manometer reservoir reset to '0' level, 'standard' samples of feedwater at t=0 collected (Nylex 10ml vials).

Run conclusion

- on completion standard pan washed out to remove salt and residual brine, constant volume pan drained via syphon, cleaned, both pans then air dried. Generally a run finished at 08:00 hr. Depending on repair and maintenance required the next run commenced one hour later or at 08:00 hr the following day.

² 'Alginox', Harcross Chemicals Pty Ltd, active ingredient 150g/litre benzalkonium chloride

Daily methodology

The experiment was operated continuously for 23 months. Daily reading and water sampling was completed about 08:00 hr. A strict daily regimen was developed as summarised below.

- check pump and circulation
- read constant volume pan feed manometer, reset by adding water to reservoir, read level of constant volume pan, adjust float counter weights as required if level is drifting
- read standard pan level with point gauge
- read temperatures in both pans and both thermal regulation pans using glass laboratory thermometers (as check against data logger files)
- take manual humidity measurement using sling psychrometer (as check against wet and dry bulb logger data)
- read anemometers, rain gauge, drift gauge, Class A pan, top up wet bulb reservoir
- take water sample plus duplicate from both pans, (Nylex 10ml vials)
- water sample centre of East Lake (Nylex 10ml vials), walk to West Lake and sample

East Lake centre of lake waters were sampled conveniently via a tap on the pump outlet. Rainwater for isotopic analysis was collected beneath silicon oil (Figure 12.4c) from a site adjacent to CSIRO Laboratories. Isolated rain events were sampled individually, frontal events were integrated and sampled once fine weather resumed (generally after 1-2 days).

12.3.4 Notes on Salinity in Evaporation Pans

Feed stock water varied from 210 to 350mg/l Cl, equivalent to approximately 0.380 to 0.663mg/l salt. Figures 12.2 d&e demonstrate salinity change in pans evaporated to dryness and evaporated at constant volume as a function of volume reduction and time. High levels of solutes reduce evaporation (Raoult's Law) by lowering the saturated vapour pressure of the evaporating water. The activities of isotopic species are likewise reduced (Dinçer 1968). Compared to fresh water, evaporating saline water exhibits less isotopic enrichment and will achieve a lower steady state δ_s when evaporated under the same meteorological conditions (Gonfiantini 1965 cited Dinçer 1968). As salinity increases ion hydration, and the incorporation of crystallisation water in saline precipitate impart additional effects (Clark & Fritz 1997).

The isotopic time course of saline waters evaporated to dryness typically display distinctive 'hooked' patterns. This phenomenon has been extensively documented in

natural salinas (Lloyd 1966, Fontes & Gonfiantini 1967, Horita & Gat 1989), in pan experiments using sea water (Gonfiantini 1965 cited Dincer 1968, Lloyd 1966) and in theoretical modelling (Sofer & Gat 1972 & 1975, Vlasova & Brezgunov 1978 cited Ferronsky & Polyakov 1982, Gat 1981c).

Using distilled water as feed stock it should be possible to run a constant volume pan for a year or longer, providing a continuous record of K . In the Perry Lakes experiments however salt accumulation from the groundwater feed stock precluded continuous operation. In the pan evaporated to dryness salinity rose exponentially as dryness was approached (Figure 12.2d). Depending on start depth (50-200mm) and feed stock, sea water salinity was reached at pan depths of 0.5 to 4.0mm (Table 12.3).

Table 12.3 Depth (mm) at which S equals sea water (35‰)

Depth at V_0	V/V_0	50mm	100mm	150mm	200mm
210mg/l Cl at V_0	0.01	0.5	1.0	1.5	2.0
350mg/l Cl at V_0	0.02	1.0	2.0	3.0	4.0

V is pan depth at time t , V_0 is initial pan depth at $t=0$

12.3.5 Notes on Fractionation Enrichment Factors and 'm'

Isotope fractionation is a physio chemical process ultimately controlled by the difference in bond strengths of isotopic species (Clark & Fritz 1997). A number of more subtle factors also affect isotopic exchange calculations. These corrections are frequently omitted in simple estimates or in reactions where fractionation is small. Where fractionation is strong or δ values large however these corrections often become significant. In depth discussions are provided by Craig & Gordon (1965) and Gat (1981c). Four fractionation factors appear in equations presented in this chapter:

ρ_L^* isotropic transport resistance of water

ε^* equilibrium enrichment factor

$\Delta\varepsilon$ kinetic enrichment factor

ε total enrichment factor (equals $\varepsilon^* + \Delta\varepsilon$)

Transport resistance ρ_L^* is small and is usually neglected (Craig & Gordon 1965). The equilibrium term ε^* is temperature dependent, increasing as temperature decreases (Dincer 1968, Table 1) being for deuterium 0.0958 at 0°C and 0.0733 at 20°C decreasing to 0.069 at 25°C (Craig & Gordon 1965). Majoube (1971) cites a value of 0.082 at 17.2 °C while experimental values determined from constant volume pans (Allison & Leaney 1982) ranged from 0.087 to 0.091 at room temperature.

The kinetic enrichment factor $\Delta\epsilon$ for deuterium is known to vary greatly depending on environmental conditions and appears to vary diurnally with humidity and wind speed (Gat 1970). Allison *et al* (1979) note that if there is a choice between the use of ^{18}O and ^2H in a water balance study, deuterium is preferable due to the smaller influence of $\Delta\epsilon$ which is both variable and difficult to determine. Merlivat (1970) determined kinetic enrichment factors in the range 0.009-0.015 (at mean relative humidity 0.5-0.65) for both ^2H and ^{18}O . Craig and Gordon (1965) cite 0.019 for ^2H at 25°C. In this study ϵ^* was set to 0.084 and $\Delta\epsilon$ 0.011 yielding ϵ of 0.095. These values are unlikely to introduce significant errors under the meteorological conditions encountered at Perry Lakes. The parameter m is frequently approximated by $h/(1-h)$ (Allison *et al* 1979) however the errors imposed by ignoring or applying incorrect the isotopic enrichment factors become unacceptable at high relative humidity (Figure 12.3d). This figure also demonstrates the relationship between h , m , and K at different ϵ & $\Delta\epsilon$.

12.4 PAN EXPERIMENT PERFORMANCE ASSESSMENT

12.4.1 Volume Regulation

The constant volume pan depth was maintained within 2mm of start depth, representing volume excursions of no more than $\pm 2.4\%$. Table 12.4 summarises pan volume data.

Table 12.4 Comparative pan statistics Runs 1-20

Run	1	2	3	4	5	6	7	8	9	10
Mean depth	85.1	84.2	84.3	84.3	83.2	82.3	82.0	81.8	82.3	82.3
Mean volume	21.80	21.58	21.60	21.60	21.32	21.10	21.02	20.97	21.10	21.10
Start depth	156	75	75	75	75	120	100	100	100	100
Start volume	40.97	19.86	19.86	19.86	19.86	31.59	26.38	26.38	26.38	26.38
Run	11	12	13	14	15	16	17	18	19	20
Mean depth	81.3	82.2	82.4	83.3	83.5	83.2	83.1	81.7	82.1	81.6
Mean volume	20.85	21.07	21.12	21.35	21.40	21.32	21.30	20.95	21.05	20.92
Start depth	100	75	75	50	50	50	100	150	200	
Start volume	26.38	19.86	19.86	13.35	13.35	13.35	26.38	39.41	52.44	

Mean depth-volume refers to constant volume pan, start depth-volume refers to pan evaporated to dryness ('standard pan')
All depths in mm, all volumes in litres

12.4.2 How Typical of the Lake was the Isotope Experiment Site?

Evaporation pans and any adjacent lake of interest must be evaporated under similar meteorological conditions if pan derived exchange parameters are to be applied to the lake with any degree of confidence. In this section we compare wind run, water temperature and evaporation over East Lake and at the pan experiment.

Wind Run

The pan site was comparatively sheltered compared to the open water surface of the lake. Table 12.5 summarises wind run. Pan anemometers were not operated runs 1-6. Figure 12.5c compares pan and lake weekly mean wind velocity for 1997.

Table 12.5 Comparative wind run at 1m over pans and East Lake

Run	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Pans (km)	1125	1021	854	1321	1625	1489	1027	1246	982	1377	1767	2169	1894	2428
Lake (km)	3020	2796	2405	3074	3460	3348	3073	3796	2779	3727	4664	5336	4130	5597
Pan:Lake %	37.3	36.5	35.5	43.0	47.0	44.5	33.4	32.8	35.3	36.9	37.9	40.6	45.8	43.4

Higher values (runs 10-12 and 18-20) occur over summer when strong easterlies alternate with strong southwest afternoon sea breezes. Lowest values (runs 13 & 14) occur in late summer and early winter marked by weak frontal activity and lighter, generally westerly winds. Average pan:lake wind run ratio was 39.3%. This large difference was expected. A site less sheltered from the wind would have been desirable but was simply not possible for security reasons. On the basis of wind run alone, the pan site would appear to be a poor analogue of the lake however the fact that pan and lake evaporation were often similar suggests that reduced wind run had little effect on the outcome of the experiment.

Temperature Control

Adequate temperature regulation was considered to be the single most important criteria in the pan experiments. The concept of operating pans isothermally with a nearby lake appears frequently in the literature (Gat 1970, Welhan & Fritz 1977, Allison & Leaney 1982) although Perry Lakes appears to be the first time the concept has been applied under field conditions. Table 12.6 summarises pan-lake thermal regulation statistics.

Table 12.6 Comparative pan:lake temperature statistics Runs 1-20

Run	1	2	3	4	5	6	7	8	9	10
Av pan T	19.1	14.9	15.8	18.3	20.5	23.5	23.7	25.4	25.8	24.8
Av lake T	19.4	14.8	16.5	19.5	22.3	24.6	25.0	26.5	27.0	25.8
Av difference	0.2	-0.2	0.7	1.1	1.7	1.1	1.3	1.2	1.2	1.0
Max lake-pan	2.6	1.4	2.1	2.3	2.9	3.3	2.6	3.0	3.3	3.9
Min lake-pan	-1.7	-1.5	-1.4	0.5	0.6	-0.4	0.1	-0.2	-0.5	-1.5
Std Dev of dif	0.49	0.32	0.43	0.37	0.39	0.54	0.38	0.65	0.83	1.05
Run	11	12	13	14	15	16	17	18	19	20
Av pan T	24.2	21.9	19.1	16.3	13.7	15.3	19.4	22.0	23.8	24.0
Av lake T	26.1	23.5	20.2	16.6	14.0	16.2	21.0	23.4	26.2	25.4
Av difference	1.8	1.6	1.1	0.3	0.3	1.0	1.5	1.3	2.4	1.4
Max lake-pan	6.3	6.0	4.2	2.4	2.6	2.6	4.4	3.6	10.6	8.2
Min lake-pan	-0.7	-0.3	-0.6	-1.7	-2.2	-1.4	0.1	-0.6	-1.8	-2.3
Std Dev of dif	1.55	1.12	0.57	0.46	0.57	0.48	0.55	0.81	2.56	2.05

Average pan and lake temperature refers to temperature in constant volume pan and lake surface temperature in centre of East Lake. Maximum and minimum are maximum difference between instantaneous lake and pan temperatures. Std Dev is standard deviation of the difference between instantaneous lake surface and pan temperatures. Temperatures recorded every hour Runs 1-5, every 10 minutes Runs 6-20. Data for Run 20 is January 20-February 14 1998 (following pump re-build).

In general thermal regulation was better over winter (Runs 1-6 and 13-18) than summer (runs 7-12 and 19-20). This occurred for the following reasons:

- greater summer head difference between inlet and pump and reduced water viscosity resulting in reduced summer pump efficiency
- reduced summer lake area (particularly Runs 19 and 20) resulted in cooling from the feed line exposed on the lake bed
- sediment build up in the feed line and general degradation of pump efficiency reduced the pumping rate as the experiments proceeded and culminated in pump failure early in Run 20 when the experiment was lacking thermal regulation for five days

Figures 12.5 a & b demonstrate typical lake-pan temperature regimes over weekly periods in early summer and early winter. Over summer the pans tended to lag behind the lake and at any time were typically about 1 degree cooler than the lake. Over winter the pans tracked lake temperature very closely. Typically the lake midday surface maximum exceeded pan temperature by about 0.5° while at other times the difference was less than 0.5° and often within 0.2°. It is worth remembering that water could not be drawn from the surface of the lake so in summer the thermal regulation water was typically 1 degree cooler than the surface and in winter (with positive sediment heat fluxes) was sometimes up to 1 degree warmer than the surface water.

Evaporation

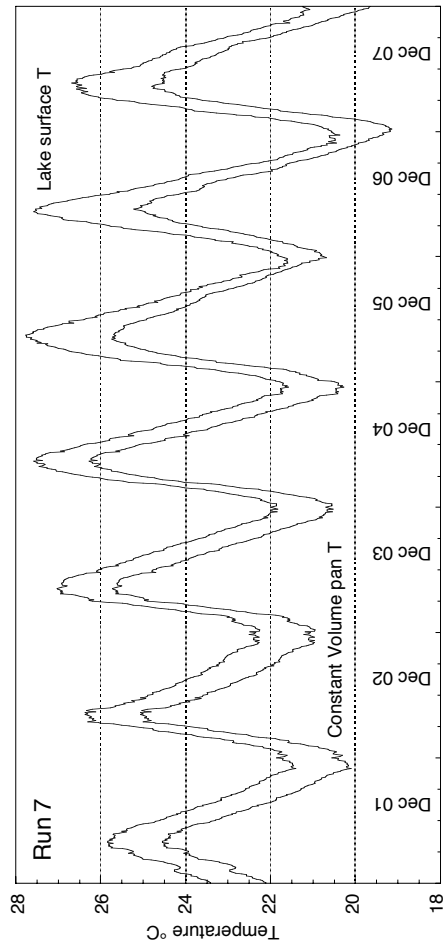
Evaporation is the best indicator of whether exchange parameters determined from pans can be applied to an adjacent lake. If evaporation in the pans and lake are similar it can be concluded that the aggregate meteorological conditions at both sites were also similar. An ideal experimental site would have allowed the pans to be located in a large flat clear area immediately adjacent to the water. No such sites were possible. The sewage pumping compound represented a less than ideal compromise.

It was expected that:

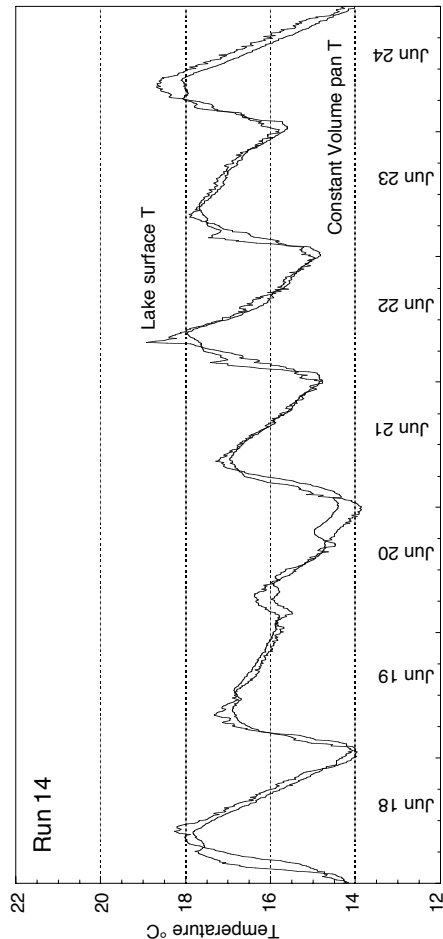
- Pan evaporation would be less than the lake due to reduced wind and little direct solar heating. Pans were partially within direct sunlight only at low winter sun angles
- Constant volume pan evaporation would more closely approximate the lake than the pan evaporated to dryness due to reduced wind exposure at low pan levels as dryness was approached

Unknown factors included the effects of radiant heating and cooling from an adjacent brick building and the metal pan shelter roof, and reduced efficiency of the pan

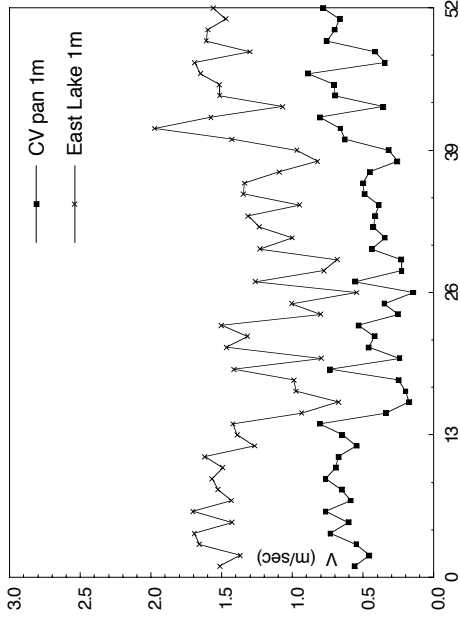
A Lake-constant volume pan temperature November 30-December 7, 1996
Maximum difference is about 2°C



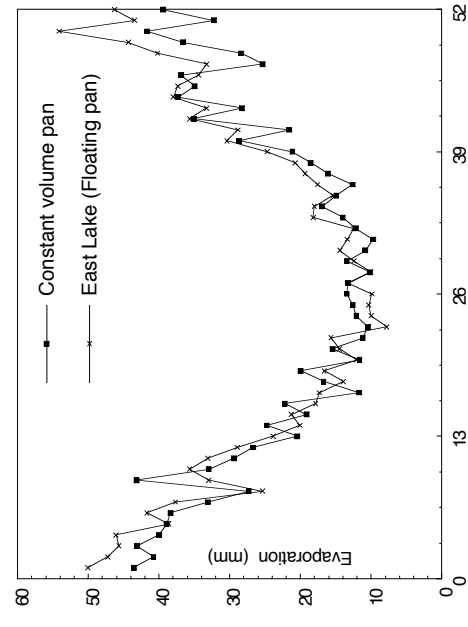
B Lake-constant volume pan temperature June 17 - 24, 1997
Lake temperature is closely tracked by the isotope experiment pan



C Weekly average wind velocity at 1m
X axis defines weeks 08:00 Day 1 to 08:00 Day 8



D Weekly evaporation total (mm)



Meteorological Comparison CV pan and East Lake

Notes

A&B: December data represents typical maximum summer difference between pans and lake. During cooler weather pans tracked with 0.5°C of lake

C: Sheltered position of the isotope experiment severely attenuated wind run compared to the lake. The lake itself is severely sheltered compared to open areas

Figure 12.5

Data 1997	Daily Av (m/sec)	Daily Run (km)	Annual Run (km)
CV pan 1m	0.51	44.2	16175
Lake 1m	1.30	112.2	41055
Lake 2m	1.38	119.0	43555
Lake 5m	1.54	132.8	48622
Perth Airport 3m	2.75	237.7	87011

temperature regulation at low summer lake levels. Pan and lake evaporation is summarised on a pan run basis (Table 12.7) and weekly (Figure 12.5d).

Table 12.7 Comparative evaporation Runs 1-20

Run	1	2	3	4	5	6	7	8	9	10
CV pan	165.6	83.8	80.7	77.5	93.8	139.6	116.6	122.7	108.0	123.7
East Lake	209.9	97.3	83.4	84.2	92.4	142.4	118.9	141.1	123.8	128.6
Pan: Lake %	78.9	86.1	96.8	92.0	101.5	98.0	98.1	87.0	87.2	96.2
Std pan	156	75	75	75	75	120	100	100	100	100
East Lake	209.9	97.3	83.4	85.2	83.5	139.9	118.9	134.8	123.8	125.0
Pan: Lake %	74.3	77.1	89.9	88.0	89.8	85.8	84.1	74.2	80.8	80.0
Run	11	12	13	14	15	16	17	18	19	20
CV pan	124.8	98.3	88.4	61.5	62.8	67.3	129.2	195.3	162.9	234.7
East Lake	118.0	105.0	82.9	58.4	63.2	76.5	152.4	213.8	207.6	265.9
Pan: Lake %	105.8	93.6	106.6	105.3	99.4	88.0	84.8	91.3	78.5	88.3
Std pan	100	75	75	50	50	50	100	150	200	
East Lake	113.0	104.0	84.0	57.7	62.5	66.8	134.3	184.8	281.8	
Pan: Lake %	88.5	72.1	89.3	86.7	80.0	74.9	74.5	81.2	71.0	

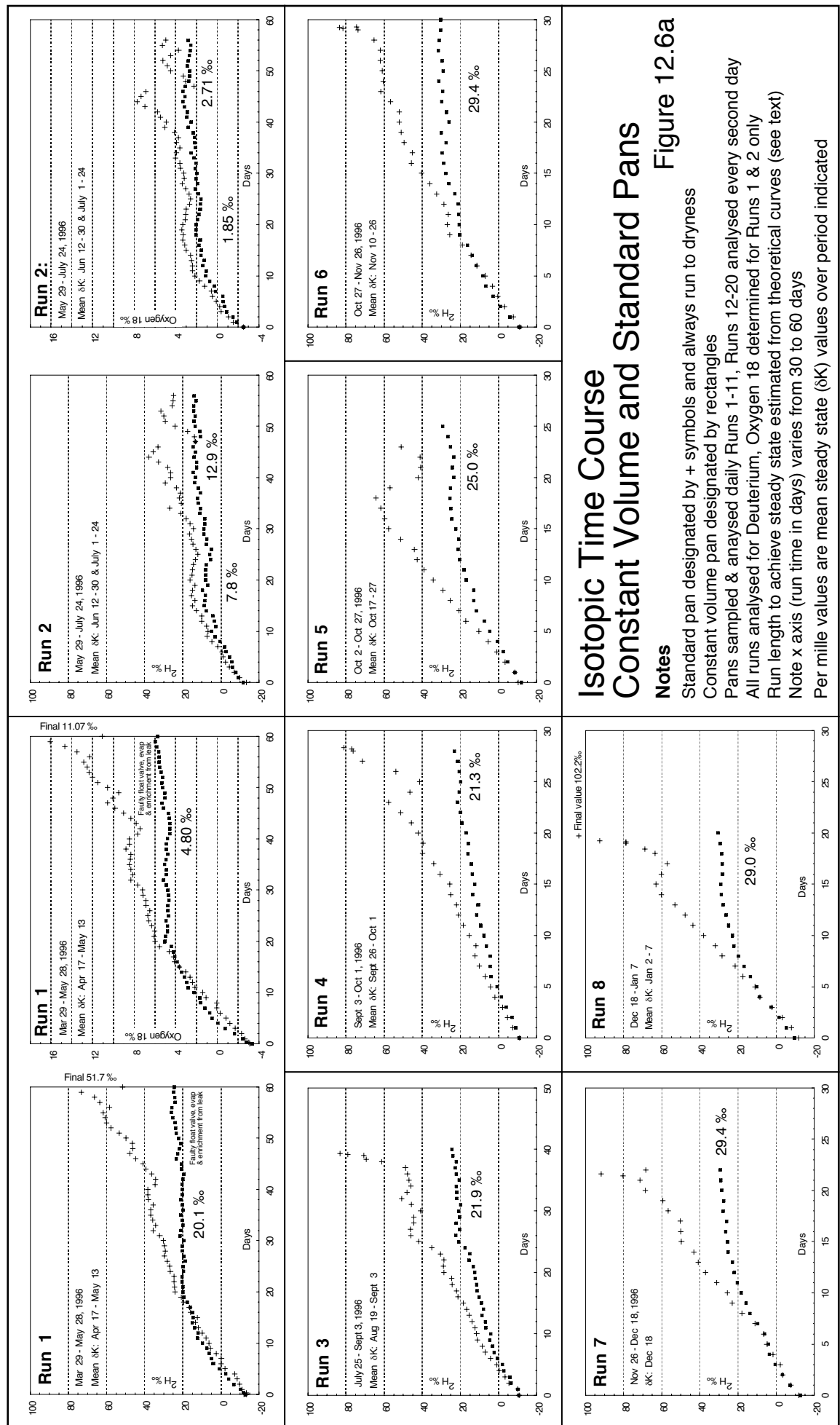
Notes: All pan and lake figures in mm. Area Constant Volume pan: 2532cm², Standard pan 2551cm². Difference represents 19cm² occupied by stilling well and float. Lake evaporation for Runs 1 & 20 partially calculated using pan:lake coefficient for Class A pan at Perth Airport.

The data largely agree with the expectation that pan evaporation would be somewhat less than lake evaporation. The only real surprise was that on four runs constant volume pan evaporation exceeded the lake by up to 6.6%, concentrated between March and June 1997. The reasons are unclear.

The isotope experiment ran continuously from March 29, 1996 to February 14, 1998 representing 688 days of continuous operation and almost two complete years of flux weighted data. Mean run time was 34.4 days. A total of 1077.3 litres of water were evaporated through the experimental pans (constant volume pan: 596.4 litres, pan evaporated to dryness: 481.9 litres).

12.5 RESULTS

Isotopic time course as raw data, Runs 1-20 for both pans is summarised in Figure 12.6 a&b. Note the frequent salt induced, sudden reduction in deuterium or 'hook' patterns (Section 12.3.4) as water volume diminished in pans evaporated to dryness. Constant volume pan steady state δ_K is apparent in all runs. Mean δ_K is indicated on each graph. Figures 12.7 a&b show graphical representation of steady state δ_S in pans evaporated to dryness. The two pan experiments simply represent different techniques for establishing the same exchange parameters. In the following section experimental results from the two techniques are presented separately. Section 12.5.9 compares exchange parameters determined using both techniques. Data appears as Appendix 12.1.



Isotopic Time Course Constant Volume and Standard Pans

Notes

Standard pan designated by + symbols and always run to dryness

Constant volume pan designated by rectangles

Pans sampled & analysed daily Runs 1-11, Runs 12-20 analysed every second day

All runs analysed for Deuterium; Oxygen 18 determined for Runs 1 & 2 only

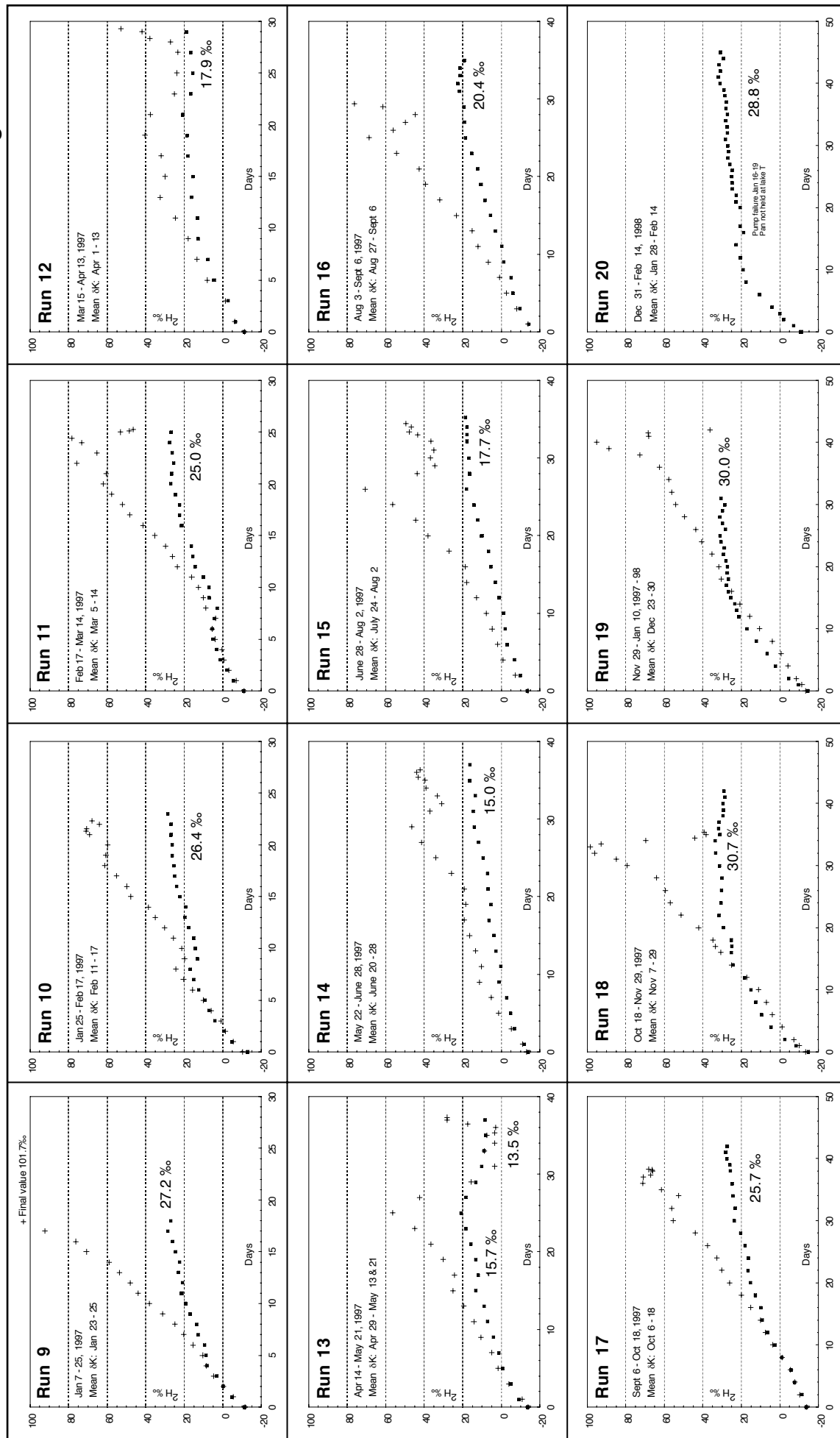
Run length to achieve steady state estimated from theoretical curves (see text)

Note x axis (run time in days) varies from 30 to 60 days

Per mille values are mean steady state (δK) values over period indicated

Figure 12.6a

Figure 12.6b



12.5.1 Graphical and Mathematical Determination of Steady State δ_S

Pans evaporating to dryness represent the more difficult technique for determining exchange parameters because as dryness is approached small meteorological changes coupled with the effects of increasingly saline water have very large effects on heavy isotope enrichment. The problem is compounded in summer when relative humidity is low. Theoretically steady state δ_S cannot be achieved under these conditions when $m < 1$ (Allison & Leaney 1982). This is the case for relative humidity less than about 50%.

Graphical solutions for δ_S were computed by fitting least squares curves. These took the form of second or third degree polynomials. Steady state δ_S was calculated at $V/V_o = 0.0001$. It is evident that steady isotopic enrichment was always possible to about $V/V_o = 0.5$ and frequently to $V/V_o = 0.1$. This 'early' data is in fact highly 'flux weighted', representing 50-90% of total evaporative loss and therefore can be used to determine steady state δ_S even where data close to dryness is absent or spurious. In Figure 12.7 different symbols indicate data points used and excluded from the curve fits.

Steady state was also computed mathematically. Rearranging equation 12.8 yields

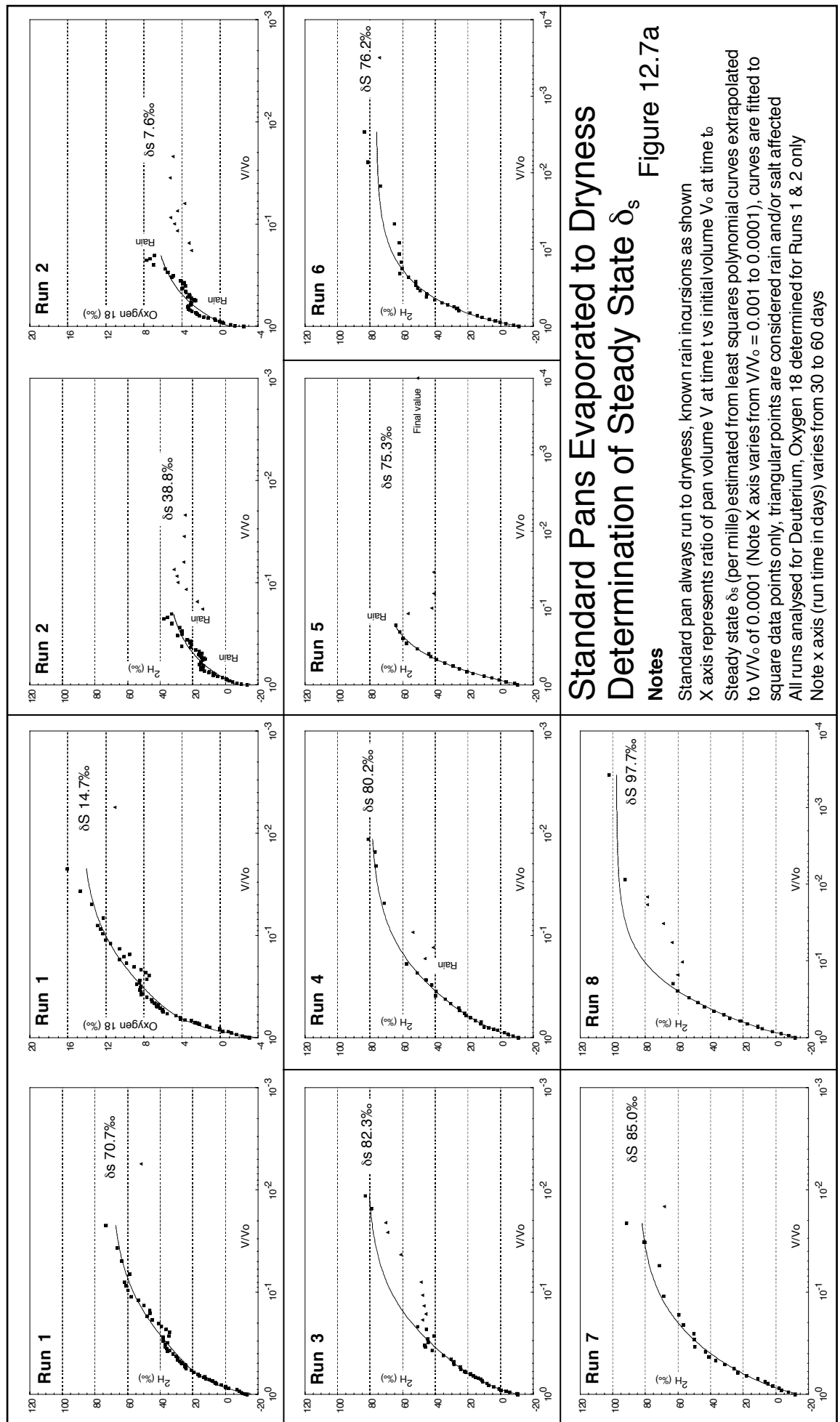
$$\delta_S = \frac{\delta - f^m \delta^o}{1 - f^m} \quad (12.22)$$

This describes δ_S for constant (in this case daily average) values of h , $\Delta\epsilon$, $E\rho_L^*$ & α^* , incorporated as m . On a daily basis, computed δ_S varies widely, however, mean daily computed δ_S was usually close to the graphical solution. Again obviously spurious data was excluded. Table 12.8 summarises the data.

Table 12.8 Comparative determination of steady state δ_S Runs 1-19

Run	1	2	3	4	5	6	7	8	9	10
Graphical	70.7	38.8	82.3	80.2	75.3	76.2	85.0	97.7	100.2	74.5
Maths (part)		38.5	59.5	67.6	110.2	113.9	99.0	117.0		86.8
Maths (full)	61.3		60.4	68.2	96.7	103.5	98.2	105.4	98.8	85.2
Run	11	12	13	14	15	16	17	18	19	
Graphical	80.3	60.8	83.6	54.9	103.5	79.4	76.4	103.0	96.8	
Maths (part)	72.9	67.8	51.2	31.9	59.6	60.5	59.2	119.3	81.0	
Maths (full)	70.7			34.3		60.1	61.0	106.8	78.2	

All values are permil (‰), graphical solution employed polynomial curve fit, extrapolated to $V/V_o=0.0001$, mathematical solutions employ equation 12.22 (Eqn 5 of Welhan & Fritz 1977), 'part' refers to initial part of deuterium time course unaffected by rain and/or salinity, 'full' employed entire data set for each pan run



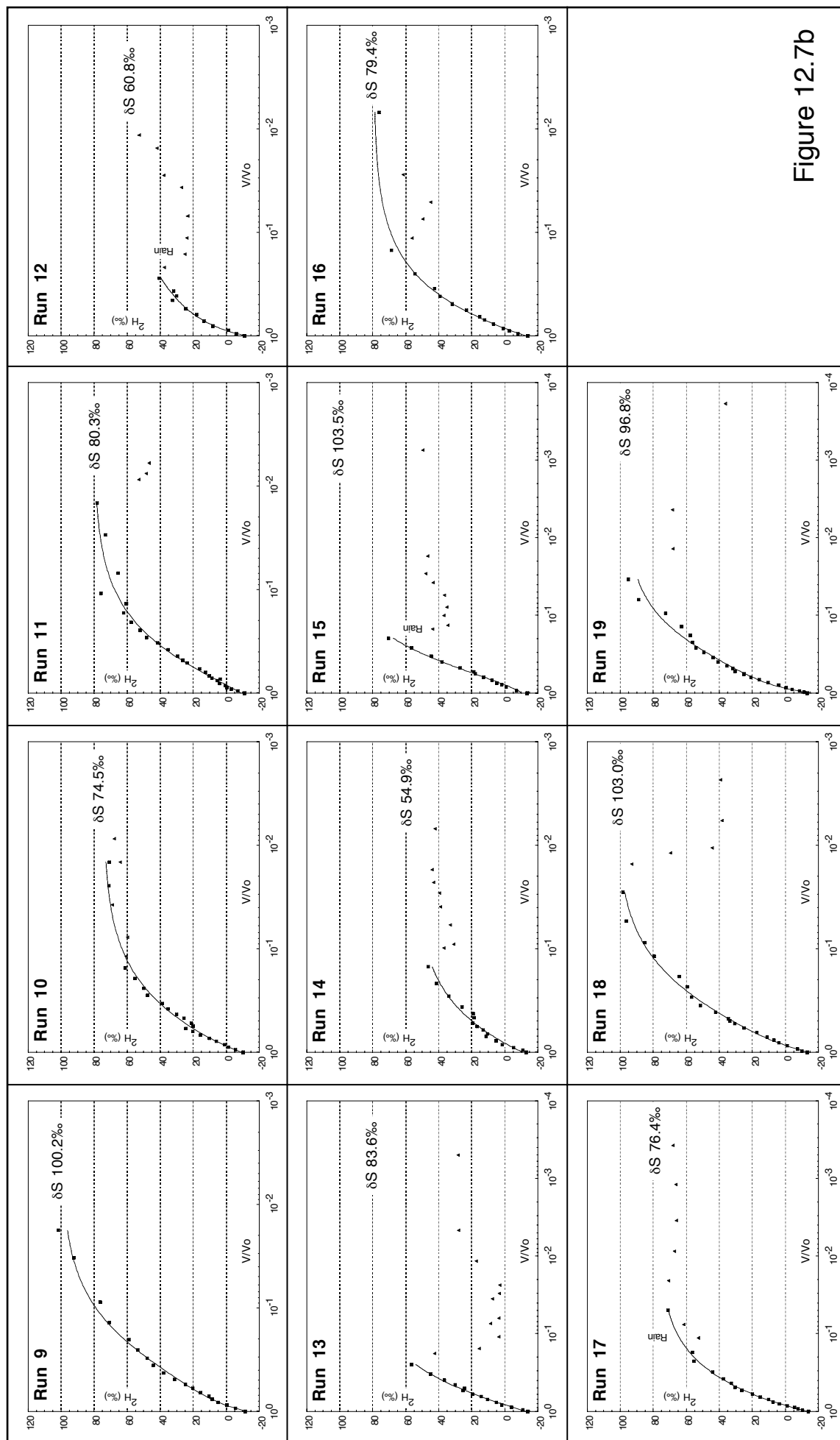


Figure 12.7b

An annual δ_S curve was developed as a cosine function fitted to graphical and theoretically derived data (Figure 12.8a). Steady state reflects meteorological parameters ultimately controlled by the annual solar cycle. Steady state maxima and minima appear to be centred on or close to the summer and winter solstice. Daily δ_S is defined by

$$35\cos 0.017214x + 75 \quad (12.23)$$

with an annual winter to summer range of 40 to 110‰ and amplitude of 70‰. An annual theoretical relative humidity function was developed in a similar fashion (Figure 12.8b) based on average bi-monthly wet and dry bulb data normalised to lake surface temperature where daily average humidity is defined by

$$11.5\cos 0.017214x + 66.5 \quad (12.24)$$

with an annual winter to summer range of 78 to 55%. Note that unlike δ_S , relative humidity is seasonally offset from the solstice with minimum on February 1 and maximum August 3. In these expressions for both δ_S and relative humidity December 21 is taken to be Day 0 and Day 366.

12.5.2 Annual δ_A from Pan Evaporated to Dryness

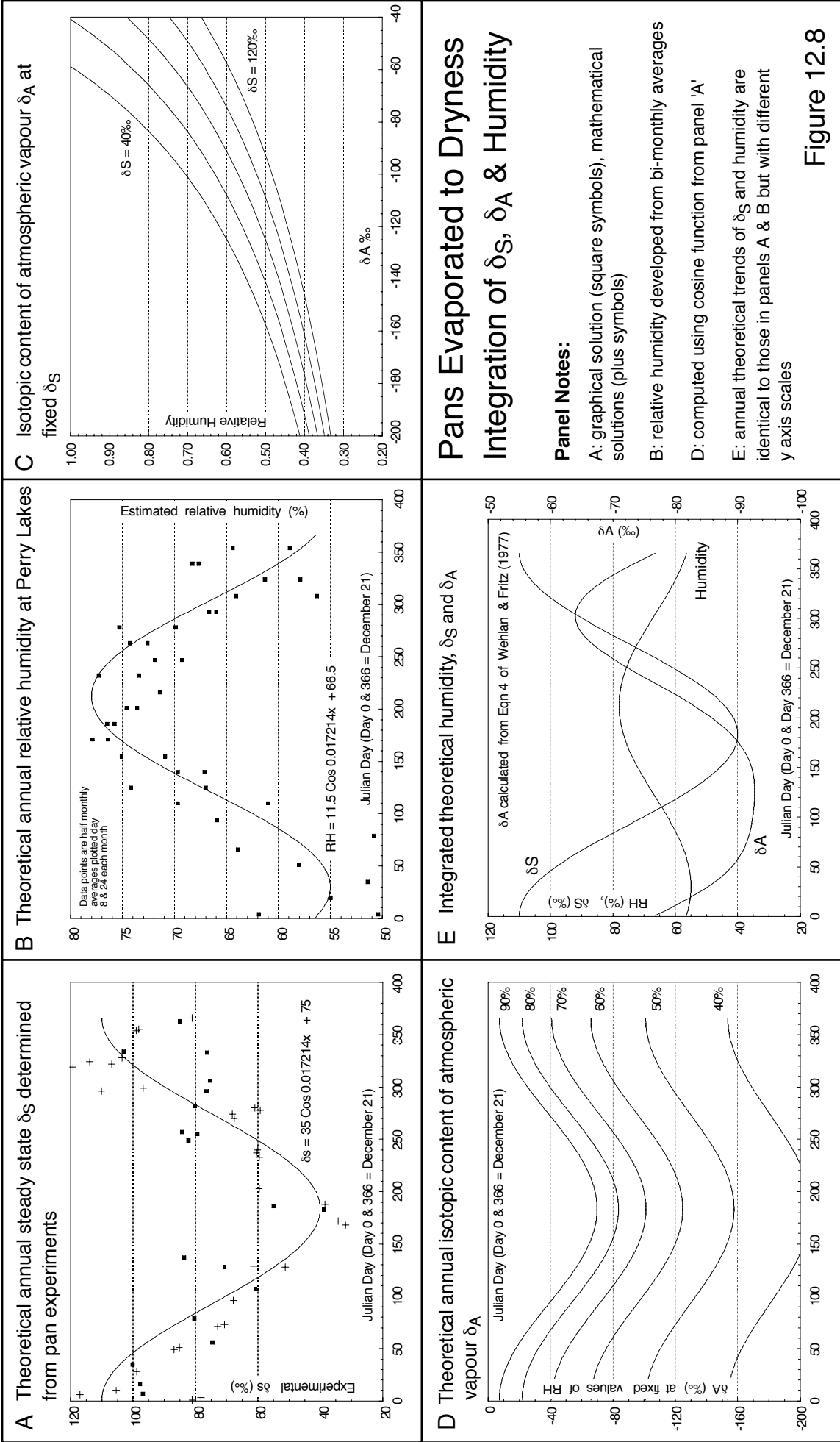
Rearranging equation 12.7 yields

$$\delta_A = \frac{\delta_S(h - \varepsilon) - \varepsilon}{h} \quad (12.25)$$

which defines δ_A for any value of δ_S , h , and ε . Setting δ_S to fixed values allows δ_A to be defined for varying relative humidity (Figure 12.8c). More realistically using equation 12.23 to define seasonal variation in δ_S , the seasonal variation in δ_A can be predicted at fixed relative humidity (Figure 12.8d).

12.5.3 Integrated Annual δ_S and δ_A from Pan Evaporated to Dryness

Defining δ_S and h by equations 12.23 and 12.24 allows a 'best guess' prediction of annual daily average δ_A calculated from equation 12.25 rearranged from equation 12.7 and equation 4 of Welhan & Fritz (1977). Figure 12.8e shows the predicted annual trend of δ_A plotted along with annual δ_S and relative humidity. The experimental δ_S data suggests that daily average δ_A will diminish (contain less deuterium) over summer and increase over winter with a range of about -92‰ to -64‰. These experimentally predicted trends are compared with measured δ_A later in this chapter.



12.5.4 Estimation of $\delta_{E(lake)}$ from Pan Evaporated to Dryness

Rearranging equation 12.14 yields

$$\delta_{E(lake)} = m_{pan} \delta_{lake} - m_{pan} \delta_{S(pan)} - \delta_{lake} \quad (12.26)$$

Theoretical families of curves for $\delta_{E(lake)}$ can then be generated for varying pan h (and hence m) and fixed pan δ_S and isotopic concentrations of lake water δ_L (Figure 12.9). All curves pass through a common point where $m = 1$. Remember that a value of unity for m is the approximate cut-off for practical development of δ_S using pans evaporated to dryness since for conditions where $m < 1$ steady state pan composition is never attained (Allison & Leaney 1982). In some plots one value of $\delta_{E(lake)}$ plots as a vertical line. This occurs where $\delta_S = \delta_L$.

Constant Volume Pan

12.5.5 Graphical Determination of Steady State δ_K

Steady state δ_K was only determined graphically. Data from Figure 12.6 are summarised as Table 12.9. Runs 1 and 2 include ^{18}O data. All other data is deuterium. The seasonal range of the experimentally derived limiting values (12.9‰ to 30.7‰) is similar to the theoretically predicted range (Table 12.2) of 16.2‰ to 34.5‰.

Table 12.9 Experimental steady state δ_K Runs 1-20

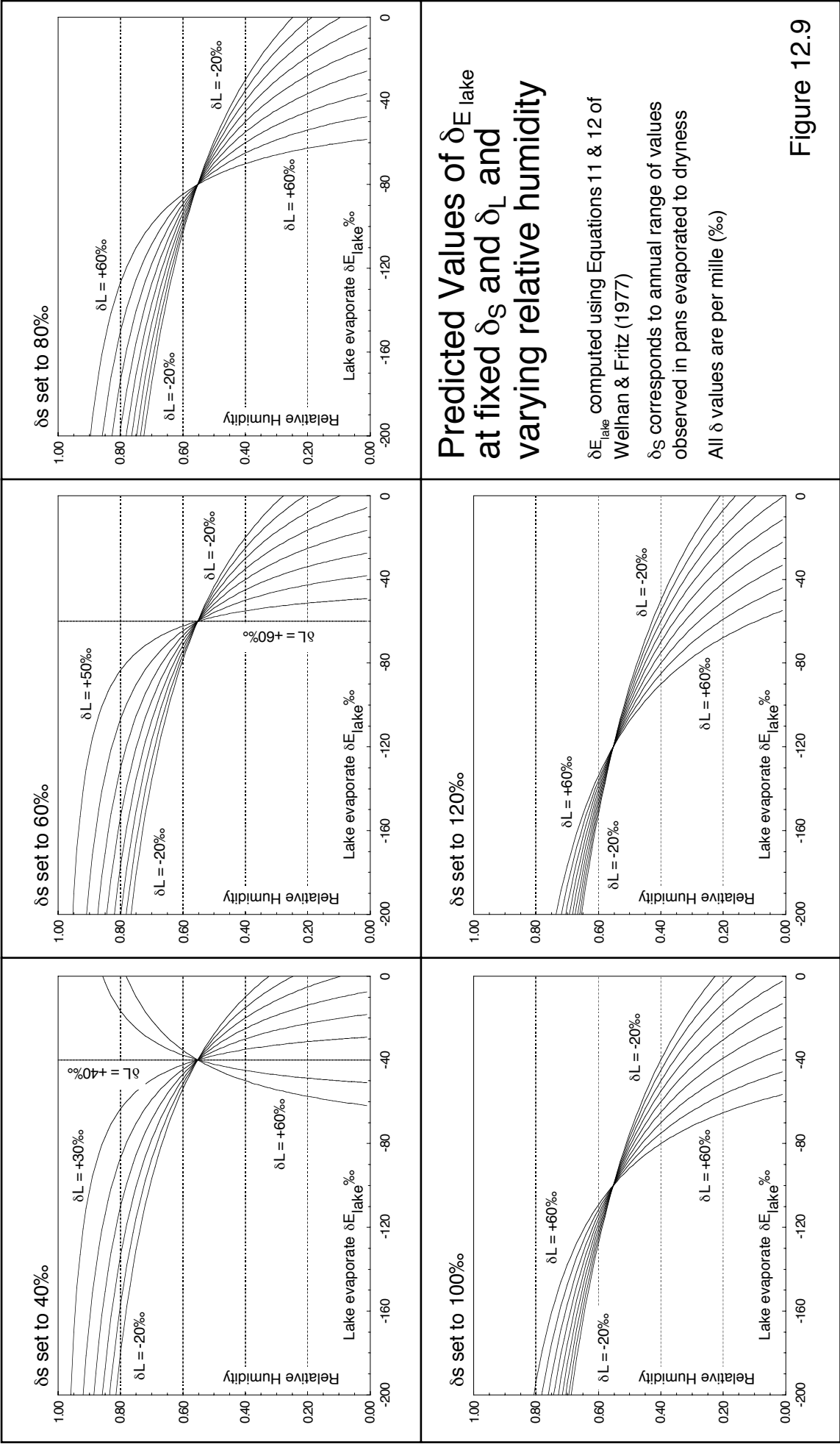
Run	1 ^2H	1 ^{18}O	2 ^2H	2 ^{18}O	3	4	5	6	7	8	9
Mean δ_K (‰)	20.1	4.80	12.9	2.71	21.9	21.3	25.0	29.4	29.4	29.0	27.2
Run	10	11	12	13	14	15	16	17	18	19	20
Mean δ_K (‰)	26.4	25.0	17.9	15.7	15.0	17.7	20.4	25.7	30.7	30.0	28.8

All data is deuterium except as indicated

An annual δ_K curve was also developed as a cosine function but fitted to graphical data only (Figure 12.10a). Again steady state maxima and minima appear to be centred on or close to the summer and winter solstice with summer to winter maximum and minimum of 30.5 to 11.5‰. Daily δ_K is defined by

$$9.5 \cos 0.017214x + 21 \quad (12.27)$$

Compared to the data developed from pans evaporated to dryness (Figure 12.8a), the constant volume pan derivation of δ_K displays far less scatter.



12.5.6 Annual δ_A from Constant Volume Pan

Rearranging equation 12.18 yields

$$\delta_A = h \left[\left[\frac{\left(K - \frac{\delta_I}{(m+1)} \right) (m+1)(h-\varepsilon)}{m} \right] - \varepsilon \right] \quad (12.28)$$

which defines δ_A for any value of K , δ_I , h and m , (containing h , $\Delta\varepsilon$ and ε). Fixing K allows δ_A to be defined for varying relative humidity (Figure 12.10c). More realistically using equation 12.27 to define seasonal variation in K , δ_A can be similarly predicted at fixed relative humidity (Figure 12.10d).

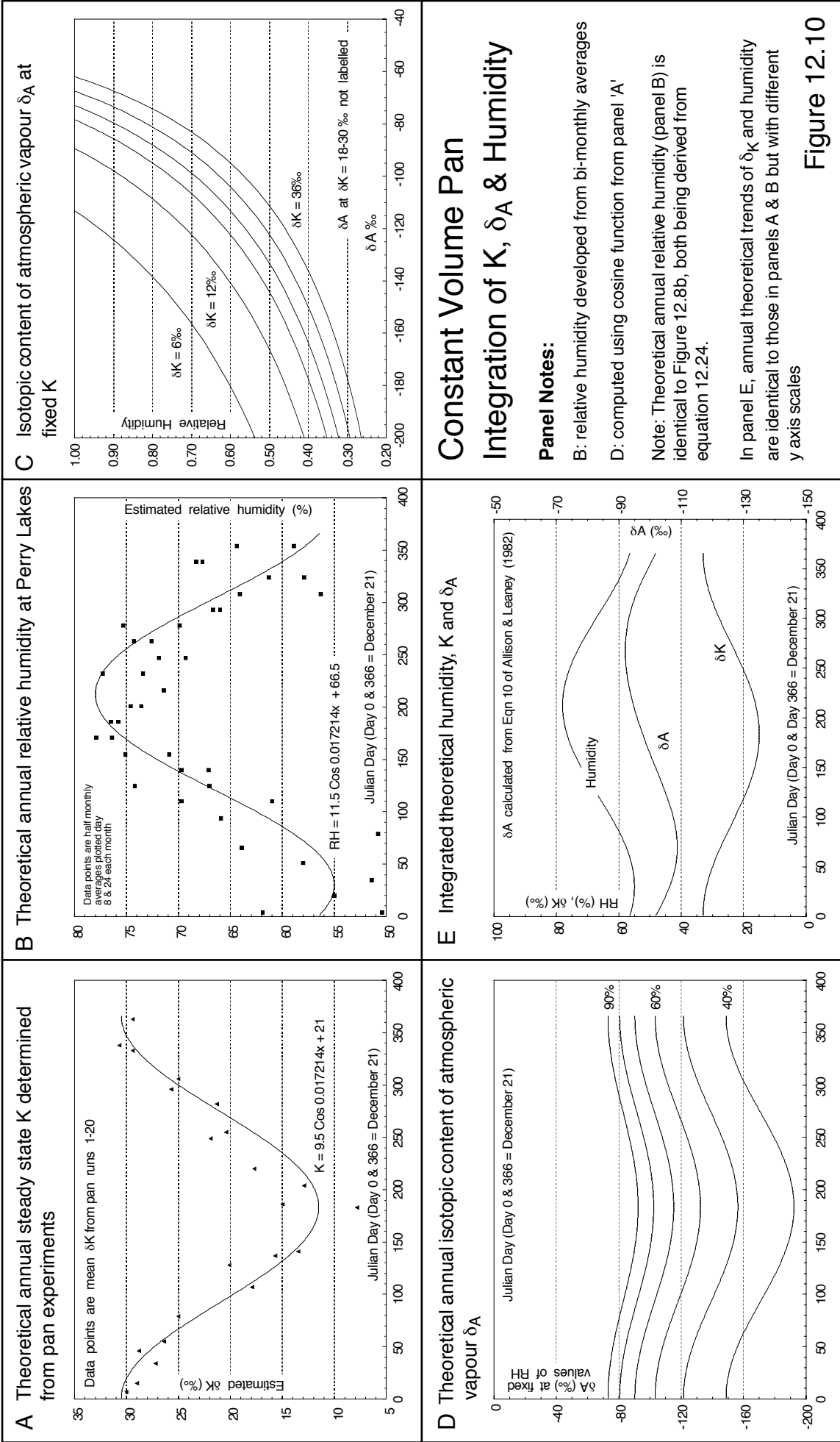
12.5.7 Integrated Annual K and δ_A from Constant Volume Pan

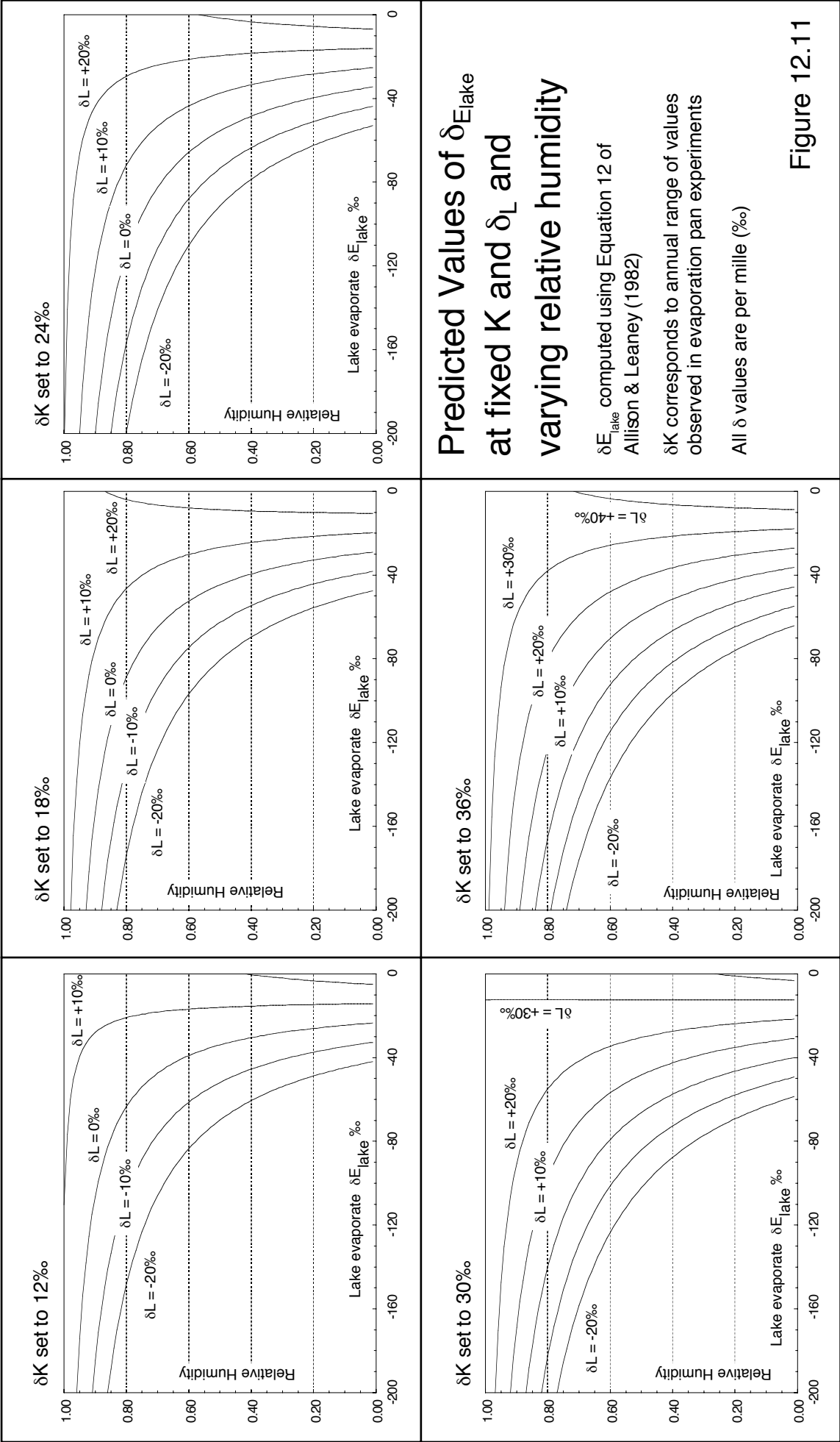
Finally, by substituting the annual trend of measured relative humidity (equation 12.24) and the annual trend of experimentally determined δ_K (equation 12.27) into equation 12.28 allows a 'best guess' prediction of annual daily average δ_A (Figure 12.10e). Plotted along with it are annual K and relative humidity. These are identical to the plots appearing in Figures 12.10 a&b but with different y axis scales.

12.5.8 Estimation of $\delta_{E(\text{pan})}$ and $\delta_{E(\text{lake})}$ from Constant Volume Pan

Employing equation 12.20, theoretical families of curves for $\delta_{E(\text{lake})}$ can then be generated for varying pan h (and hence m) and fixed pan K and isotopic concentrations of lake water δ_L (Figure 12.11). Pans evaporated at constant volume will achieve steady state K regardless of h (and hence m). The range of daily average relative humidity recorded during the pan experiments (Table 12.10) demonstrates that for all runs there were days when average relative humidity was less than 50% and steady state could not be obtained in a pan evaporated to dryness. During summer, days when the minimum daily average relative humidity is less than 50% are quite common. The commonness of this condition demonstrates the benefit of determining exchange parameters from a constant volume pan.

Table 12.10 also shows the recorded range of δ_{lake} . It is evident that where $K = \delta_{\text{lake}}$ then $\delta_{E(\text{lake})}$ is constant for all values of h . In Figure 12.11, if K is set at -12.4‰, then $\delta_{E(\text{lake})}$ plots as a vertical line. This is analogous to the situation where $\delta_S = \delta_L$ in pans evaporated to dryness.





Predicted Values of δE_{lake} at fixed K and δ_L and varying relative humidity

δE_{lake} computed using Equation 12 of Allison & Leaney (1982)

δK corresponds to annual range of values observed in evaporation pan experiments

All δ values are per mille (‰)

Figure 12.11

Table 12.10 Comparative daily average humidity and δ_{lake} Runs 1-20

Run	1	2	3	4	5	6	7	8	9	10
Min daily av RH	39.7	49.8	43.1	43.2	41.5	33.6	38.2	31.6	36.2	39.3
Max daily av RH	78.0	88.2	87.1	75.2	73.6	75.3	62.3	54.6	59.9	69.9
Min δ_{lake}	-6.8	-16.1	-6.2	2.5	5.1	5.1	11.1	10.2	9.9	-2.7
Max δ_{lake}	3.1	-1.9	2.3	7.1	14.5	16.6	18.4	18.9	18.5	13.3
Run	11	12	13	14	15	16	17	18	19	20
Min daily av RH	39.0	43.7	42.9	50.6	41.7	45.5	36.3	30.0	36.2	37.4
Max daily av RH	75.3	83.2	87.8	88.4	83.4	82.0	72.5	70.8	64.7	77.5
Min δ_{lake}	-1.0	-6.4	-3.9	-10.9	-5.7	-4.6	-20.3	5.5	-0.5	ND
Max δ_{lake}	8.8	17.0	6.9	0.5	-1.2	1.8	1.8	33.2	67.7	ND

Relative humidity (RH) normalised to constant volume pan temperature (= lake surface temperature), ND = no data

12.5.9 Comments on $\delta_{E(\text{lake})}$ determined from δ_S and K

Even a cursory examination of Figures 12.9 and 12.11 confirms that estimates of $\delta_{E(\text{lake})}$ made using exchange parameters determined from δ_S and K will not be the same. Equations developed to determine such parameters are premised on numerous assumptions not the least of which is the condition of steady evaporation and humidity. Evaporation usually reaches a maximum in early afternoon and a minimum just before dawn. Relative humidity displays exactly the opposite pattern. Instantaneous (10 minute) relative humidity at Perry Lakes ranged from 9% to 100% over the course of the pan experiments. Evaporation pans smooth or integrate these fluctuations to provide 'flux weighted' estimates of m and δ_S or K . The steady state parameters δ_S or K are applied somewhat differently to further estimate $\delta_{E(\text{lake})}$ resulting in curve families which are similar but far from identical. The same comments apply to annual trends in daily average δ_A (Figures 12.8e and 12.10e) predicted from δ_S or K .

12.6 ANNUAL RELATIONSHIP BETWEEN δ_S AND δ_K

Combining field data from the pan experiments and theoretical curves allows mean monthly steady state estimates to be developed for Perry Lakes (Table 12.11).

Table 12.11 Relationship between δ_S and δ_K , median monthly values

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
δ_K (‰)	29.6	26.6	22.2	17.2	13.4	11.6	12.3	15.4	20.1	24.9	28.7	30.5
δ_S (‰)	106.8	95.5	79.4	61.1	47.0	40.2	42.8	54.3	71.5	89.2	103.5	109.8

Minimum values occur June 21 (11.5‰ and 40.0‰) and maximum values December 21 (30.5‰ and 110.0‰). The theoretical trigonometric functions describe a simple linear relationship between δ_S and δ_K such that

$$\delta_S = 3.68\delta_K - 2.36 \quad (12.29)$$

12.7 DIRECT FIELD MEASUREMENT OF δ_A AND $\delta_{E(\text{lake})}$

The isotopic composition of ambient water vapour δ_A and humidity are the principal factors influencing heavy isotope enrichment of a water body undergoing evaporation (Simpson *et al* 1987). Under conditions of low relative humidity vapour flux from a water surface can be approximated by a Rayleigh distillation where

$$\delta = -1000(1 - f^{a^*}) \quad (\text{Whitehead 1990 Eqn 7}) \quad (12.30)$$

Where relative humidity is high some evaporation and Rayleigh distillation do occur, however isotopic composition of the residual water becomes dominated by exchange of isotopes between air vapour and the water surface. The water now approaches isotopic equilibrium with respect to air vapour δ_A .

Knowledge of δ_A is required in isotopic water balance determinations (Chapter 6) and evaporation pans can be used to estimate δ_A (this chapter). Direct field measurement represents a second approach and is useful as a validation of pan derived values. Field measurement however is costly and time consuming rendering continuous direct measurement of δ_A impractical. Therefore such measurements only provide a 'snap shot' of δ_A over the air sampling period, typically several hours. As a result little detail is known regarding the isotopic composition of atmospheric water vapour in Australia (Whitehead 1990). In general δ_A varies diurnally, primarily in response to humidity and seasonally in response to this and other factors such as varying air mass provenance.

12.7.1 Direct Field Measurement of δ_A

Sampling of atmospheric vapour must be done without fractionating the isotopes (Yurtsever & Gat 1981). Typically this has been accomplished by freezing out the water at extremely low temperatures using dry ice or liquid air (Craig & Horibe 1967, Merlivat & Coantic 1975, Sofer & Gat, 1975). Atmospheric water vapour at Perry Lakes was collected using glass vapour traps after the design of Zundel *et al* (1978). These consist of a primary inlet chamber and a secondary coiled scavenging trap. With reference to Figure 12.4a, the traps are immersed in ethanol chilled to approximately -60°C by means of a 'Heidelberg' cooler³. The cooler comprises a single stage compressor and cooling chamber containing three ethanol filled wells allowing three traps to be operated simultaneously. The vapour traps are immersed in these wells. Air is drawn through the

³ The cooler uses R502 gas which under single stage compression will theoretically cool to -70°C . Thermocouple tests indicated actual ethanol temperature was about -50 to -55°C . The cooling vessel was further insulated with insulfoam (high density rubber foam). Styrofoam and insulfoam inserts were made to fit over the ethanol wells. Under daytime summer field conditions typical operating temperature was -58°C .

traps via a vacuum pump, each trap being controlled by a separate needle valve and gas flowmeter (Figure 12.4b). A minimum of about 5ml liquid water is required for ²H and ¹⁸O analyses.

Condensation and freezing are fractionating processes, however if all vapour is collected the frozen vapour when thawed and mixed within the sealed trap is representative of the atmospheric vapour, the critical point being that all vapour must be trapped. Zundel *et al* (1978) reported a 99.9% extraction efficiency at flow rates of 1m³/hr. Tests at this rate using two traps in series indicated over 5% of vapour was not being frozen in the first trap. Optimum rate (extraction efficiency, sample size and run time) was found to be 4 litres/min (0.24m³/hr). Merlivat & Coantic (1975) using dry ice cooled traps recommended 2.5 litres/min to achieve complete extraction. By running two traps in series, extraction efficiency was calculated for each sampling run. Average extraction efficiency over 108 runs was 99.3%. The lowest extraction efficiency was 96.0% (sample A047, June 9, 1997). There was never sufficient water in the second trap to analyse however possible errors were tested using a mass balance calculation of the form

$$\delta_{sample} = \frac{massT1 \cdot \delta T1 + massT2 \cdot \delta T2}{mass(T1 + T2)} \quad (12.31)$$

where *massT* is water mass (grams) in trap and δT is deuterium ratio of the water (expressed as permil). Sample A047 (measured $\delta T1$ -90.7‰) was used as a 'worst case' example. Assuming extreme fractionation and setting $\delta T2$ in the range -80.0‰ to 0.0‰ the maximum fractionation effect on δ_{sample} was only about 3‰ (Table 12.12).

Table 12.12 Fractionation effect of incomplete recovery in Trap 1 Sample A047

δ Trap 2 (‰)	-80	-70	-60	-50	-40	-30	-20	-10	0.0
δ Sample (‰)	-90.3	-89.9	-89.5	-89.1	-88.7	-88.3	-87.9	-87.5	-87.1

mass T1: 5.743g, mass T2: 0.239g

Quite clearly even extreme fractionation from vapour escaping trap 1 would not be sufficient to significantly perturb the measured isotopic composition of trapped vapour. Average sampling time was 4 hours representing an air volume of 0.96m³ however in practice, this varied anywhere from 45 minutes (0.18m³) to 5hr 45 minutes (1.38m³). Air was sampled from a height of 2m adjacent to the isotope pan experiment. As time progressed the sampling routine was modified from one four hour run once a week to more numerous shorter runs. The cooler, which was permanently mounted in a light commercial van, was frequently left running overnight so that it could be used immediately while other routine sampling work was carried out during the early morning.

Method Detail

Methodology for a typical δ_A sampling run was as follows:

- start cooler and allow trap wells to reach operating temperature (about 1 hour)
- connect inlet and outlet tubing to traps and insert in ethanol wells, wait 5 minutes to allow traps to chill and ethanol to re-cool to -60°C
- start vacuum pump, adjust flow to 4 litres/minute, periodically readjusting as required
- at completion, remove tubing from traps and seal trap inlets & outlets with mini bungs
- remove traps, allow ice to melt and weigh traps after they have reached room temperature with contained water and bungs (ensuring there is no condensation on the outside of the traps). Each trap had an identifying number and dedicated bungs which were included in the empty weight
- remove bungs and transfer water gently into clean, dry 10ml Robertson bottle, cap immediately
- purge trap with ethanol and blow out with dry nitrogen, heat trap in drying oven at 105°C for minimum 2 hours, purge while hot with dry nitrogen and seal with bungs

Pouring the water from the trap to the bottle is the only point where trapped water is momentarily exposed to evaporation. Ideally water should be vacuum distilled from the traps however lacking such equipment, gentle pouring in which the water is exposed to evaporation for only several seconds is considered to introduce negligible error (J. Dighton⁴, pers com). Figure 12.12a shows results of all δ_A sampling. Data appears in Appendix 12.2.

Diurnal Variation

Diurnal changes in δ_A occur in response to air mass changes (land and sea breezes for example), temperature (condensation and dew fall at night should further deplete heavy isotopes in the vapour), near ground effects such as temperature inversions and evaporation from nearby water bodies and the soil under low wind conditions. At Perry Lakes there appeared to be a progressive enrichment in heavy isotopes from dawn to dusk during 1997 (Table 12.13).

Table 12.13 Diurnal changes in δ_A deuterium

	Jul 07	Aug 11	Aug 18	Oct 06	Oct 13	Nov 23	Nov 30	Dec 07
Dawn					-90.5	-88.9	-83.6	-98.1
Day	-92.8	-96.1	-86.5	-89.4	-79.4	-84.5	-78.4	-85.0
Dusk	-89.3	-91.5	-79.1	-85.7				

Samples collected consecutively, average sampling time 3 hours. Insufficient sample precluded many ^{18}O determinations

⁴ Isotope technician, CSIRO Land & Water, Glen Osmond, South Australia

At Perry Lakes this may (in part) be explained by the abundance of phreatophytic vegetation within the immediate vicinity. Note that transpiration is non fractionating (Clark & Fritz 1997). During the day such vegetation will transpire vapour whose composition is similar to local groundwater (about -12.4‰ and -2.72‰ ²H and ¹⁸O respectively). Unfortunately we only had four Zundel traps so were unable to collect multiple sequential samples over one 24 hour period to properly test this hypothesis.

Seasonal Variation

Winter weather on the west coast of Australia is dominated by moisture bearing frontal systems moving off the Indian Ocean. Winds are predominantly westerly. Summer weather is dominated by continental high pressure systems (subtropical anticyclones) resulting in a persistent easterly flow of dry continental air (Gentilli 1972). Also over summer moist oceanic air originating from the tropics is frequently funnelled south by the 'West Coast Trough' (Sturman & Tapper 1996). Surprisingly there is little average seasonal variation in Perry Lakes δ_A measurements by season and thus air mass provenance (Table 12.14).

Table 12.14 Perry Lakes δ_A measurements seasonal means

	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
Day and Night Data	-85.5	-93.8	-84.7	-82.6
Day time ONLY	-85.5	-95.3	-85.0	-82.4

Mean of all data (108 analyses) is -85.2‰. The most isotopically depleted samples (for example -121.4‰ deuterium 12 May 1997) tended to be associated with dry easterly winds moving from the centre of the continent.

Land breeze and sea breeze experiments

Extreme diurnal heating of the land relative to the ocean produces strong sea breezes along the west coast. Consecutive δ_A samples collected during east winds followed by a sea breeze display a slight isotopic enrichment from the air moving off the ocean (Table 12.15). Clearly however these are local effects which operate on a much smaller scale than the continental air masses noted above.

Table 12.15 Land-sea breeze experiments

Date	Oct 6	Oct 13	Nov 23	Nov 30	Dec 7
Land breeze	-89.4	-90.5	-88.9	-83.6	-98.1
Sea breeze	-85.7	-79.4	-84.5	-78.4	-85.0

All dates are 1997

The greatest enrichment of δ_A appears to be associated with moist tropical air during west coast trough conditions. These were particularly common during early summer 1997 and corresponded with three vapour sampling sessions (Table 12.16). Mean trough air mass δ_A was -74.4‰ .

Table 12.16 δ_A during west coast trough

Date	Nov 4	Nov 9	Dec 11
δ_A trough air	-72.6	-75.8	-74.8

All dates are 1997

The observation that isotopic enrichment is enhanced in air masses of tropical origin compared to air masses from higher latitudes is consistent with other observations from Australia (Brunel *et al* 1992) and from North America (White & Gedzelman 1984).

12.7.2 Direct Field Measurement of $\delta_{E(\text{lake})}$

Introduction

Craig & Gordon (1965) provide a model of the physical processes (including stable isotope fractionation) which occur at an air-water interface. They assumed a multi layered process (Figure 12.12c). Within the lake well mixed water is overlain by a thin laminar layer where fractionation may occur through molecular diffusion. The fluid-atmosphere interface is a thin vapour layer within which humidity decreases from a saturated lower contact and approaches local atmospheric humidity at the top. The isotopic concentration of the vapour in this interface is δ_E . Above this is a laminar vapour layer where again molecular diffusion and fractionation may occur. Above this turbulent mixing predominates with rapid transition to local atmospheric isotopic concentration δ_A . The fractionation paths are shown schematically by heavy lines. Similar models have been proposed by Sverdrup (1937), and Brutsaert (1975) comprising a diffusive sub layer 'd' directly over the interface and an overlying 'fully turbulent layer'.

Sampling requires attempting to capture vapour from the base of the laminar air layer. Merlivat and Coantic (1975) provide experimental estimates of the thickness of this layer 'd' under varying air velocities (Figure 12.12e). Curve fitting and extrapolation provided estimates of 'd' as still air is approached (Table 12.17). This suggested that under still air conditions, sampling within several cm of the water surface would approach the base of the laminar layer.

Table 12.17 Thickness of laminar layer 'd' as still air conditions are approached

Air V (cm/sec)	500	200	70	50	20	10	5	1
Air V (km/hr)	18.0	7.2	2.5	1.8	0.72	0.36	0.18	0.036
Thickness 'd' (mm)	0.7	2.2	6.5	9.8	27.7	60.7	132.9	820.5

Craig & Gordon (1965) provide estimates of marine δ_E as a mass balance where mean δ_E must be equal to the mean isotopic enrichment of precipitation being returned to the sea. They also provide an equation describing the relationship between δ_E and the composition of a water body (at constant volume without liquid outflow) undergoing evaporation:

$$\delta_E = \frac{\alpha * \delta_L (1 + E\rho_{iL}) - h\delta_A - \varepsilon}{(1 - h) + \Delta\varepsilon + \alpha * E\rho_{iL}} \quad (\text{Craig \& Gordon 1965 Eqn 23}) \quad (12.32)$$

Allison & Leaney (1982) present a simplified form as Eqn 7. This expression for δ_E shows it to be largely a function of the isotopic composition of atmospheric water vapour δ_A , relative humidity and the isotope fractionation factors for the isotope of interest. From a practical point of view δ_A is seldom known with any degree of accuracy. Alternative methods of estimating δ_E using pan derived exchange parameters have been explored earlier in this chapter. The literature provides little in the way of practical field methodology for confirming theoretically derived estimates of δ_E . Allison *et al* (1979) note that estimation of δ_E under field conditions of varying wind, temperature and humidity is virtually impossible. Merlivat & Coantic (1975) sampled vapour under controlled conditions within a large (40m long) sealed wind tunnel. The author is not aware however of any other practical field measurement of evaporate from a water body.

Method

On cold still mornings at Perry Lakes vapour is frequently visible rising from the warmer water into the cooler air. This is evaporated lake water vapour, made temporarily visible through condensation. Initial experiments to sample lake evaporate were carried out by fixing the open end of a sampling line on the East Lake staff gauge support. The open end was positioned about 2cm above the water surface. The feed line was weighted, sinking into the water column which was 10-11°C warmer than the air, thus precluding any condensation in the feed line. The Heidelberg cooler unit was positioned on the lake shore and operated in an identical manner to that used for δ_A sampling. The small length of exposed feed line between the water and the vapour trap was insulated with high density rubber foam pipe insulation, maintained at or above lake temperature with heat lamps. At completion any feed line condensation was purged using dry nitrogen, passed through the vapour trap. Two such experiments carried out on dead still nights between

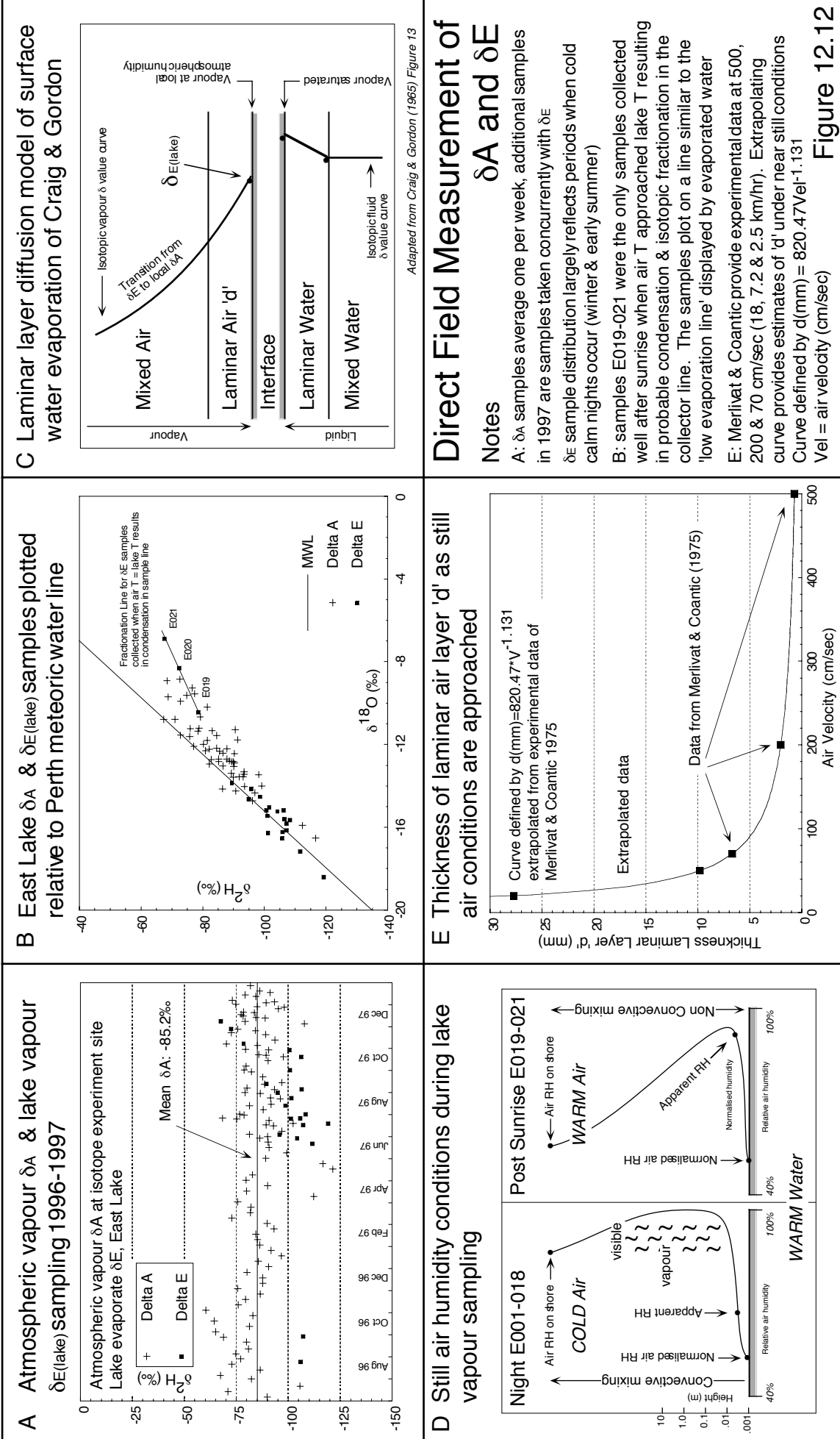


Figure 12.12

midnight and dawn confirmed the viability of sampling lake evaporate however the experimental procedure was cumbersome. Possibly the greatest problem was the unpredictability of when satisfactory sampling conditions were likely to occur. If any number of samples were to be collected, a sampling technique was required which could be rapidly deployed on an opportunistic basis.

The most time consuming aspect of the initial tests was deploying the pickup line in the lake and supplying 240 volt power via 200m of extension cords from the isotope experiment. A floating sampling system (Figure 12.4d) was designed which could be left permanently in place. The principal features of this system were:

- a permanently installed inlet line bathed in lake water, connected to the shore and bathed in return water (approximately $1^{\circ}\text{C} < \text{lake}$) from the pan experiment in the service conduit
- a system of pressure controlled inlet valves which remained closed except under conditions of vacuum suction (when sampling) or purge back pressure (when purging with dry nitrogen)
- an anchored floating inlet which maintained a constant inlet height of 5mm above the water surface

In operation the van containing the Heidelberg unit was positioned adjacent to the isotope experiment pans. The final feed from the service conduit to the vapour traps was insulated and warmed by heat lamps as before. At completion this section of line was purged via the vapour traps with dry nitrogen as was the feed line back to the floating pickup. An inspection point at the lake edge (the coolest point in the line) allowed inspection of a clear insert to check for line condensation. Occasional very minor misting occurred, however estimates of possible fractionation error using equation 12.31 and data plots relative to the local meteoric water line (Figure 12.12b) suggested minimal line fractionation.

During δ_E sampling, a simultaneous δ_A sample was collected in the normal manner (Figure 12.12a and Appendix 12.2). Using this system a total of 21 lake evaporate samples were collected. The floating pickup allowed opportunistic sampling not only during the night but also during normal data collection activities at dawn and at dusk.

Results

Data are plotted (along with δ_A) in Figure 12.12a and are summarised in Table 12.18. Here humidity of the air and humidity normalised to the lake surface temperature correspond to the average recorded during the sampling period (typically 45 to 240 minutes). K (pan average) is the mean seasonal value determined from pan experiments, K (instantaneous) is K calculated for the sampling period only using equation 12.18.

There is a very large difference between the two, the former being 'flux weighted' over many days, the latter being that occurring only over several hours. Lake δ_E is shown as measured and as calculated from equation 12.20 in three different ways:

- normalised relative humidity and pan averaged K
- non normalised relative humidity and pan averaged K
- normalised relative humidity and instantaneous K

The quantity 'apparent RH' is the relative humidity which would be required in equation 12.20 to produce the sampled value for δ_E assuming averaged K. It is evident from equation 12.18 that K incorporates δ_A . Calculating δ_E using equation 23 of Craig & Gordon (1965) (equation 12.32) and measured δ_A produces identical estimates of δ_E suggesting that measured δ_A and experimentally derived K are essentially correct. Raw data appear as Appendix 12.3.

The δ_E measurements were made at dusk, night and dawn under varying meteorological conditions, the only uniform criteria being still air. Three general observations can be made:

- 1: for all measurements taken at night, early dawn and most taken at dusk (E001-E018) 'apparent RH' tends to lie between air RH and normalised RH and $\delta_E < \delta_A$
- 2: for measurements taken after sunrise (E019-E021), 'apparent RH' exceeds air RH and $\delta_E > \delta_A$
- 3: δ_E calculated using normalised RH and instantaneous K closely approximates δ_E measured directly by vapour sampling

Discussion

The 'night time' data (E001 to E018 in Table 12.18) suggests that under conditions of warm lake surface and cool still air, there is a relative humidity gradient immediately above the water surface (Figure 12.12d). Warm air and lake evaporate rise convectively into the cold overlying air. Normalised relative humidity is that of the local air mass (as measured nearby on shore) normalised to the lake surface temperature. Sampling occurs in the 10-20mm zone above the air-water interface and may have an effective normalised relative humidity (under still non mixing night time conditions) intermediate between that of the local air mass and the air-water interface (Figure 12.12d). Tendrils of visible vapour were frequently observed rising up to 10m above the lake. The tendrils do not form at the water surface but a few mm above it. Their appearance coincides with the height where moist air cools to saturation point. Their disappearance with height suggests that maximum excess of saturation occurs in a blanket several metres thick over the lake. Above that height, humidity probably decreases approaching that measured nearby on shore.

The 'sunrise data' (E019 to E021) presented unique and unusual conditions where vapour was collected well after sunrise in early summer but still under windless conditions. On all previous sampling occasions $T_{\text{air}} \ll T_{\text{lake}}$. Here however air temperature was approximately equal to lake temperature. Under these conditions natural convective mixing would be less (or absent) and perhaps replaced by mechanical or molecular mixing. A blanket of humid air effectively forms at the air-water interface. In the case of E021 the apparent normalised humidity of the air approached saturation (Figure 12.12d) with δ_E approaching or exceeding δ_A measured nearby. Plotting all data relative to the Perth meteoric water line (MWL) however suggests that isotopic fractionation occurred while sampling E019-021 (Figure 12.12b). These three samples plot below the MWL. It is likely that as air temperature approached lake water temperature, some condensation occurred in the sample feed line. Estimating δ_E from very short term (non flux weighted) values of K generally produces the closest approximations of the experimental data, however these short term (effectively instantaneous non flux weighted) K values are strongly influenced by δ_A .

With reference to equation 12.20 and Figure 12.11 it is apparent that δ_E is particularly sensitive to changes in humidity at given values of δ_I , δ_L and δ_K . This is particularly so at high relative humidity when very small changes in humidity result in very large changes in δ_E . Under such conditions accurate measurements using wet and dry bulb thermometers are suspect since Bureau of Meteorology wet bulb depression tables for non ventilated thermometers assume a minimum natural (wind) ventilation of $1\text{--}3\text{ m sec}^{-1}$. Lack of ventilation raises the wet bulb temperature resulting in an over-estimation of true vapour content (Fritschen & Gay 1979 p150). This is apparent in the calculated δ_E which exhibits very large excursions from the experimentally measured δ_E . These extremes largely reflect errors in measuring humidity.

Therefore any attempt to compare theoretical and experimental measures of $\delta_{E(\text{lake})}$ must include accurate measurement of relative humidity at the vapour sampling site. This is complicated by the meteorologically 'abnormal' conditions under which vapour was collected, at night with nil wind and a pronounced air temperature gradient from the warm water surface to cold air. Under such conditions the experimental data suggest that relative humidity measured on land adjacent to the lake will be too high (and possibly subject to additional errors due to non ventilation) and this same data normalised to lake surface temperature will be too low. In other words the true relative humidity at the sampling site under still, convective mixing meteorological conditions is likely to be between the two. Finally, estimating δ_E using equation 12.32 also indicates a high sensitivity to δ_A . Errors in measuring δ_A (or its proxy K) will likewise have large effects on calculated δ_E .

Table 12.18 Direct measurement of $\delta_{E(\text{lake})}$ deuterium

Sample	E001	E002	E003	E004	E005	E006	E007
Date	05-09-96	08-10-96	14-06-97	21-06-97	26-06-97	07-07-97	10-07-97
Start Time (hr)	03:45	00:50	19:00	21:10	18:00	20:00	18:00
Duration (hr)	2.8	4.7	4.0	3.5	3.5	3.5	4.0
Lake T (°C)	19.1-16.3	23.3-21.8	17.3-16.1	16.7-16.1	18.8-17.2	14.0-12.8	14.0-12.4
Air T (°C)	6.6-5.5	13.1-10.5	9.6-6.7	10.5-11.2	14.8-11.2	7.0-4.5	6.8-2.7
Av Norm RH	45.8	46.0	51.6	67.1	71.8	59.0	55.5
Av Air RH	90.0	89.5	87.3	91.5	92.5	90.8	92.9
Apparent RH	84.8	86.4	79.1	81.8	82.2	80.9	82.0
δL	4.8	7.9	-8.8	-4.4	-2.2	-4.5	-5.7
δK (pan average)	21.5	23.1	15.0	15.0	15.0	16.4	16.6
δK (instantaneous)	53.6	53.5	49.0	35.9	36.0	40.5	35.6
δE at Norm RH	-40.1	-37.6	-56.5	-64.7	-66.1	-57.8	-57.2
δE at Air RH	-150.1	-131.9	-170.7	-197.4	-195.5	-198.8	-261.0
δE (instantaneous K)	-93.3	-88.2	-119.4	-120.9	-131.6	-110.3	-95.3
δE measured	-105.9	-107.2	-111.6	-104.2	-95.7	-107.1	-119.2
δA measured	n/a	n/a	n/a	-86.3	-81.4	-89.3	-102.3
Sample	E008	E009	E010	E011	E012	E013	E014
Date	16-07-97	17-07-97	22-07-97	02-08-97	11-08-97	18-08-97	23-08-97
Start Time (hr)	17:45	17:40	05:00	17:45	17:45	17:45	05:00
Duration (hr)	4.2	3.0	2.4	2.2	2.0	2.0	1.8
Lake T (°C)	13.9-12.3	14.2-13.2	11.1-10.1	19.5-18.1	16.4-15.7	17.1-16.2	15.3-14.7
Air T (°C)	11.3-8.0	10.7-5.2	2.3-0.9	13.7-10.5	12.4-8.7	13.6-8.9	9.8-7.0
Av Norm RH	52.9	56.9	50.2	60.2	61.8	57.2	55.7
Av Air RH	76.5	79.9	88.4	87.6	83.6	76.8	82.4
Apparent RH	80.4	82.3	83.1	80.3	77.0	76.0	80.7
δL	-3.1	-2.2	-1.2	-1.6	-4.5	-3.2	-1.2
δK (pan average)	17.0	17.0	17.7	18.0	19.0	19.4	19.8
δK (instantaneous)	53.8	55.2	54.8	44.7	36.7	48.4	40.8
δE at Norm RH	-50.6	-52.2	-46.4	-56.3	-67.2	-59.5	-54.8
δE at Air RH	-87.2	-95.3	-148.8	-144.9	-135.6	-97.5	-115.0
δE (instantaneous K)	-120.4	-131.4	-113.2	-116.0	-108.3	-120.0	-97.1
δE measured	-101.2	-105.8	-108.3	-98.6	-101.5	-94.9	-106.5
δA measured	-75.2	-68.4	-76.6	-81.4	-91.5	-79.1	-93.4
Sample	E015	E016	E017	E018	E019	E020	E021
Date	30-08-97	17-09-97	04-10-97	13-10-97	21-10-97	09-11-97	19-11-97
Start Time (hr)	18:10	18:30	04:00	05:00	06:15	06:40	06:20
Duration (hr)	1.8	2.0	2.0	1.5	0.8	0.8	1.5
Lake T (°C)	19.2-18.5	23.4-22.7	20.4-20.1	21.4-21.4	21.9-22.1	21.8-22.3	19.9-20.6
Air T (°C)	14.5-11.8	17.5-14.6	11.8-11.6	10.2-10.5	19.4-21.1	15.0-20.2	11.5-19.4
Av Norm RH	54.4	53.3	55.4	48.4	51.3	49.6	47.7
Av Air RH	72.4	81.4	87.5	92.3	54.9	62.9	65.3
Apparent RH	77.7	62.1	82.1	74.4	70.4	83.4	100.3
δL	0.7	-14.7	5.0	0.0	4.3	19.1	30.2
δK (pan average)	20.4	23.0	24.5	25.7	26.5	30.7	30.7
δK (instantaneous)	44.8	51.4	38.4	48.8	57.7	55.7	55.2
δE at Norm RH	-51.0	-84.6	-51.4	-57.0	-53.2	-33.0	-13.3
δE at Air RH	-75.2	-187.6	-144.0	-280.8	-56.4	-40.2	-13.7
δE (instantaneous K)	-98.8	-139.0	-79.4	-97.1	-110.5	-77.5	-55.4
δE measured	-89.4	-100.9	-106.2	-100.6	-78.5	-72.4	-67.6
δA measured	-88.6	-78.8	-97.7	-90.5	-70.2	-75.8	-79.2

Notes: All delta ' δ ' values are in permil (‰) notation, δL set to -12.4‰ (mean of 41 samples, SD = 1.4‰), ϵ set to 0.095 and $\Delta\epsilon$ 0.011, lake temperature is surface temperature in centre of lake, air temperature taken with shielded laboratory thermometer 1.5m above ground level at isotope pan experiment site, RH determined from non aspirated wet & dry thermistors & loggers at isotope pan experiment site (10 minute readings), 'Norm' RH is air RH normalised to the lake surface water temperature, all temperatures are range from start to end of δE sampling period, δE calculated using Eqn 12 of Allison & Leaney (1982), δE at air and normalised RH estimated using pan averaged K for period, δE (instantaneous K) uses K calculated (Allison & Leaney Eqn 10) for sampling period only, δA where noted sampled concurrent with δE , lake δL interpolated from samples collected every four days (refer Water Balance Data Sheets), δK (pan average) interpolated graphically from isotopic pan experiment. Apparent RH - refer text.

Conclusions

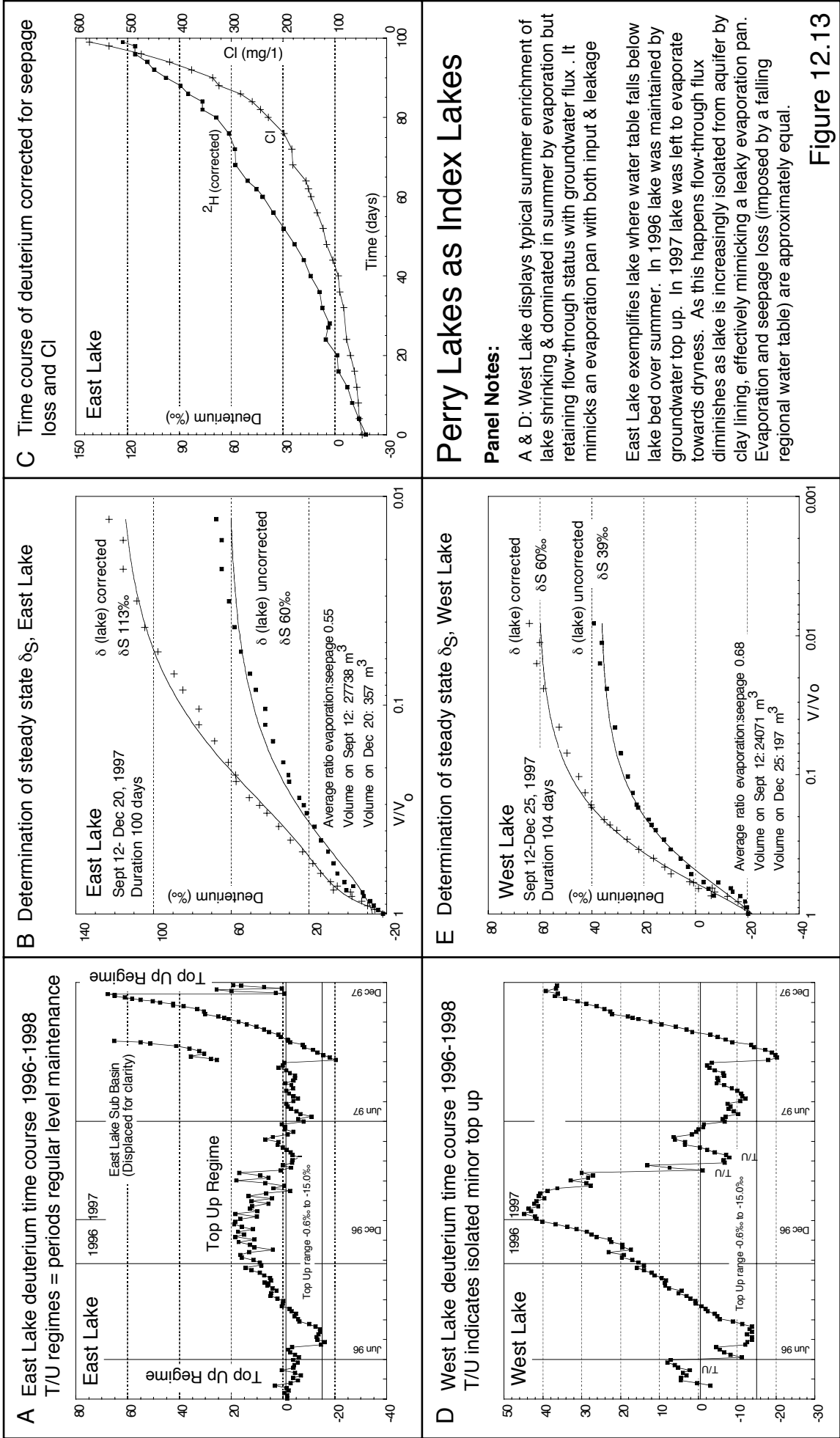
Direct measurement of δ_E is possible but only under highly abnormal meteorological conditions. Theoretical estimates using equation 12.20 are compromised by the difficulties in measuring relative humidity at the air-water interface under such conditions.

Certainly the field experiments were valuable in confirming that directly measured δ_E is in many cases similar to δ_E calculated by other means. Probably the single most important observation was the confirmation that δ_E calculated using equation 12.32 (Craig & Gordon 1965 eqn 23) and measured δ_A produced identical estimates of δ_E calculated using equation 12.20, suggesting that measured δ_A and experimentally derived K were essentially correct. This provided the confidence to apply δ_E derived experimentally from the pan experiments in the final isotopic balances (Chapter 6).

12.8 LAKE AND PAN LIMITING VALUES

The whole objective of pan experiments is to use a small controlled evaporation environment (a pan) as a simple physical model of an adjacent lake. Figure 12.13 a&d show the time course of deuterium in East and West Lake over two years. West Lake shrinks to a small pond over summer. Small amounts of groundwater are added occasionally to ensure sufficient habitat for long necked tortoises, but in general levels are controlled solely by the falling regional groundwater table and a local groundwater gradient controlled by frequent top up pumping into East Lake. West Lake retains a partially sandy bottom at all but its lowest summer levels and mini piezometer tests (Chapter 7) confirm a flow through regime is maintained in summer. Over summer 1996 and 1997 West Lake shows a steady rise in deuterium enrichment, peaking around years end. This peak reflects both an annual solar cycle (identical to the same cycles described in the pans) and the increased effect of groundwater recharge as a local groundwater mound builds up around East Lake. Small increases in the West Lake stage occur within hours of water being added to East Lake where top up pumping peaks in January and February. We know from our inability to integrate the mass, solute and isotopic balances however (Chapter 6) that this apparent peak was, in fact, an effect of achieving an isotopic steady state.

At East Lake the regional groundwater table has fallen below the lakes deepest basin for a number of summers. In 1996 the lake was subject to a routine level maintenance regime commencing with occasional top up from October onwards peaking in January and February. The top up water comes from a number of bores and has variable deuterium levels in the range -0.6 (bore 1 lying in the East Lake release zone) to -15.0‰



Perry Lakes as Index Lakes

Panel Notes:

A & D: West Lake displays typical summer enrichment of lake shrinking & dominated in summer by evaporation but retaining flow-through status with groundwater flux . It mimicks an evaporation pan with both input & leakage

East Lake exemplifies lake where water table falls below lake bed over summer. In 1996 lake was maintained by groundwater top up. In 1997 lake was left to evaporate towards dryness. As this happens flow-through flux diminishes as lake is increasingly isolated from aquifer by clay lining, effectively mimicking a leaky evaporation pan. Evaporation and seepage loss (imposed by a falling regional water table) are approximately equal.

Figure 12.13

(bores 2-7 lying up gradient and within an unevaporated groundwater field, Figure 6.7). During summer 1996-97 deuterium enrichment in East Lake never exceeded +20‰.

In late 1997, the wetland managers agreed to let East Lake recede almost to dryness. The time course of deuterium (and Cl) is evident in Figures 12.13 a&c. Treating this as a pan evaporating to dryness (Figure 12.13b) an apparent limiting steady state of about 60‰ was achieved. Mini piezometer tests during this period (Chapter 7) confirm that a flow through regime is maintained as dryness is approached, however recharge appears to be << discharge because the lake becomes insulated from the aquifer by its clay lining. Then daily volume reduction is a combination of approximately equal parts evaporation and seepage loss to a falling regional water table. Gat (1981d) notes that in the general case of a lake with both inflow and outflow the enrichment of heavy isotopes is reduced in proportion to the weight of the non-fractionating outflow relative to evaporation. Setting recharge to zero, $\delta_{\text{(lake)}}$ was corrected against evaporation and discharge as calculated in the daily mass balances (Figure 12.13b), suggesting a true $\delta_{\text{S(lake)}}$ of about 113‰ around December 20th. This is in reasonable agreement with the equivalent $\delta_{\text{S(pan)}}$ of 103.0‰ and 96.8‰ (Runs 18 and 19) covering the same period.

Importantly this data strongly suggests that exchange parameters determined from evaporation pans adjacent to Perry Lakes can provide valid approximations of the same parameters in the lake and validates equations 12.13, 12.14 and 12.20.

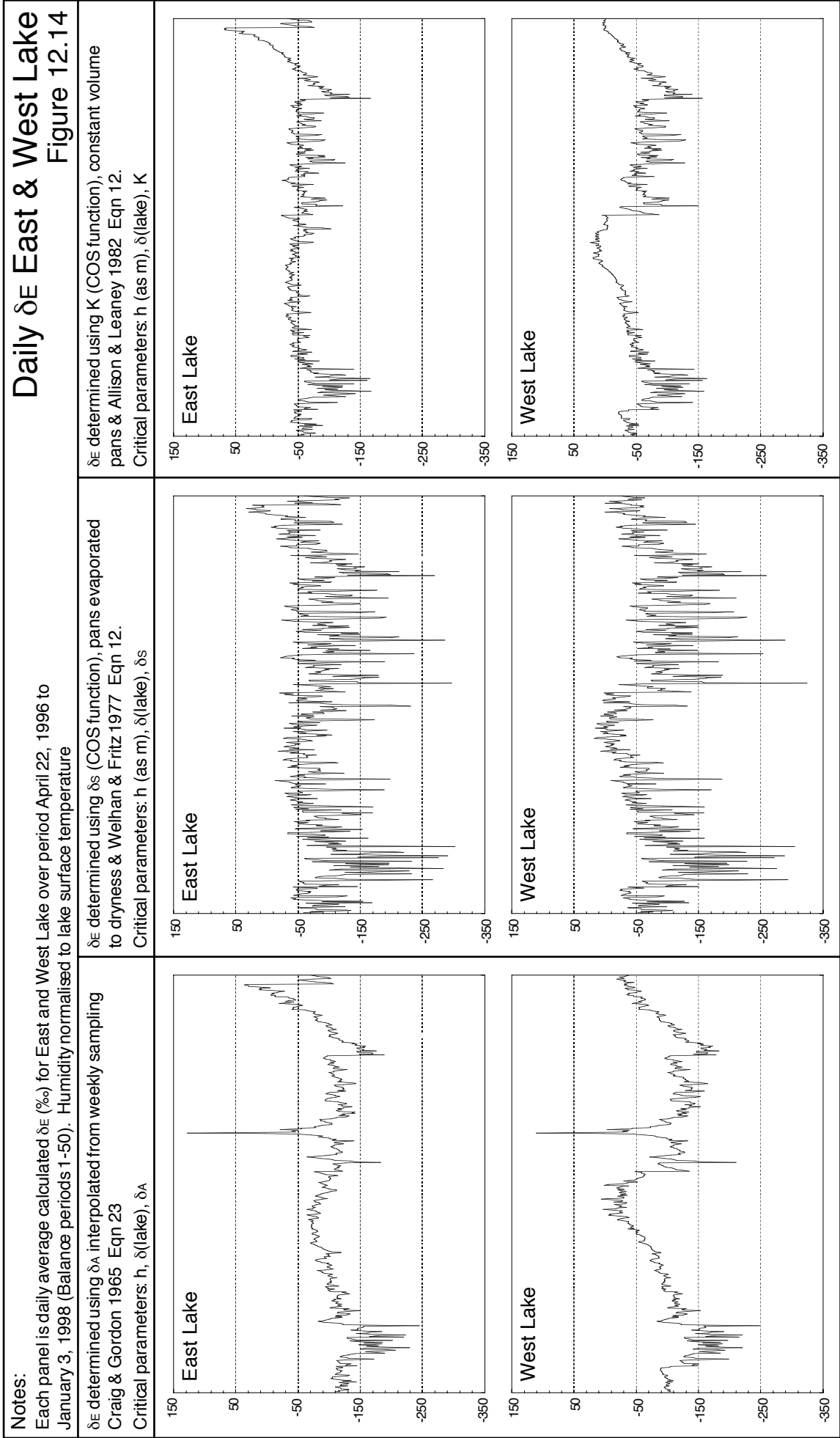
Data was similarly corrected for West Lake however this is not strictly valid because a groundwater flux is maintained such that steady state of about 39‰ is maintained. This is obviously similar but not directly equivalent, to values of K obtained from the constant volume pan of 30.7‰ & 30.0‰ (Runs 18 & 19).

12.9 APPLICATION TO DAILY WATER BALANCES AT PERRY LAKES

12.9.1 Calculation of Daily δ_A and $\delta_{\text{E(lake)}}$

Average daily $\delta_{\text{E(lake)}}$ was estimated using three different methods:

- 1: Equation 23 of Craig & Gordon (1965), critical parameters humidity, $\delta_{\text{(lake)}}$, δ_A with daily estimated average δ_A computed by interpolating weekly atmospheric sampling.
- 2: Equation 12 of Welhan & Fritz (1977), critical parameters humidity (as m), $\delta_{\text{(lake)}}$, and δ_s calculated from pans evaporated to dryness
- 3: Equation 12 of Allison & Leaney (1982), critical parameters humidity (as m), $\delta_{\text{(lake)}}$, and K calculated from pans evaporated at constant volume



In all cases humidity was normalised to lake surface temperature. Daily δ_E calculated for East and West Lake using each method can be compared in Figure 12.14. The differences reflect the differing critical parameters upon which each is based and the assumptions used in extrapolating exchange parameters from pans to lake. The same calculations were made using non normalised humidity. Mean values of daily average δ_E were calculated for balance periods 1-50 (22 April 1996 to 03 January 1998) and for calendar year 1997 (Table 12.19). The table includes non normalised data.

Table 12.19 Mean values of $\delta_{E(\text{lake})}$ East and West Lake (per mille)

	RH (air) K (Cos)	RH (norm) K (Cos)	RH (air) δ_S (Cos)	RH (norm) δ_S (Cos)	RH (air) Craig & Gordon	RH (norm) Craig & Gordon
East Lake						
Bal 1 to 50	-65.5	-53.3	-131.9	-84.1	-107.3	-101.7
Year 1997	-63.2	-50.5	-128.9	-81.8	-96.6	-92.7
West Lake						
Bal 1 to 50	-57.5	-46.0	-123.9	-76.8	-85.2	-94.5
Year 1997	-58.0	-44.4	-123.7	-75.7	-88.1	-86.6

In East Lake the mean $\delta_{E(\text{lake})}$ calculated by pan derived K was 42.2‰ greater than the value calculated using Craig & Gordon (1965) equation 23. The data however is much smoother than that using pan derived δ_S although this is closer to the Craig & Gordon figure in terms of annual mean, being just 10.9‰ greater. Daily isotopic balances were computed and integrated with mass and solute balances (Chapter 6) using both method 1 and method 3. Final balances used the locally derived pan data of method 3. The difference between the two methods (in terms of water balance mass) was less than 1%.

Allison & Leaney (1982) show how errors in $\delta_{E(\text{lake})}$ estimated from pan parameters are minimised by choosing δ_I such that K is approximately equal to δ_{lake} . This approach involves 'spiking' the feed water to produce the desired δ_I . Under such conditions relatively large errors in evaluating m (up to 30%) can be tolerated since they result in relatively small errors in estimated $\delta_{E(\text{lake})}$. This study took the approach of using groundwater such that δ_I in the pan experiments was identical to the isotopic content of groundwater discharge in the adjacent lake. At Perry Lakes where multiple experiments using large quantities of water were run continuously over two years the use of 'spiked' feed water was considered unwarranted on the basis of added complication and cost.

Notation Chapter 12

I	rate of inflow per unit area to a water body
δ_I	isotopic composition of inflow
O	rate of outflow per unit area from a water body
δ_L	isotopic composition of lake water
P	precipitation on water body surface per unit area
δ_P	isotopic composition of precipitation
E	evaporation rate
δ_E	isotopic composition of evaporating water from a lake surface
$E\rho_{iL}$	liquid transport resistance (very small and usually ignored)
K	limiting steady state isotopic composition of water remaining in pan held at constant volume
T	temperature °C
V	evaporation pan volume
f	the fraction V of original volume of liquid V_o remaining, $f = V/V_o$
f^{a*}	fraction of residual water (f), a^* combined equilibrium and kinetic fractionation factors
h	relative humidity, relative humidity normalised to surface water temperature
m	refer text
t	time since initiation of pan run, start $t=0$
δ, δ_L	isotopic composition of a well mixed body of water subject to evaporation only
δ^*	isotopic steady state limiting value of Gat (1981)
δ_A	isotopic content of atmospheric water vapour
δ_E	isotopic composition of evaporating water vapour
δ_K	alternate designation for K
δ_L^{ss}	isotopic steady state in a terminal lake
δ_{in}	isotopic content of inflow to a terminal lake
δ_I	isotopic composition of feed water in a constant volume pan
δ^0	initial isotopic content of water in a constant volume pan at $f = 1.0$
δ_S	limiting steady state isotopic composition of water remaining under E with no flow
α^*	equilibrium isotope fractionation: $\left(R_{vapour}/R_{liquid}\right) < 1$ where R is the ratio of isotopic water molecules DHO/H_2O or H_2O^{18}/H_2O^{16}
$\Delta\epsilon$	kinetic enrichment factor
ϵ^*	equilibrium enrichment factor = $1 - \alpha^*$, $\alpha^* = 1 - \epsilon^*$
ϵ	total enrichment factor, equals: $\epsilon^* + \Delta\epsilon$
ρ_L^*	isotopic transport resistance in the liquid