### 激光同位素技术在水文学研究中的应用与实践

北京理加联合科技有限公司

孙宝宇

## 先进的科学仪器是推动科技创新的重要支撑



面向世界科技前沿,面向国家重大需求,面向国民经济主战场,率先实现科学技术跨越发展,率先建成 国家创新人才高地,率先建成国家高水平科技智库,率先建设国际—流科研机构。

----中国科学院办院方针

首页 组织机构 科学研究 成果转化 人才教育 学部与院士 科学普及 党建与科学文化 信息公开

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#### 高端科研仪器国产化值得期待

2019-04-15 来源: 人民日报 吴月辉 刘诗瑶 喻思南 谷小凯 蔣建科

【字体: 大中小】



语音播报

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#### 要想成为科研强国,必须首先成为仪器强国

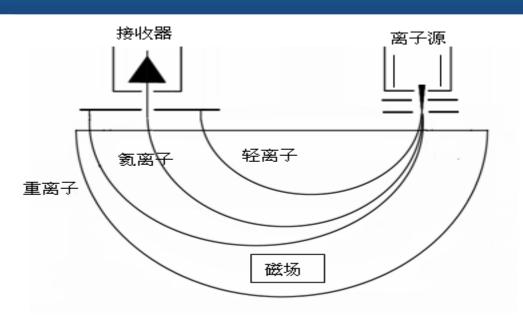
日前,人类历史上首张黑洞"正面照"发布,在全世界引起广泛关注。这张"照片"是由来自全球30多个研究所的科学家们通过分布在全球不同地区的8个射电望远镜阵列组成的一个虚拟望远镜网络拍摄到的。

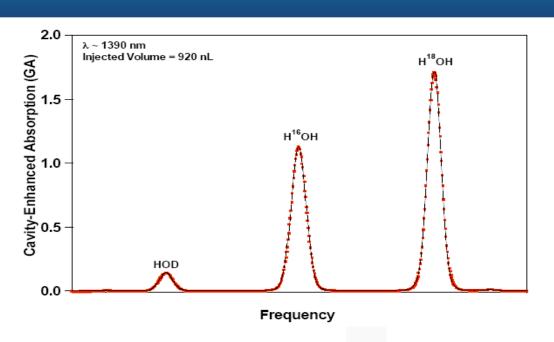
黑洞"照片"的成功拍摄,离不开射电望远镜的使用。现代科技发展实践表明,重大科学研究成果的取得,往往是以科学仪器和技术手段上的突破为先导;科学仪器的进展一定程度上代表着科学前沿的方向,也是推动科技创新的重要支撑。

据不完全统计,诺贝尔自然科学类奖项中,68.4%的物理学奖、74.6%的化学奖和90%的生理学或医学奖成果借助各种先进的科学仪器完成,或直接与新仪器方法或功能的发展相关。



## LGR激光同位素技术原理



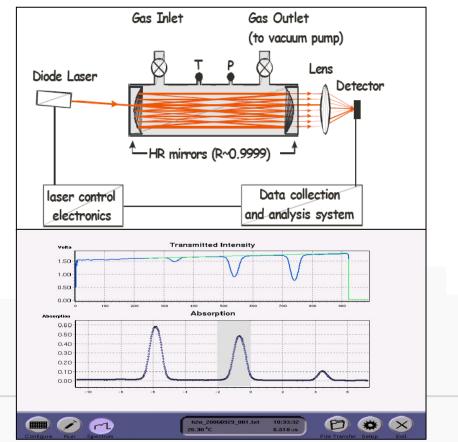


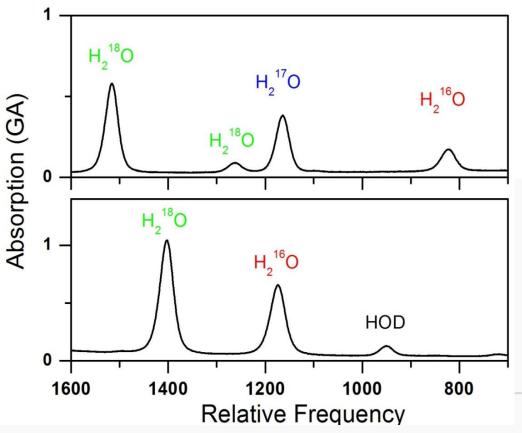
- ▶ 以水分子为例,有九种水分子组合,最常见的分子有:
  - H<sub>2</sub><sup>16</sup>O;
  - HD<sup>16</sup>O;
  - · H<sub>2</sub><sup>18</sup>O.
- > 这对于激光分析仪来说是三种不同的气体



## LGR激光同位素技术原理

- LGR是通过测量特定光谱的光强吸收而确定特定物质浓度,符合经典的Lambert-Beer定律。
- LGR利用两个高反射镜面制造一个光腔,使激光在两个镜面间进行大量反射,增加吸收强度。
- 利用LGR离轴入射专利技术 (OA-ICOS), 消除了光腔中的干涉影响。
- 目前OA-ICOS技术已经广泛的使用于LGR各种分析仪。









IWA-35/45 水同位素分析仪



LWIA-30d 液态水同位素分析仪

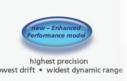


IWA-45EP

δD: 0.2‰,  $\delta^{18}$ O: 0.03 ‰ &  $\delta^{17}$ O: 0.03 ‰

catch some air









水汽同位素分析仪,2Hz

多路器

水汽同位素标气发生器



### 水同位素分析仪





- 1.  $\delta D$ : 0.2‰,  $\delta^{18}O$ : 0.03‰,  $\delta^{17}O$ : 0.03‰;
- 2. 水同位素分析仪中国大陆用户已超过150余台;
- 3. 2006年国际原子能机构 (IAEA) 在全球开始推广,目前IAEA在全球的实验室已拥有超过100台激光水同位素分析仪;
- 4. 可广泛应用于液态水、植物水、土壤水、酒水 饮料、医药检测、果实等。



### 液态水同位素分析仪



- 1.  $\delta D$ : 0.2‰,  $\delta^{18}O$ : 0.03 ‰,  $\delta^{17}O$ : 0.03 ‰;
- 2. 样品盐度: < 4% (样品盐度超过4%时, 需要缩短维护时间间隔);
- 3. 工作温度: 0~45℃;
- 4. 样品温度: 0~50℃;
- 5. 800注射/天,速度可调;
- 6. 能通过SCI修正有机污染;



### 水汽同位素分析仪



- 1. 浓度范围: 100 60000 ppm (non-condensing);
- 2. 重复性/精度 (1 σ , 10秒/100秒):

 $\delta D: 0.5\% / 0.2\%$   $\delta^{17}O: 0.15\% / 0.05\%$ 

 $\delta^{18}O: 0.15\% / 0.05\% [H<sub>2</sub>O]: 0.2\% / 0.07\%;$ 

- 3. 测量频率: 最快可达2 HZ;
- 4. 工作温度: 0~40°C;
- 5. 采样温度: -30~50℃。





ABB Los Gatos Research 公司(原美国LGR公司), 1994年创立于硅谷, 隶属于ABB集团, 公司致力于开发激光痕量气体与稳定同位素分析仪。作为CRDS、ICOS及OA-ICOS等激光测量技术的专利(>12项)所有者, LGR是目前激光分析仪的全球领导者。设备主要用于前沿科学研究、工业过程监控与质量控制、空气质量与排放监控、痕量温室气体与稳定同位素的测量。











# LGR水同位素分析仪在水文学与生态学中的应用



## LGR激光氢氧稳定同位素技术的应用

### 加入IAEA的"水同位素分析实验室间比对" (WICO)

### 天然水样 (已经过滤)

|        | Assigned<br>Values |                       |              | TIWA<br>Measured Values |                       |              |
|--------|--------------------|-----------------------|--------------|-------------------------|-----------------------|--------------|
| Sample | δ²H [‰]            | δ <sup>18</sup> Ο [‰] | d-excess [‰] | δ²H [‰]                 | δ <sup>18</sup> O [‰] | d-excess [‰] |
| WICO 1 | -77.4 ± 0.9        | -10.80 ± 0.02         | 9.0          | -77.6 ± 0.1             | -10.83 ± 0.01         | 9.0          |
| WICO 2 | -41.7 ± 1.1        | -5.11 ± 0.03          | -0.8         | -42.3 ± 0.1             | -5.13 ± 0.02          | -1.3         |
| WICO 3 | -168.3 ± 1.0       | -22.01 ± 0.05         | 7.8          | -168.9 ± 0.0            | -22.07 ± 0.02         | 7.6          |
| WICO 4 | 0.5 ± 1.1          | -0.50 ± 0.05          | 4.5          | -0.1 ± 0.2              | -0.55 ± 0.08          | 4.3          |

Table 3 Intercomparison between ABB LGR TIWA measured values and assigned IAEA values for natural water samples

环境水的2H和18O是水文地质、气象、海洋学和生态学研究的主要分析方法。准确的分析可以提供可靠的科学信息,来指导水和环境的管理决策。

国际原子能机构(IAEA)同位素水文实验室组织了一次水同位素比对(WICO),以各种技术进行国际实验室天然水稳定同位素测定( $\delta^{18}$ O和 $\delta^2$ H)的能力评估。共235个实验室加入。ABB LGR的水同位素分析仪(TIWA)也加入了此次比对。

## LGR激光氢氧稳定同位素技术的应用

### 加入IAEA的"水同位素分析实验室间比对"

### 甲醇污染的水样

|          | Assigned<br>(‰) | Measured uncorrected (‰) | Measured<br>corrected (‰) |
|----------|-----------------|--------------------------|---------------------------|
| δ²H      | -114.3 ± 1.1    | -100.1 ± 0.3             | -114.0 ± 0.2              |
| δ18Ο     | -15.68 ± 0.02   | -6.36 ± 0.06             | -15.42 ± 0.21             |
| d-excess | 11.1            | -49                      | 9.4                       |

Table 4 Assigned, measured, and corrected values for WICO 5

对于甲醇污染的水样,通过光谱污染修正软件校正以后与标准值的一致性较好。



### 加入IAEA的"水同位素分析实验室间比对"

### 贫化水、富集水和盐化水

|        | Assigned<br>Values |               |              | TIWA<br>Measured Values |               |              |
|--------|--------------------|---------------|--------------|-------------------------|---------------|--------------|
| Sample | δ²H [‰]            | δ¹8O [‰]      | d-excess [‰] | δ²H [‰]                 | δ¹8O [‰]      | d-excess [‰] |
| WICO 6 | -323.7 ± 0.9       | -41.41 ± 0.04 | 7.6          | -323.7 ± 0.0            | -41.44 ± 0.01 | 7.9          |
| WICO 7 | 55.7 ± 1.6         | 5.61 ± 0.08   | 10.8         | 54.6 ± 0.1              | 5.63 ± 0.03   | 9.5          |
| WICO 8 | 17.6 ± 1.2         | -3.45 ± 0.10  | 10.0         | -18.8 ± 0.1             | -3.50 ± 0.04  | 9.2          |

Table 5 Intercomparison between ABB LGR TIWA measured values and assigned IAEA values for depleted, enriched, and salty samples

在测量富集的、贫化的以及盐化水中δ2H和δ18O时,TIWA也能提供极好的结果。



## LGR激光氢氧稳定同位素技术的应用

# 背景

- 利用激光氢氧稳定同位素技术,可以确定植物水分来源。
- 不同水体的氢氧稳定同位素还可用于水汽输送、土壤水运移和补给机制、补给源和地下水机制、水体蒸发、植物蒸腾和土壤蒸发的区分以及径流的形成和汇合等方面的研究。因而引起了水文学家,生态学家以及气候学家等的广泛关注。基于此,研究者们利用该技术进行了大量的科学试验以揭示相关的水文过程。



### 植物水分来源

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DOI: 10.1002/eco.2078

#### RESEARCH ARTICLE

WILEY

Responses of two desert riparian species to fluctuating groundwater depths in hyperarid areas of Northwest China

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Abstract

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#### 2.3 | Stable isotope analysis and calculation

Water from plant xylem and soil samples was extracted with cryogeni vacuum distillation method (Sternberg, Deniro, & Savidge, 1986; West, Patrickson, & Ehleringer, 2006). The stable hydrogen (δ<sup>2</sup>H) and oxygen (δ18O) isotopic compositions of all samples were analysed DLT-100: Los Gatos Research Inc., Mountain View, CA, USA). The δ<sup>2</sup>H and 518O raw values were normalized to the Vienna Standard Mean Ocean Water (V-SMOW) scale based on three laboratory standards (LGR 3C, LGR 4C, and LGR 5C). The long-term analytical uncertainty was determined to be 1% for  $\delta^2H$  and 0.1% for  $\delta^{18}O$ . The stable isotopic ratios were calculated as:

from fully exposed, south-facing branches of each selected individual,

In the hyperarid region of Northwest China, frequent variations in hydrological

environments present challenges to the persistence of riparian plants. The main

objective of this study was to determine whether two desert riparian species (Populus

euphratica and Tamarix ramosissima) differed in their water uptake patterns and

ecophysiological responses to fluctuating groundwater depths (GWDs). This study

was conducted in typical desert riparian ecosystems in the downstream Heihe River

basin, Northwestern China, where the GWD continuously increases during growing

season. Stable oxygen composition (δ<sup>18</sup>O) in xylem water, soil water, and groundwa-

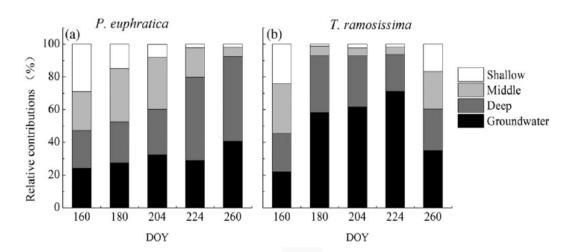
ter, as well as leaf water potential and gas exchange were monitored. Results showed

that P. euphratica used a higher ratio of soil water, whereas T. ramosissima relied more

on groundwater and deep soil water. As the GWD increased during the growing sea-

and then measured immediately after being cut from plants. The maximum net photosynthetic rate (Amax; µmol CO2m-2 s-1) and maximum leaf stomatal conductance (gmax; mol H2Om-2 s-1) were measured with an LI-6400 portable photosynthetic system (Li-COR Inc., Lincoln, NE, USA). The measurements were carried out between 08:00 a.m. and 10:00 a.m. solar time when maximum photosynthetic rate values for the two species were expected according to our preliminary diurnal measurements (data not shown). For each species, five sun-exposed shoots were measured from each of the five individuals. Three measurement replications for each shoot at the intervals of 15 s were made. Gas exchange measurements were not conducted on 22 July (DOY 204) because of equipment failure.

研究黑河流域荒漠 河岸生态系统中的 胡杨林和多枝柽柳 的水分利用格局以 及对地下水深度波 动的生理生态响应。



胡杨林利用较大比例的土壤水,多枝柽柳主要依赖于地下水和 深层土壤水。随着地下水深度的变化,胡杨林对深层土壤水和地下水的吸 收比例增加。而多枝柽柳在其关键生长阶段对地下水的吸收比例增加。

随着地下水深度的变化,两个物种转向于利用更可靠的水源, 对胡杨林而言,水源的转变并不能充分补偿干旱胁迫对气体交换的影响。



### 植物水分来源



Contents lists available at ScienceDirect

#### Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Seasonal variation in water uptake patterns of three plant species based on stable isotopes in the semi-arid Loess Plateau



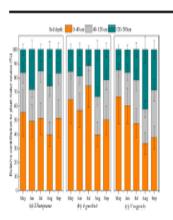
Jian Wang ab, Bojie Fu a, Nan Lu a, Li Zhang c

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- State Key Laboratory of Vegetation and Environmental Change, Institute of Botany, Chinese Academy of Sciences, Beijing 100093, China

#### HIGHLIGHTS

- Seasonal variations of water uptake pattern were determined by dual stable isotopes (5D and 6<sup>18</sup>O) and MixSIAR model
- Soil water in the 0-120 cm depth contributed 75-80% to the total water uptake in the growing season.
- Vitex negundo displayed larger degree of ecological plasticity to switch water between shallow and deep soil layers.
- Functionally dimorphic root systems were related to flexible water uptake pattern.

#### GRAPHICAL ABSTRACT

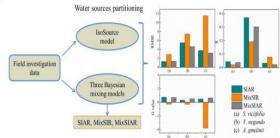


基于氢氧稳定同位 素并结合MixSIAR 模型研究了黄土高 原半干旱区代表植 物本氏针茅、细裂 叶莲蒿以及黄荆水 分利用模式的季节 性变化,结果发现 黄荆具有更大程度 的生态可塑性。

### Inter-comparison of stable isotope mixing models for determining plant water source partitioning

Science of the Total Environment (IF 5.589) Pub Date: 2019-02-19, DOI: 10.1016/j.scitotenv.2019.02.262

Jian Wang, Nan Lu, Bojie Fu



Water sources used for plant identification coupled with stable isotopes are essential to improving the understanding of eco-hydrological processes and ecological management in water-limited ecosystems. Many approaches associated with stable isotopes have been used to determine plant water source apportionment. However, inter-comparisons of different methods are still limited, especially for Bayesian mixing models. In this study, we tested linear mixing models (IsoSource) and Bayesian models (SIAR, MixSIR and MixSIAR) to identify sources of water absorbed by *Vitex negundo* and *Sophora viciifolia* (shrubs) and *Artemisia gmelinii* (subshrub) during the growing season in the semiarid Loess Plateau. The results showed that there was no significant difference in the predicted plant water source fractions using only stable hydrogen isotope ( $\delta^{18}$ O) with the IsoSource model. No significant difference was found in plant water source

在IsoSource模型中仅用δD或δ<sup>18</sup>O来预测植物水分吸收无明显差异,就木本植物而言, SIAR和Mix-SIAR模型植物水分分配结果更好。

## 应用-溪水水分来源

• Berman等 (2009) 在LGR液态水同位素上增加一个简单的外部设备,采用自动原位取样、连续测量的方式,在三次强降雨过程中同时测量溪水和降水的稳定同位素组成以确定溪水的水分来源。



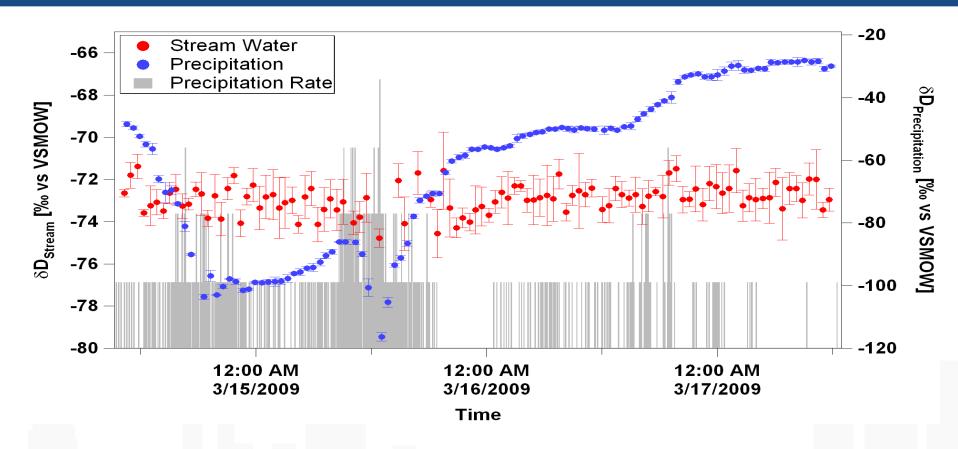








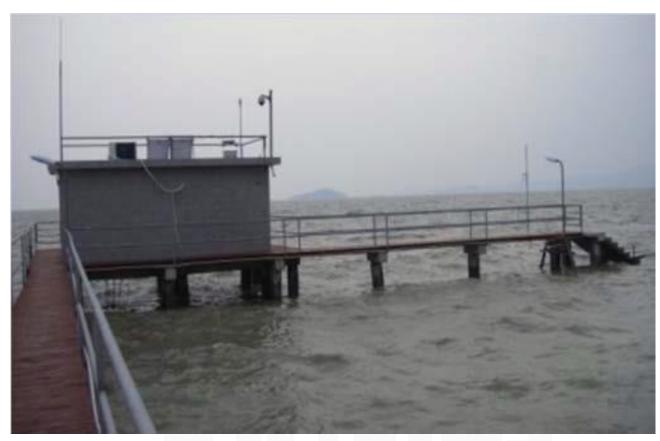
## 应用-溪水水分来源



Manish Gupta, Elena Berman, Chris Gabrielli, Tina Garland, J. McDonnell High-Frequency Field Deployable Isotope Analyzer for Hydrological Applications *Water Resource. Research*, doi:10.1029/2009WR008265



## 耶鲁大学-南京信息工程大学大气环境中心





湖泊蒸发是地表水耗散中不可忽视的一项,影响区域地表<mark>能量平衡</mark>,甚至会影响区域降水状况和干湿特征,乃至全球的气候变化



## 应用-湖泊蒸发

第50卷 第1期 2019年 1月 海洋与湖沼 OCEANOLOGIA ET LIMNOLOGIA SINICA

Vol.50, No.1 Jan., 2019

### 氢和氧稳定同位素示踪湖泊蒸发的对比研究\*

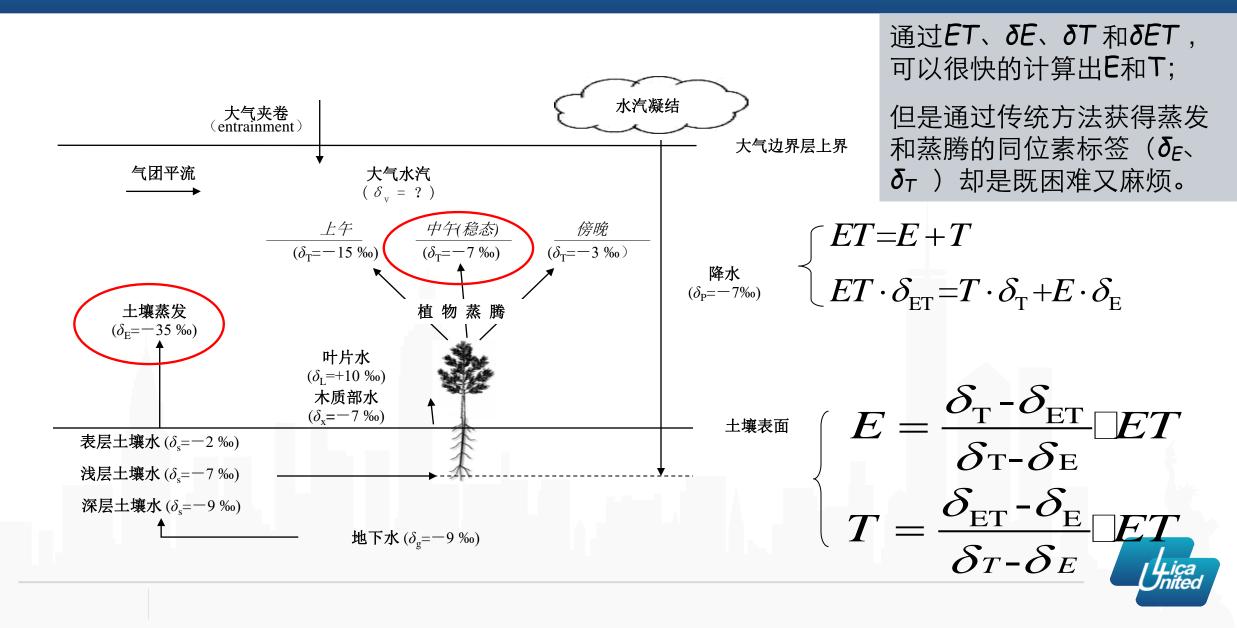
谢成玉1 肖 薇1,20 徐敬争3 朱珊娴4 胡勇博1 李旭辉1

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摘要 氢氧稳定同位素被广泛用于水文循环过程的研究。本文观测了 2015 年太湖湖水  $H^2HO$  和  $H_2^{18}O$  组分,分析了它们的时空变化规律及其控制因子,探讨亚热带大型浅水湖泊的同位素富集机制;基于稳定同位素质量守恒法计算太湖蒸发量;评价了动力分馏学系数的传统湖泊算法与海洋算法的适用性;重点分析了  $H^2HO$  和  $H_2^{18}O$  示踪湖泊蒸发的效果,对比二者之间的差异。研究结果表明,在空间上,太湖湖水和河水的氢氧同位素在南部特别是东南部较为富集但在北部区域较为贫化,这主要是受水流方向的控制,东南部湖水经历的蒸发时间较长,因此湖水中同位素累积较多;在季节上,冬季湖水同位素较贫化、春夏季较富集。对于 2015 年太湖的年蒸发量,用氢同位素示踪的结果与观测值较一致,为 880mm;氧同位素的示踪结果略低,为 690mm。使用传统湖泊研究中对动力学分馏系数的取值,会导致蒸发被显著低估,而氧稳定同位素的示踪结果对动力学分馏系数的取值更为敏感,同时氢稳定同位素在同位素分馏过程中主要是平衡分馏效应占主导,因此  $H^2HO$  在动力学分馏系数的参数化方案中影响较小,在实际应用中更为稳定。本文的研究结果表明了稳定同位素水

将同位素质量守恒方 程和Craig-Gordon模型相 结合计算湖面蒸发量, 对比 <sup>2</sup>H和<sup>18</sup>O在整个参数化方案 中的差异及在同位素分馏机 理上的差异, 重点检验采用 两种同位素作为示踪剂的情 况下稳定同位素质量守恒法 在大型开放浅水湖泊中的适 用性。

## 应用-区分蒸腾和蒸发



# 应用-野外廓线



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#### Agricultural and Forest Meteorology

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Partitioning oak woodland evapotranspiration in the rocky mountainous area of North China was disturbed by foreign vapor, as estimated based on non-steady-state <sup>18</sup>O isotopic composition

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### LI-2100 全自动植物土壤水分真空抽提系统

LI-2100是LICA自主研发的一款全自动真空冷凝抽提系统,且已通过CE认证。从根本上解决了植物和土壤水分提取采集的难题,克服了传统液氮冷却的繁琐,不仅可以防止同位素分馏,而且安全且效率高,不会对植物和土壤造成破坏。可与LGR水同位素分析仪配套使用。

## LI-2100 全自动植物土壤水分真空抽提系统

### 特点





- 1. 沿用传统经典的真空蒸馏冷冻方法,数据可靠
- 2. 无需液氮:压缩机制冷,提高安全性
- 3. 快速高效:一次可同时提取14个样品
- 4. 全自动抽提: 全过程无人值守
- 5. 安全便捷: 自我断电与自我保护功能
- 6. 质量控制: 故障提示与自动报警
- 7. 全球首创: 专利技术
- 8. 氢氧稳定同位素前处理



# LI-2100安装案例











## LI-2100和水同位素分析仪应用案例

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Stable isotope evidences for identifying crop water uptake in a typical winter wheat-summer maize rotation field in the North China Plain



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- · A full crop water uptake diagram was obtained for winter wheat and summer
- · Stable isotope and hierarchical cluster analysis were used to classify soil layers
- · Dry root weight density negatively corresponded to wheat's water uptake
- · Soil water content positively corresponded to both wheat and maize's water uptake.
- · Irrigation should be suspended from the pooting to flowering stages of wheat

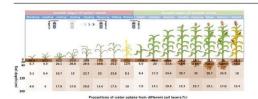
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#### GRAPHICAL ABSTRACT



Better managing agricultural water resources, which are increasingly stressed by climate change and anthropo genic activities, is difficult, particularly because of variations in water untake patterns associated with crop type and growth stage. Thus, the stable isotopes 6180 and 62H were employed to investigate the water uptake pattern: of a summer maize (Zeg mays L.) and winter wheat (Triticum gestivum L.) rotation system in the North China Plain Based on the soil water content, soil layers were divided into four groups (0-20 cm, 20-40 cm, 40-120 cm, and 120-200 cm) using a hierarchical cluster analysis. The main soil layer of water uptake for sum mer maize was from 0-20 cm at the trefoil (77.8%) and jointing (48.6%) stages to 20-40 cm at the booting (33.6%) and heading (32.6%) stages, became 40-120 cm at the silking (32.0%) and milking (36.7%) stages, and then returned to 0-20 cm at the mature (35.0%) and harvest (52.4%) stages. Winter wheat most absorbed water from the 0-20 cm soil water at the wintering (86.6%), seedling (83.7%), jointing (45.2%), booting (51.4%), heading (28.8%), and mature (67.8%) stages, but it was 20-40 cm at the flowering (34.8%) and milking (25.2%) stages. The dry root weight density was positively correlated with the contributions of the water uptake for winter wheat However, no similar correlation was found in summer maize. Regression analysis indicated that the soil volume ric water content (SVWC) was negatively correlated with the contribution of the water uptake (CWU) for sum mer maize (CWU = -0.91 × SVWC + 57.75) and winter wheat (CWU = -2.03 × SVWC + 92.73). These different responses to water uptake contributions suggested that a traditional irrigation event should be post poned from the booting to flowering stage of winter wheat. This study provides insights into crop water uptake and agricultural water management

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#### 2.3. Measurement and analysis

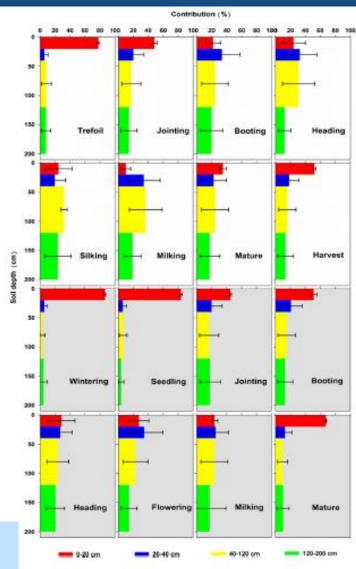
Soil water content at depths of 10 cm, 20 cm, 30 cm, 40 cm, 60 cm, 80 cm, 100 cm, 120 cm, 150 cm, and 200 cm were monitored at 30 min intervals using a Water-Content-Profile probe (EnviroSCAN, Sentek Pty Ltd., Stepney, Australia) connected to a CR200X data logger (Campbell Scientific, Inc. Logan, UT, USA) in the field.

Water in xylem and soil samples were extracted using a fully automatic vacuum condensation extraction system (LI-2100, LICA United Technology Limited, Beijing, China). The extraction rate of water from samples was >98%. Xylem water, soil water, and precipitation (0.5– 1.5 ml) (manual book edited by Los Gatos Research, Inc.) were analyzed for  $\delta^{18}$ O and  $\delta^{2}$ H. The isotopic compositions were analyzed using a water isotope analyzer (WIA-35d-EP, Model 912-0026, Los Gatos Research, Mountain View, CA, USA). Each sample was analyzed six times, and the first three results were discarded to minimize the memory effect. The isotopic compositions were reported in standard  $\delta$ -notation, representing ‰ deviations from the Vienna Standard Mean Ocean Water standard (V-SMOW), expressed as  $\delta(\%) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{expected}}} \times 1000 =$  $(\frac{R_{sample}}{R_{gandard}}-1) imes 1000$ . The analytical uncertainties for  $\delta^{18}O$  and  $\delta^{2}H$  were 0.15% and 0.5%, respectively. Corrections using a standard curve for  $\delta^{18}$ O and  $\delta^{2}$ H in xylem water samples were conducted to avoid methanol and ethanol contamination (Schultz et al., 2011).

Roots were washed, sieved, and then oven-dried at 65 °C to a constant weight to achieve dry root weights. The dry root weight density was calculated by dividing the dry root weight (g) by the soil volume (cm<sup>3</sup>) (Guan et al., 2015; Li et al., 2010).

The Bayesian mixing model (MixSIR 1.0.4) was employed to quantify the proportion of water uptake from each water source based on the mass balance of the isotope (Moore and Semmens, 2008).

华北平原典型冬小麦-夏季玉米轮作田作物吸水的稳定同位素研究。在华北 平原,作者利用 $\delta^{18}$ O和 $\delta^{2}$ H研究了冬小麦和夏季玉米轮作田的水分吸收模 式。















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