德州休斯敦工业VOC排放监控

Greg Yarwood，侯敏

RAMBOLL

CLEAN AIR ASIA VOC WORKSHOP, SHANGHAI
DECEMBER 15, 2016

致谢

资源链接见最后一页

- 德州环境质量委员会(TCEQ)
- 德州空气质量研究计划(AQRP)
- 德克萨斯大学奥斯汀分校(UT)
- 瑞典FluxSense遥感技术探测公司
- 英国国家物理实验室
- Picarro公司
- Entanglement Technologies公司
- NOAA 地球系统研究实验室

休斯敦航道


Houston Ship Channel
Image courtesy of Cregan Design


Houston
TX

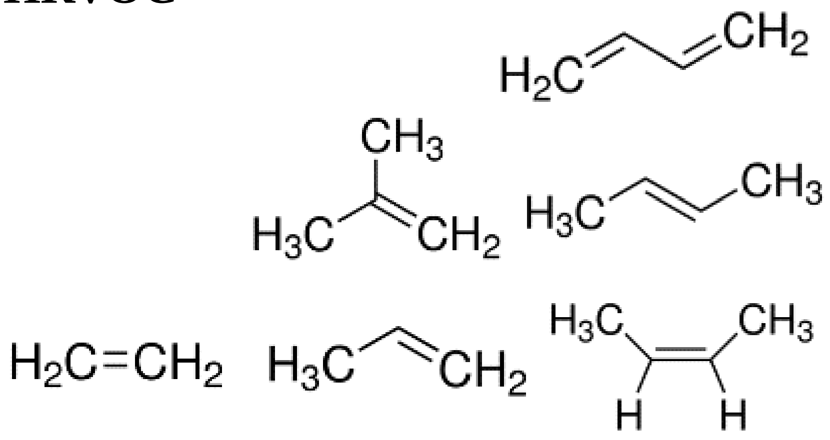

Refinery
Neighborhood
Neighborhood

休斯敦工业VOC – 重点

- 高活性VOC (HRVOC)
  - 烯烃 ≤ C4
  - 强作用力的臭氧前体物

- 毒性VOC
  - 苯
  - 1,3-丁二烯
  - 界区暴露和公共健康

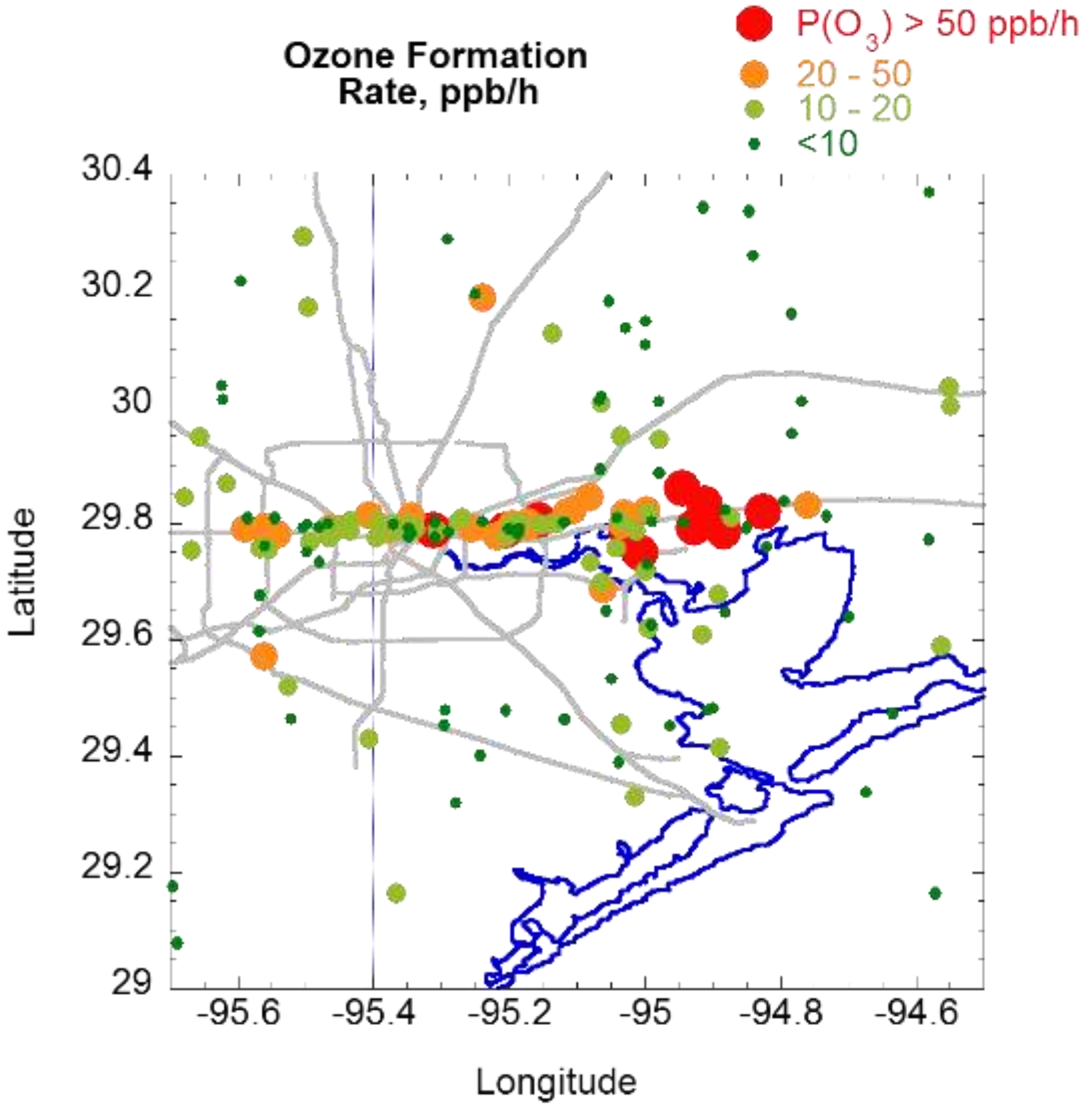
HRVOC



2000年休斯敦臭氧和HRVOC情况

- TexAQS 2000年实地调查
- 飞机“飞行试验”采集的数据
  - 臭氧
  - 氮氧化物
  - VOC，气相色谱法测定

- HRVOC排放迅速生成臭氧 P(O3)
- 工业烟流的臭氧生成效率 (O_3 /氮氧化物)是城市烟流的2倍
  - 排放清单低估了HRVOC排量



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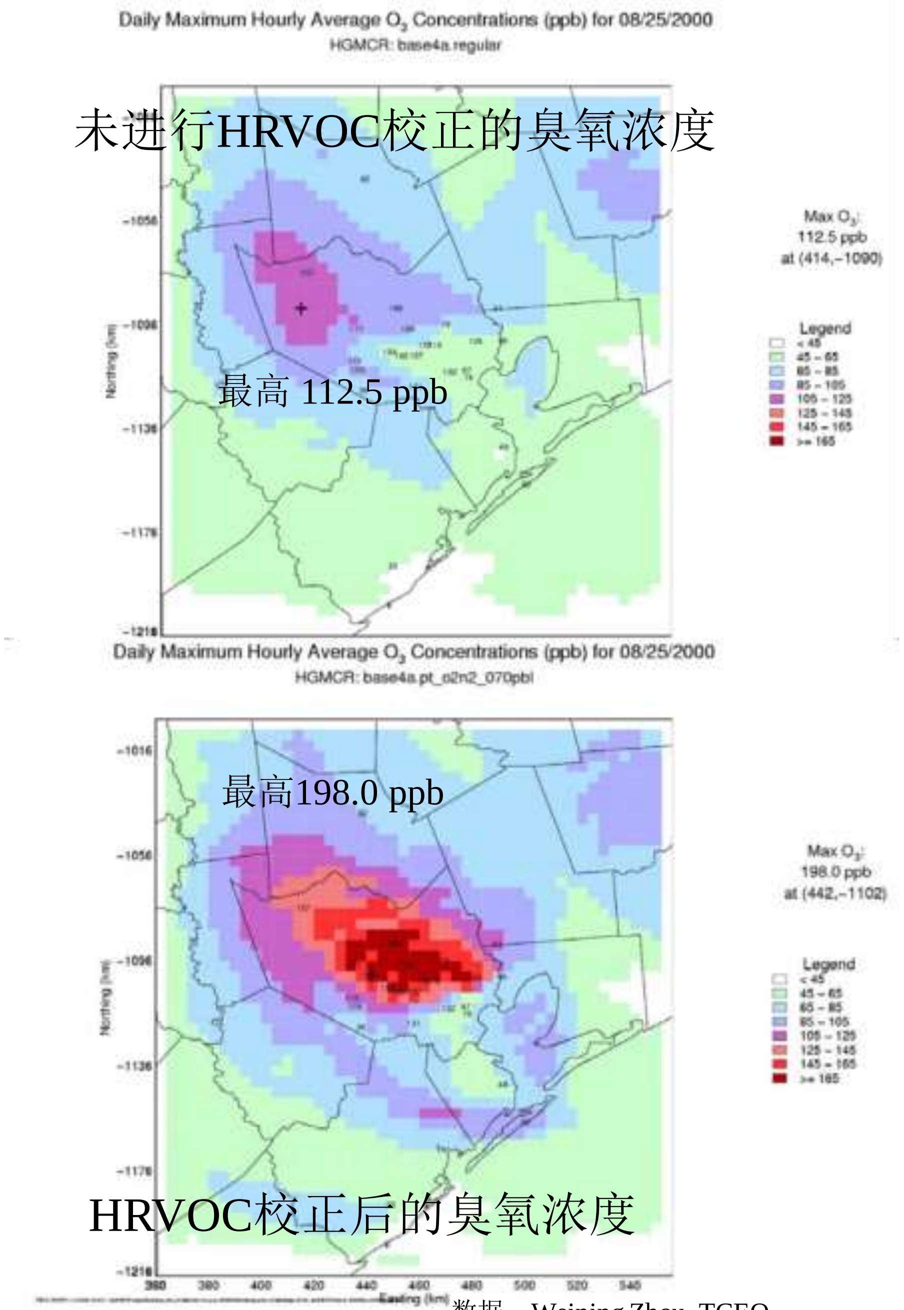
通过模型确认HRVOC对臭氧的影响

- TCEQ臭氧模型
  - 调整排放清单，以反映TexAQS的HRVOC观察结果：VOC点源排量从6,742 kg/hr增至12,386 kg/hr
  - 使用修正后的排放清单的模型模拟结果与观测结果一致性大大改善
  - TCEQ使用了Ramboll的CAMx模型：www.camx.com

- TCEQ引入了HRVOC法规：
  - 由公司监测HRVOC排放
  - 制定企业长期和短期HRVOC总排量上限
  - 规则涵盖火炬、无组织排放、过程排气口和冷却塔

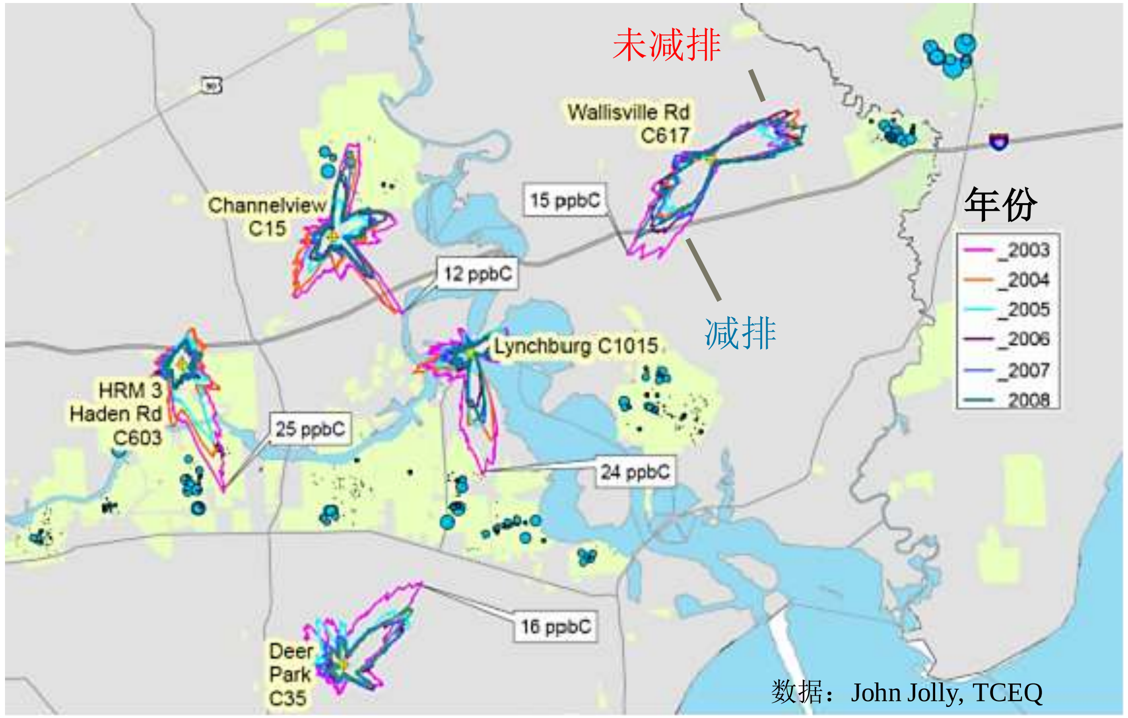


数据：Weining Zhou, TCEQ

休斯敦Auto-GC网络观测到HRVOC下降

- Auto GC网络全天候运行
- 狭窄、有方向性的烟流显示排放源方位，但不能明确具体排放源
- TCEQ的三角测量分析表明，工业点源是HRVOC主要排放源
- 2003年到2008年的趋势表明，部分排放源大幅减少了排放，而其他排放源未减少
- TCEQ的HRVOC规则极大地改善了排放和臭氧情况

乙烯 (ppbC)年几何均值随风向分布图



Auto-GC和气象观测系统、臭氧、氮氧化物等观测系统部署在一处

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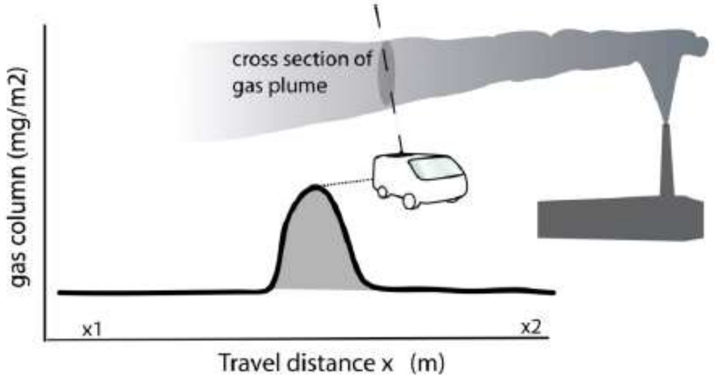
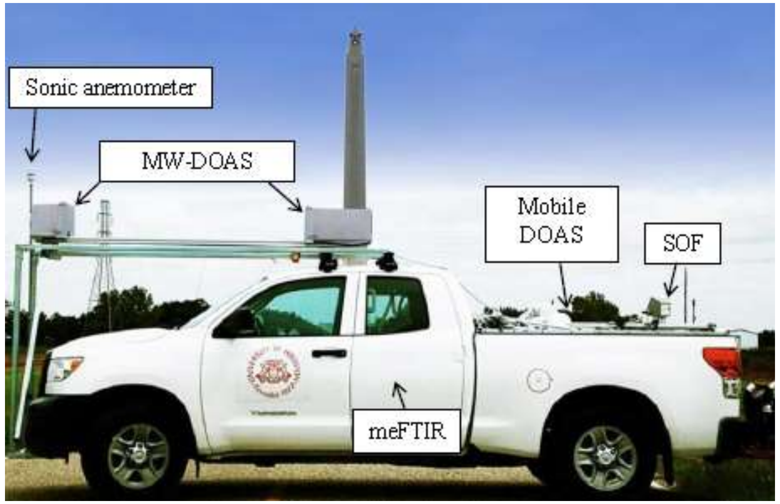
排放通量 (g/s)移动监测

- 光学方法测量气柱质量 (g/m^2)
  - 红外掩日通量法（SOF）: FTIR分析仪：VOC、HRVOC、NO_2
  - 差分吸收光谱法（DOAS）：UV分析仪：NO_2、 SO_2、HCHO
- 整合烟流宽度(m)上的气柱
- 测量风速 (m/s)
- 通量= (g/m^2) x m x (m/s) = g/s
  - 风速影响准确性
  - 准确性一般为±35%
  - 比大部分排放清单更准确
  - 需要的是气柱质量，不是地面浓度
  - 更多信息：*www.fluxsense.se*





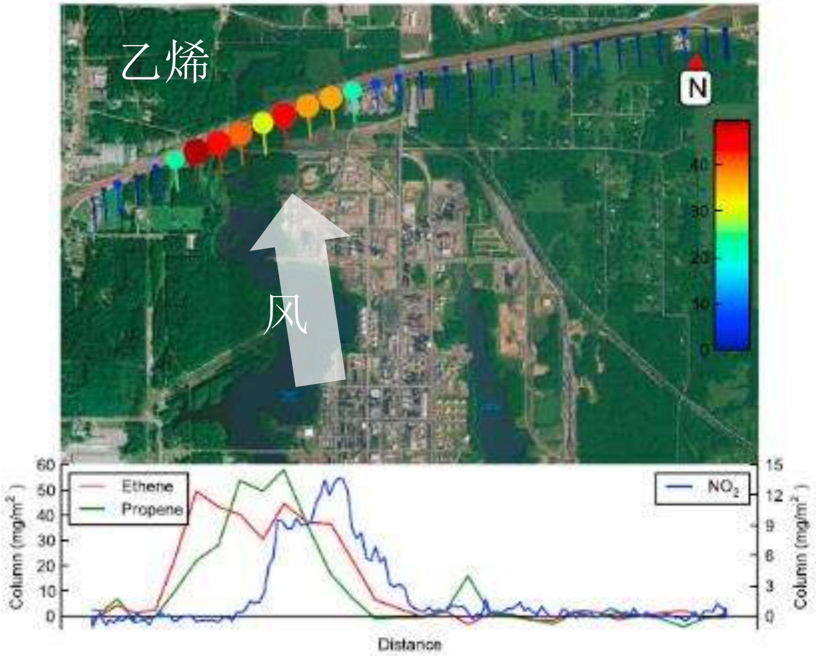
石化设施附近的SOF

Emission measurements of alkenes, alkanes, SO_2, and NO_2 from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS

John K. E. Johansson[1], Johan Mellqvist[1], Jerker Samuelsson[1], Brian Offerle[1], Barry Lefer[2], Bernhard Rappenglück[2], James Flynn[2], and Greg Yarwood[3]

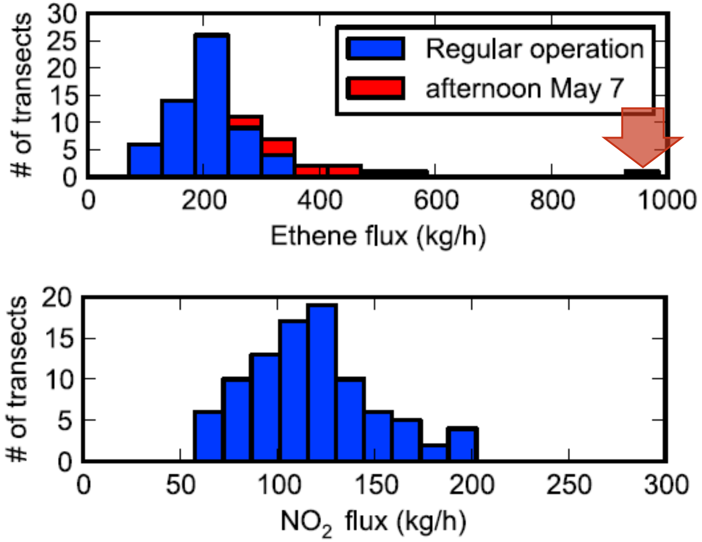
http://onlinelibrary.wiley.com/doi/10.1002/2013JD020485/full

单次监测（横断面）



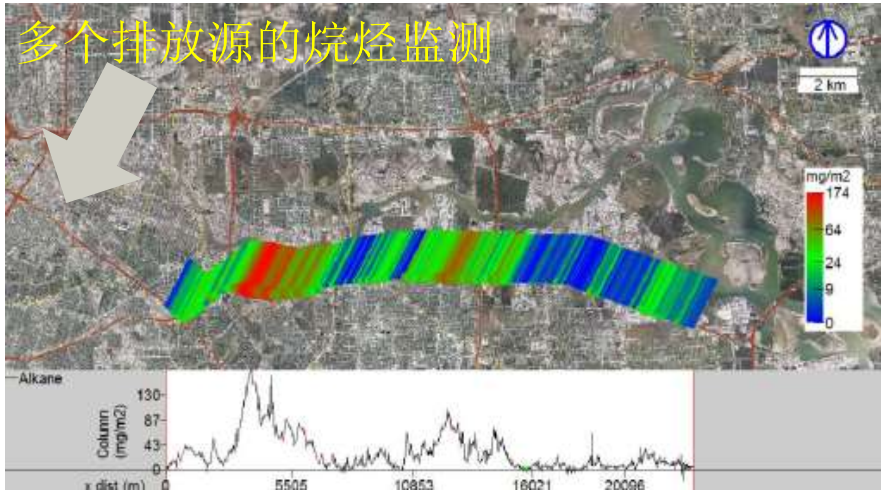
监测车

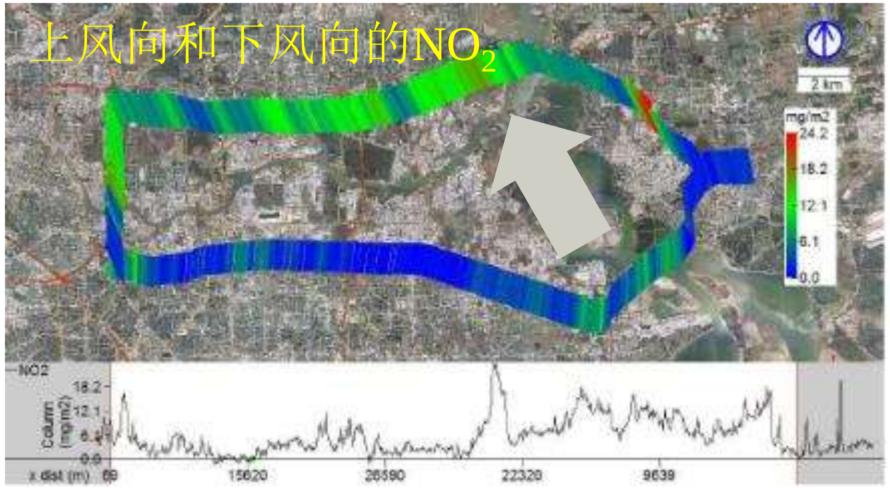
10天的通量监测

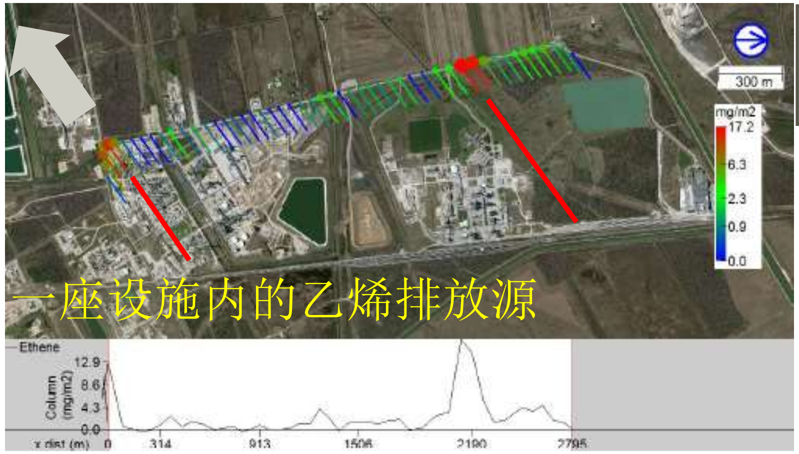


- 排放通量在变化
- 乙烯在某一天的最高值约为中位数的5倍
- NO_2 更稳定

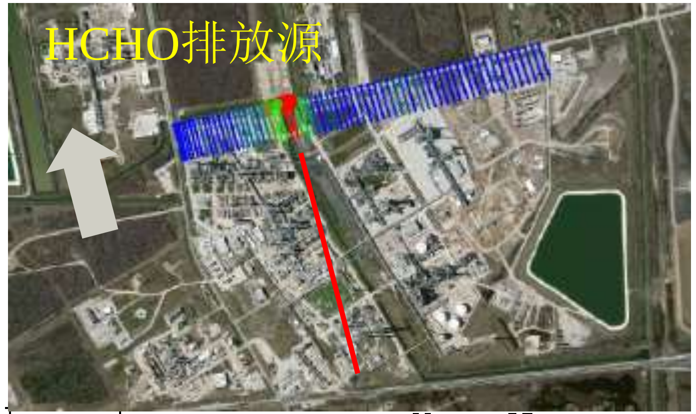
SOF其他示例







界区内监测，提高精度



Day	N	Start	Stop	Mean (kg/h)	SD (kg/h)
130909	2	150902	152137	7.1	3.7
130913	4	141718	145658	13.2	6.3
130922	3	121834	125155	9.0	3.1
130923	5	130800	161137	8.2	3.0
	14	**121834**	**161137**	**9.7**	**4.5**

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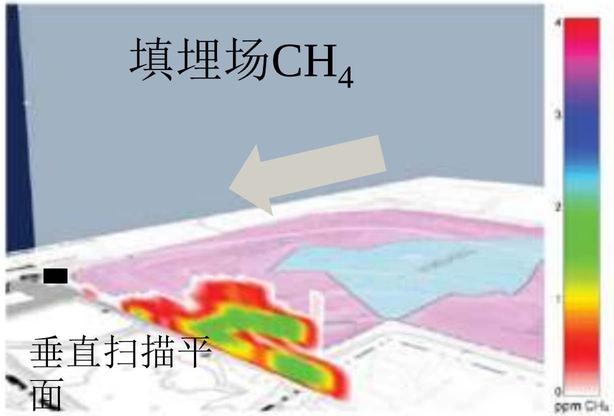
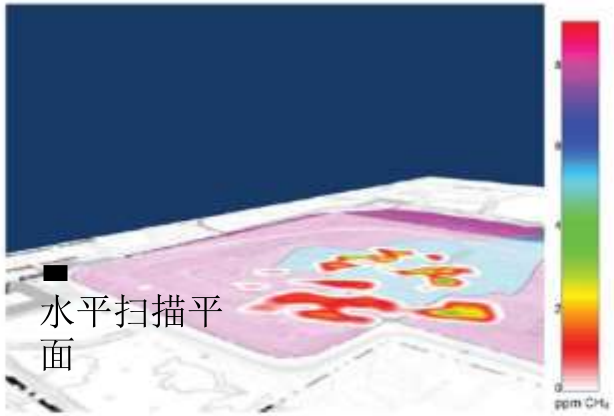
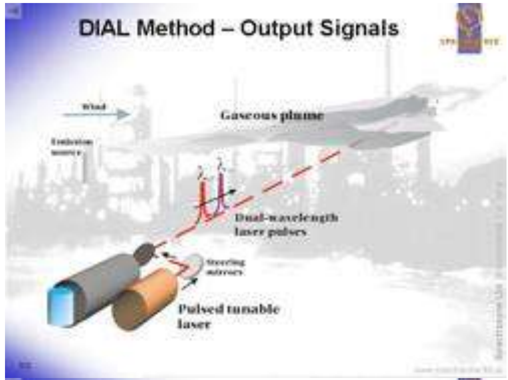
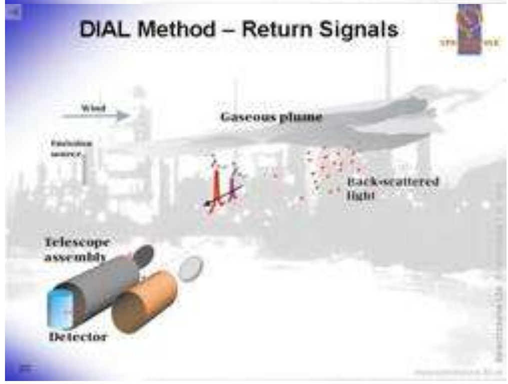
激光烟流扫描：差分吸收激光雷达（DIAL

- DIAL：差分吸收激光雷达
  - 光学方法测量气柱质量 (g/m²)
  - IR分析仪：VOC、HRVOC 、 NO_2
  - UV分析仪：NO_2 、 SO_2 、 HCHO 、 BTEX
- 利用垂直扫描平面计算通量 (g/s)
  - 风速影响准确性
  - 准确性一般为±25%
  - 比大部分排放清单更准确
  - 更多信息：www.npl.co.uk
- 配备仪器的大型车辆
  - 停车扫描
  - 来自英国；通过海运发送车辆
  - 在休斯敦炼油厂开展调查研究

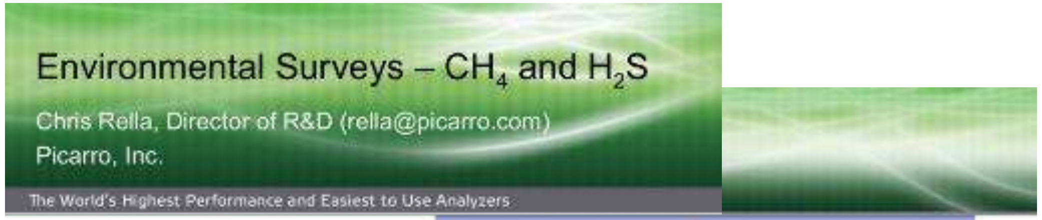




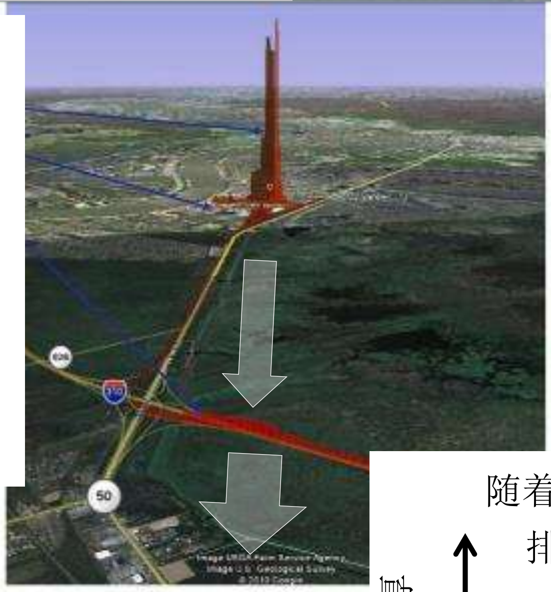




移动浓度测量



- 炼油厂CH_4烟流
- 10公里距离上3个横断面
- 排放源附近的CH_4峰值>背景值上1.5 ppm
- 下风向CH_4峰值接近背景值



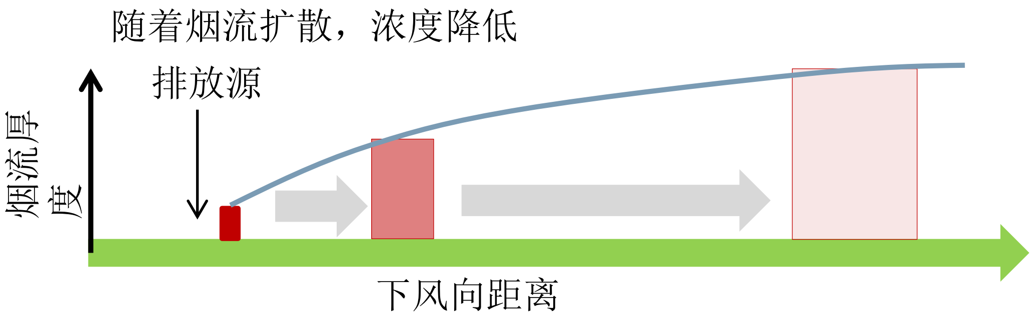
PICARRO

Picarro公司光腔衰荡光谱技术（CRDS）测量

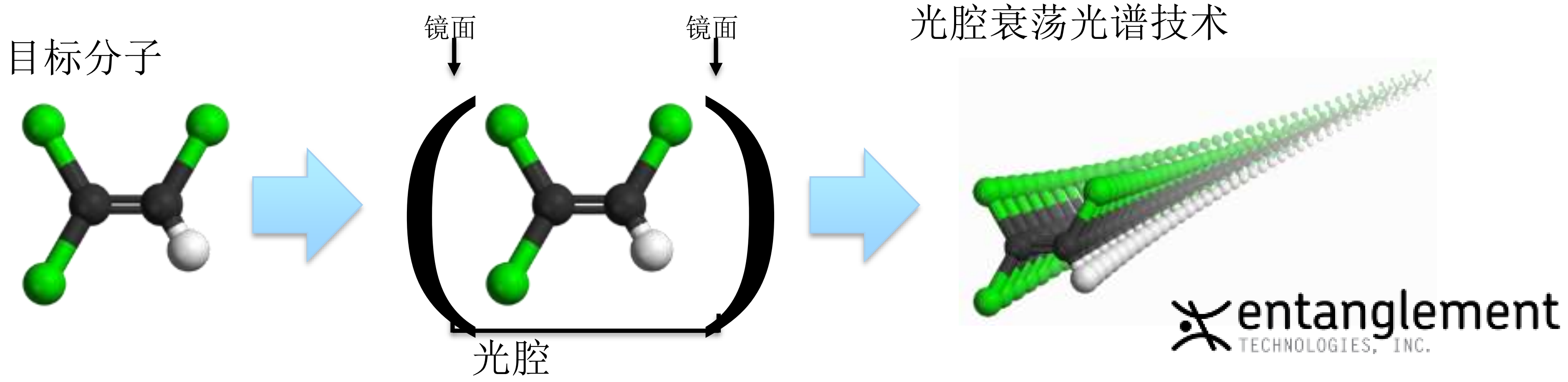
CH_4

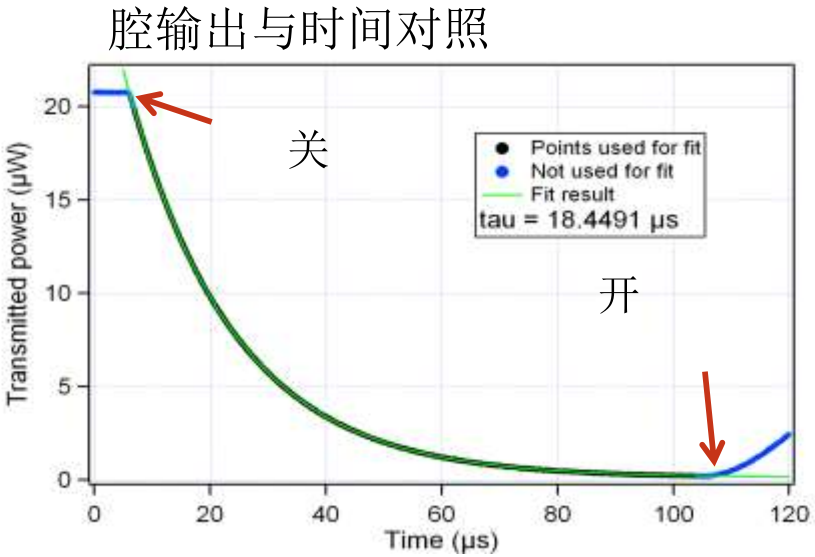
优点
- 灵敏度高
- 响应快
- 车辆安装良好
- 查找烟流

缺点
- 计算排放通量需要有烟流厚度
- 检测不到高空烟流



CRDS能力在增长





- 光吸收增强高达400,000x
- 通过测量“衰荡”时间确定吸收量

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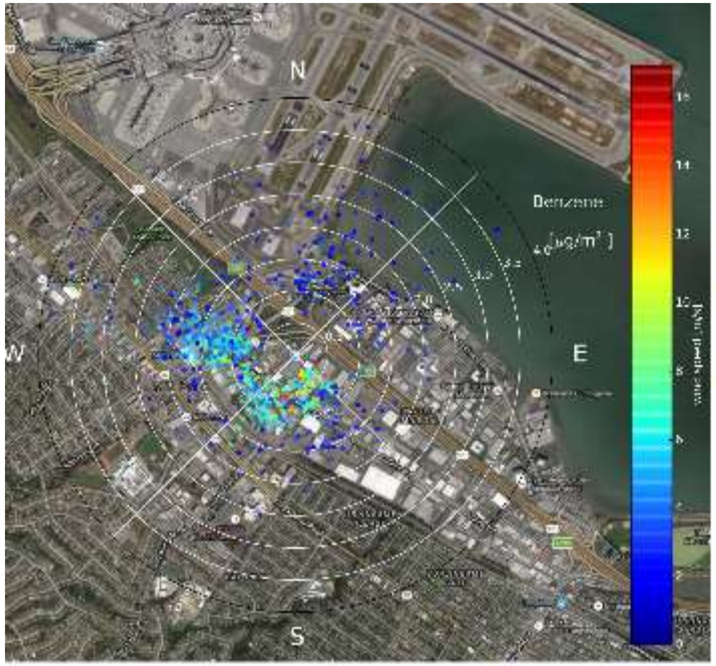
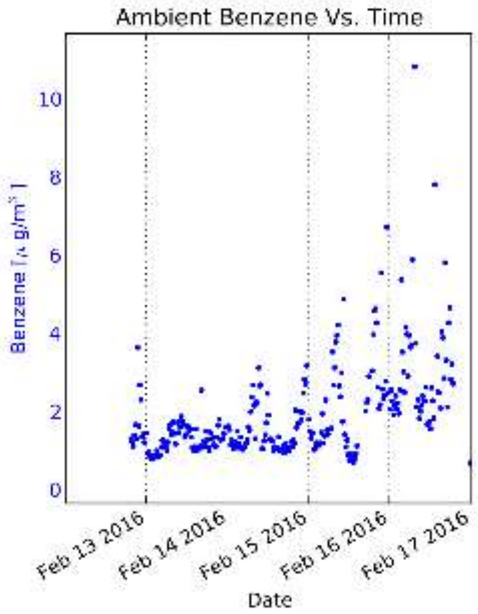
CRDS测量环境苯（也有三氯乙烯）





entanglement TECHNOLOGIES, INC.

- 环境浓度1-10 $\mu g/m^3$的苯污染增长和时间序列
- 地点位于旧金山的Entanglement实验室
- 排放源可能是道路交通和国际机场
- 仪器性能 （15分钟，1-西格玛）：

  <0.06 $\mu g/m^3$ 三氯乙烯
  <0.05 $\mu g/m^3$ 苯

方法综合

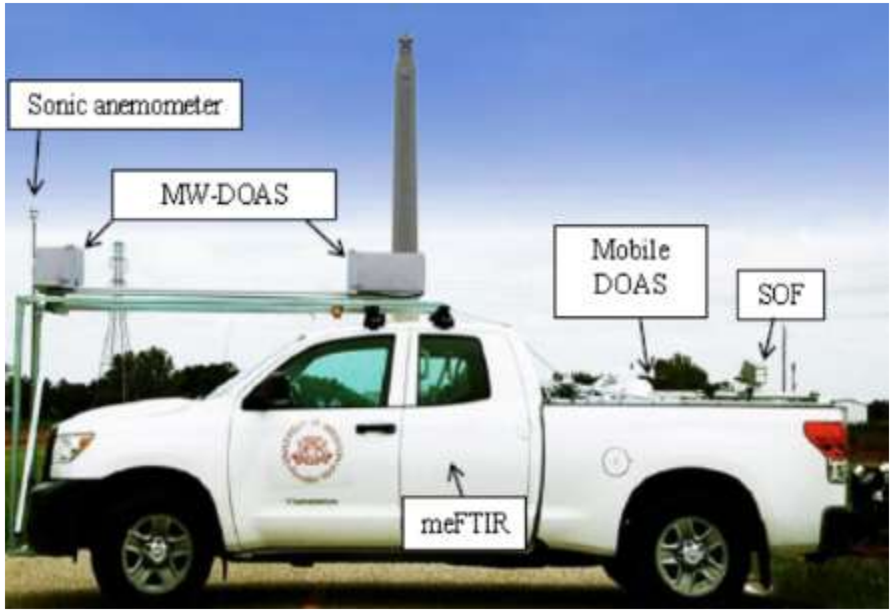
FluxSense

•利用SOF和/或DOAS检测烟流

- 作为补充信息的地面浓度
    - UV DOAS带有多次反射装置，用于二甲苯芳烃
    - 抽气式FTIR，用于VOC

NOAA地球系统研究实验室

- 利用Picarro CRDS检测CH_4烟流
- 利用罐装样本和气相色谱法分析VOC
    - 不连续
    - 利用VOC/CH_4 比值



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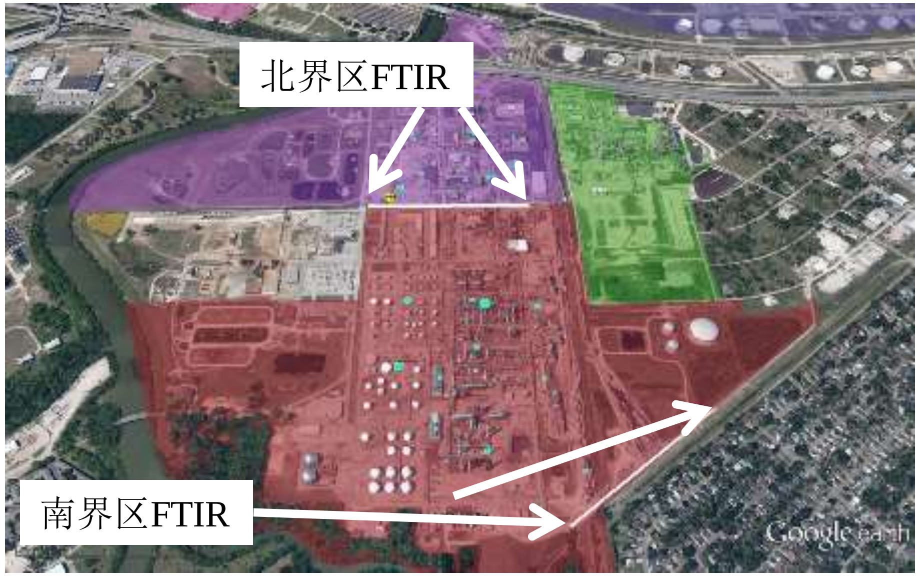
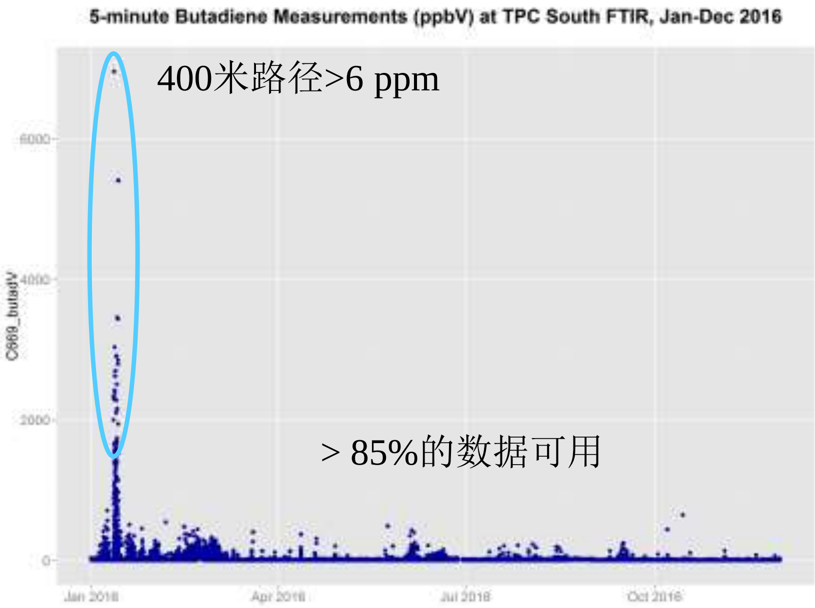
界区FTIR用于分析毒性VOC种类

- 3座相邻设施，2台界区FTIR分析仪
  - 1,3-丁二烯和苯乙烯
  - 400米路径：按照距目标排放源地点300、200、100、50米的距离观测排放事件

- 目的是改善经营实践，最大程度减轻影响



数据：John Jolly, TCEQ



南界区丁二烯，
2016年1-12月

TCEQ火炬操作员培训

- TCEQ发现有时火炬操作效率较低
- UT为TCEQ开发了一套在线培训课程

低效火炬操作

- 低热值排气
- 辅助空气或水蒸气太多
  - 努力避免烟雾
- 运行时只使用最大燃烧量的极小部分
  - 使用安全火炬控制过程排放

TCEQ

Supplemental Flare Operations Training for Plant Personnel

THE UNIVERSITY OF TEXAS AT AUSTIN

https://sfot.ceer.utexas.edu/

Welcome to the Supplemental Flare Operations Training

Purpose and Objective of the Training

The purpose of this site is to provide supplemental online flare operations training to plant personnel who monitor elevated, industrial-scale chemical and petrochemical flares used for routine service. This training is intended to supplement flare site-specific training provided by the trainees own company.

The objective of the training is to enhance plant personnel's understanding of industrial flare operation and provide practical information about variables affecting flare performance, with the aim to maximize flare destruction and removal efficiency (DRE) of dual-purpose assisted flares consistent with state and federal regulations using existing on-site resources.

Training Overview

Employing results of past and recent full-scale flare studies, scientific information available in the published literature, flare manufacturer's data, governing state and federal regulations, and the expertise of content experts, environmental organizations and consultants, this Internet-based training program has been developed for plant personnel. The training is organized into five short modules plus a final comprehensive assessment. Each module focuses on a different topic/subject area pertinent to the understanding of how flares operate and/or how flare performance can be impacted. Upon successful completion of all five modules and the comprehensive assessment, a certificate of completion will be awarded. This certificate certifies that you have completed the Supplemental Flare Operations Training and Comprehensive Assessment but is not a substitute for site-specific training. A refresher module is also available as a high-level refresher presentation to review the Supplemental Flare Operations Training for Plant Personnel.

The training consists of these five modules and an assessment as well as a refresher module and assessment. It is recommended that you complete the training in numerical order.

- Module 1 - Introduction (approximately 9 min.)
- Module 2 - History of Flares, Applicable Regulatory Codes and Flare Types (approximately 22 min.)
- Module 3 - Approaches to Monitoring Flare Emission Performance (approximately 36 min.)
- Module 4 - Flare Performance Parameters Investigated in Recent Industrial Flare Studies (approximately 24 min.)
- Module 5 - Factors that Impact Flare Performance (approximately 21 min.)
- Supplemental Flare Operations Training Comprehensive Assessment
- Supplemental Flare Operations Training Certificate of Completion

Trainers and Training Personnel

A Resource Toolkit for Trainers is available to training personnel who would like to have access to the instructor notes as well as the images, videos, and animations used within the Supplemental Flare Operations Training modules for utilization within their own site-specific training. This Resource Toolkit is available as organized zipped files for download.
Trainers must create a new account to access the toolkit.

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结论

- 欧洲成功实施VOC通量测量已有20年历史
  - 主要是DIAL和SOF两种方法
  - 改善了排放性能
  - 清单低估过程
- 移动系统可以找到未知的排放源
- 排放改善潜力
  - 火炬操作规程
  - 工业废水处理
  - Ramboll可以帮助你

Greg Yarwood， PhD

安博英环（美国）加州诺瓦托办公室

电话：**1 415 899 0704**

邮件： **gyarwood@ramboll.com**

Min Hou， CIH

安博英环（中国）北京办公室

电话：**86 155 1033 7040**

邮件： **mhou@ramboll.com**

Ling Huang， PhD

安博英环（中国）上海办公室

电话：**86 173 1632 9863**

邮件： **lhuang@ramboll.com**

数据来源

- 德州环境质量委员会 (TCEQ): https://www.tceq.texas.gov/
- 德州空气质量研究计划 (AQRP): http://aqrp.ceer.utexas.edu/
- 瑞典FluxSense遥感技术探测公司：http://wwww.fluxsense.se
- 英国国家物理实验室：http://www.npl.co.uk/people/rod-robinson
- Picarro公司：https://www.picarro.com
- Entanglement Technologies公司：http://www.entanglementtech.com
- NOAA地球系统研究实验室：http://www.esrl.noaa.gov/csd/news/topics/oilandgas.html