On the Distribution of the Blank (B)

L.A. Currie and J.M. Conny -- NIST (March 2003)

- The blank as the fundamental limiting factor

- Relation to detection decisions and limits, and uncertainties of low-level measurements

- Environmental blanks: normal and *ab*-normal

- Case study of TOA filter-blanks for OC and EC

  Importance for remote carbonaceous aerosol:

  SUMMIT, GREENLAND **air** (0.3^+ μg/m^3) and **snow** (9^+ μg/kg) [TC]

Detection -- The Concept

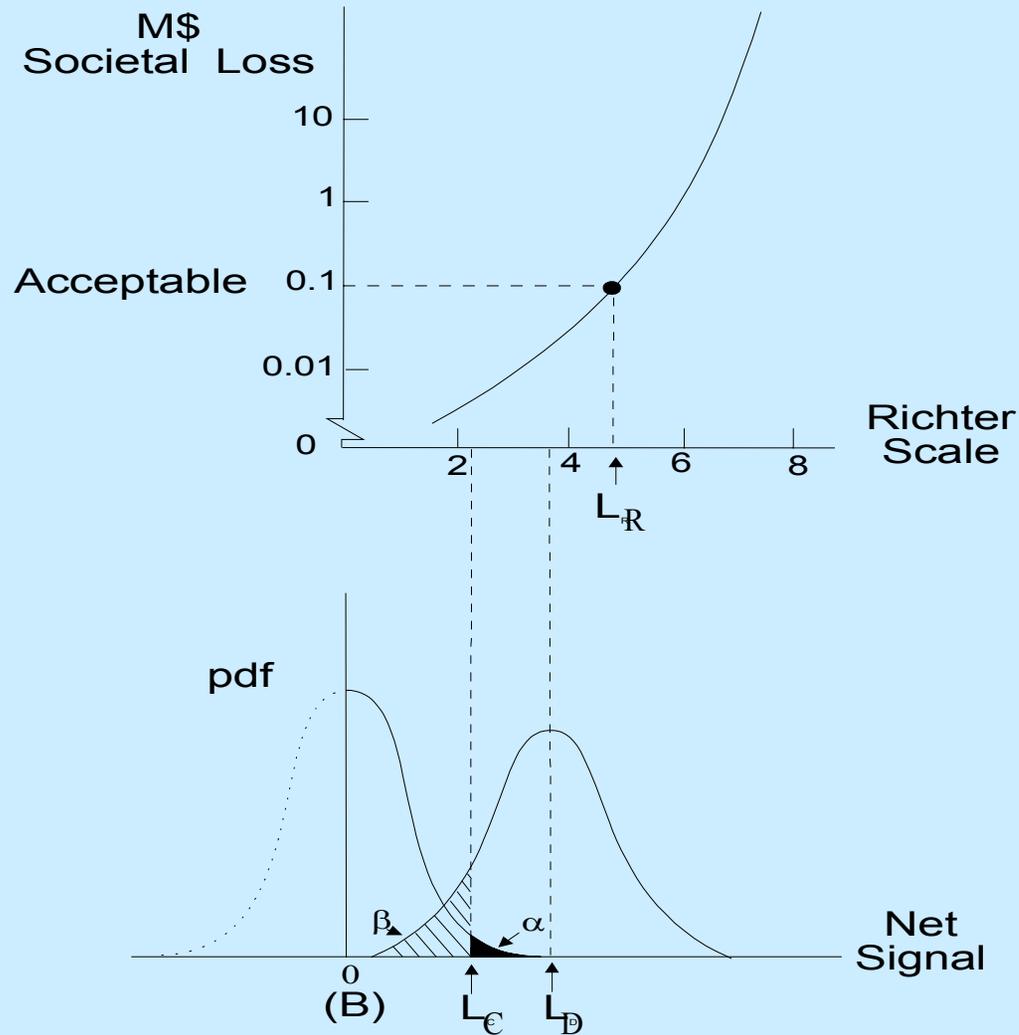- **Dual Questions:**

  - Q1 - How little can be detected (quantified)?

  - Q2 - Has something been detected (how much)?

- **Popular Responses:**

  - **Intuitive** (sound experience, non-quantifiable)

  - **Ad Hoc** (rigid formula, dictum, vote, ...)

  - **Signal/Noise** (assuming white noise, Q2 only)

  - **Avoidance** (small signals not worth considering)

  - **Hypothesis Testing** (false positives and false negatives)

Detection Needs and Capabilities
L_C: critical level, L_D: detection limit, L_R: requisite limit

Answer -- question 2

Detection Decision (Critical Value) $(L_C; \alpha = 0.05)$

- **Defining relation** (IUPAC, 1995, 1998):

    (1) $\Pr(L > L_C \mid L = 0) \leq \alpha$

- **Simplified relations** (IUPAC, 1995, 1998)

    (2a) $L_C = z_{1-\alpha}\, \sigma_o \rightarrow 1.645\, \sigma_o$

    (2b) $L_C = t_{1-\alpha, \nu}\, s_o \rightarrow 2.132\, s_o$ [4 df]

    ....

   For paired measurements: $\sigma_o = \sigma_B \sqrt{2}$

B - Distributions

- S (materials, atmospheric particles: n-large)

- ^{14}C (atmospheric particles: n-small)

- OC, EC (unused Lab and Field filter blanks)

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S, ^{14}C: Currie, "Case studies of skewed .. distributions .. in low-level environmental research," *Fresenius J Anal Chem* 370 (2001) 705-718.

OC, EC: Conny & Slater, "BC and OC in aerosol particles from crown fires in the Canadian boreal forest," *J Geophys Res* 107, D11 (2002) 10.1029/2001JD001528.

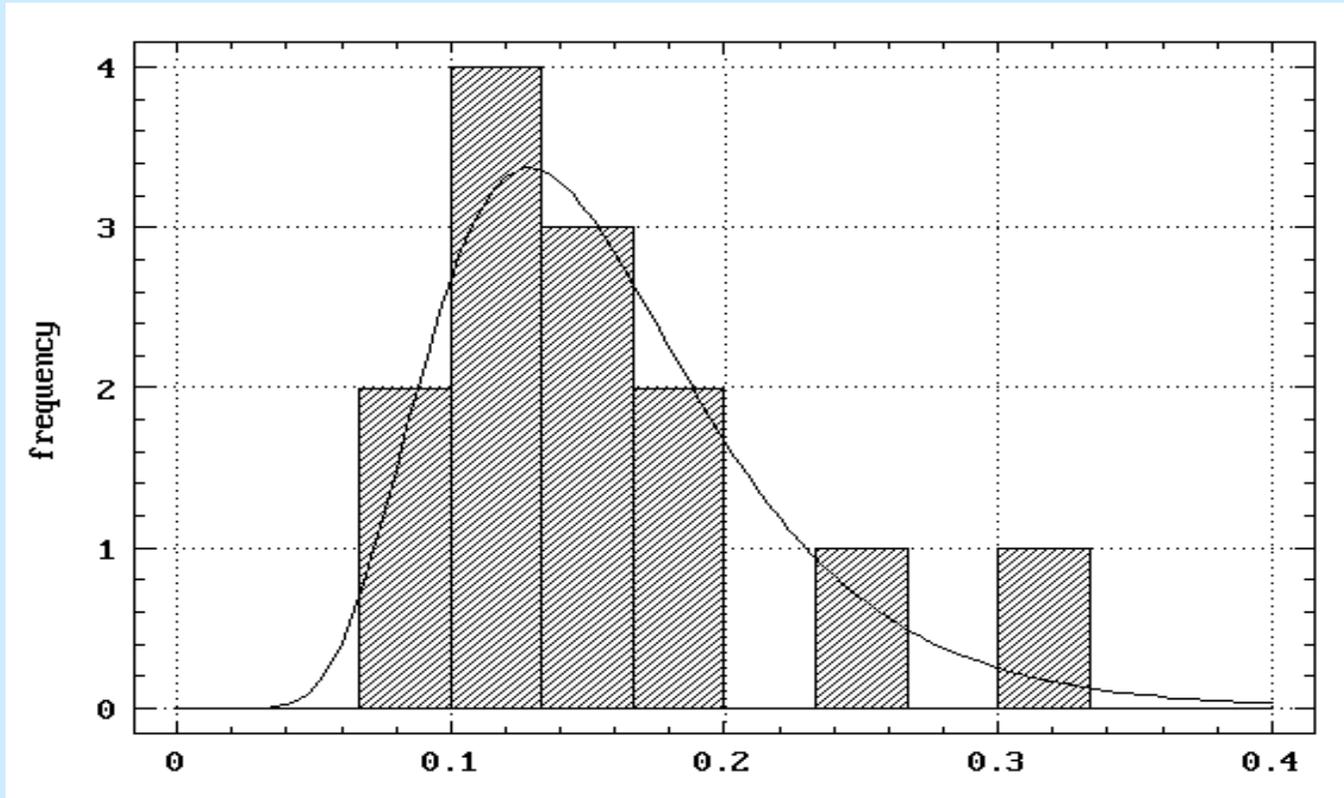# Sulfur Blank Distribution (W.R. Kelly, 1994)[6]
(n = 179; mean [rsd] = 0.27 µg [0.74])

<BUT: It depends on the weather!>
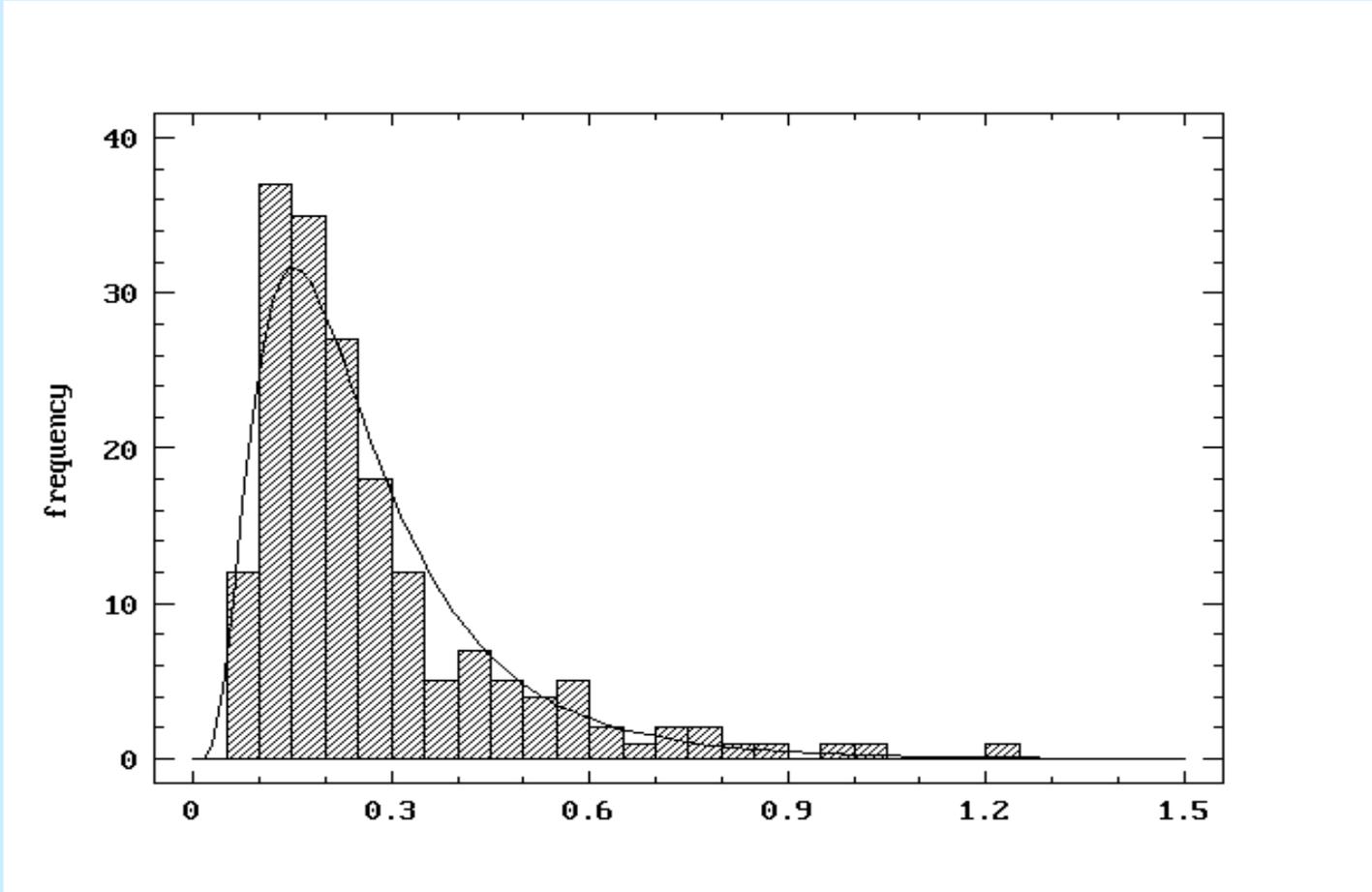
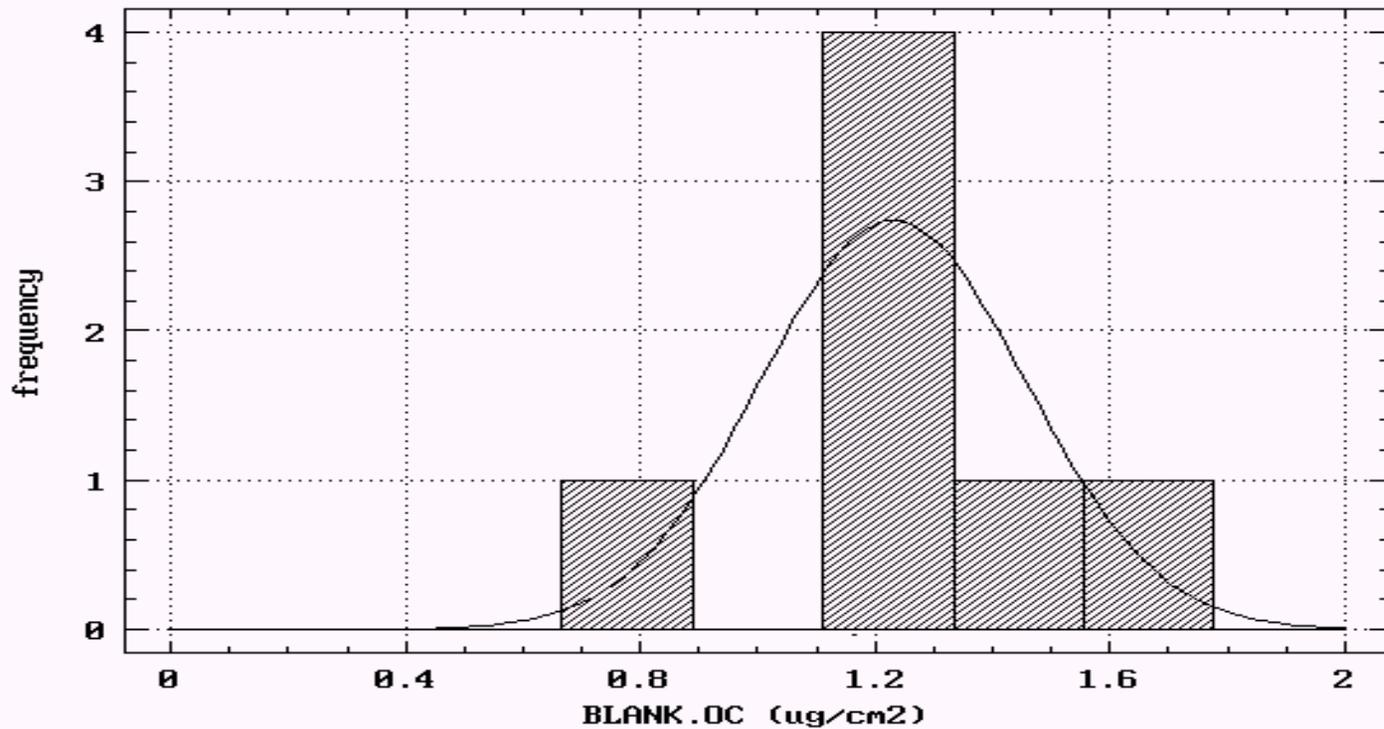# Modern Carbon (^{14}C) Blank Distribution (Currie, 2000)[5]
(n = 13; mean [rsd] = 0.16 [0.06] μg C)

Issues:

- EC must be isolated for AMS measurement

- Combustion tube (AMS) blank controlled via 'thermal discriminator'

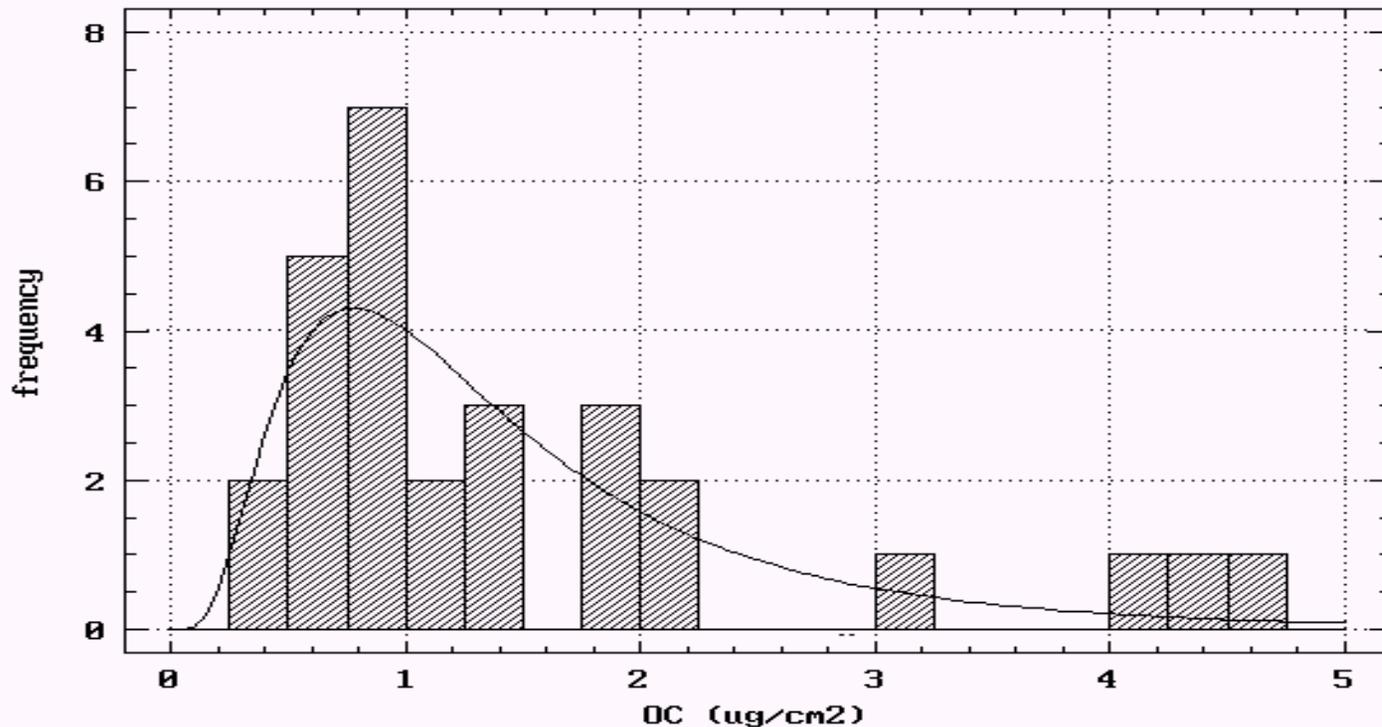- Approximate normality via (B_i - B_j) [paired observations]

OC Lab Filter Blank (mean, s=1.23, 0.23 μg/cm²) n=7

$$L_C \text{ (paired)} = t_{6,0.05}\, s_B \sqrt{2} = 0.62 \ \mu g/cm^2$$

[N]

OC Field Filter Blank (mean, s=1.53, 1.18 µg/cm^2) n=28
<ASSUMPTION INVALIDITY: Not Normal!>

L_C (N,0.05) ≈ 1.93 µg/cm^2 L_C (N,0.01) ≈ 2.73 µg/cm^2 [not paired]

L_C (LogN)/ L_C (N) = 1.09 L_C (LogN)/ L_C (N) = 1.56

EC Field Filter Blank (mean, s=0.007, 0.051 μg/cm²) n=28

<ASSUMPTION INVALIDITY: Not Normal!>
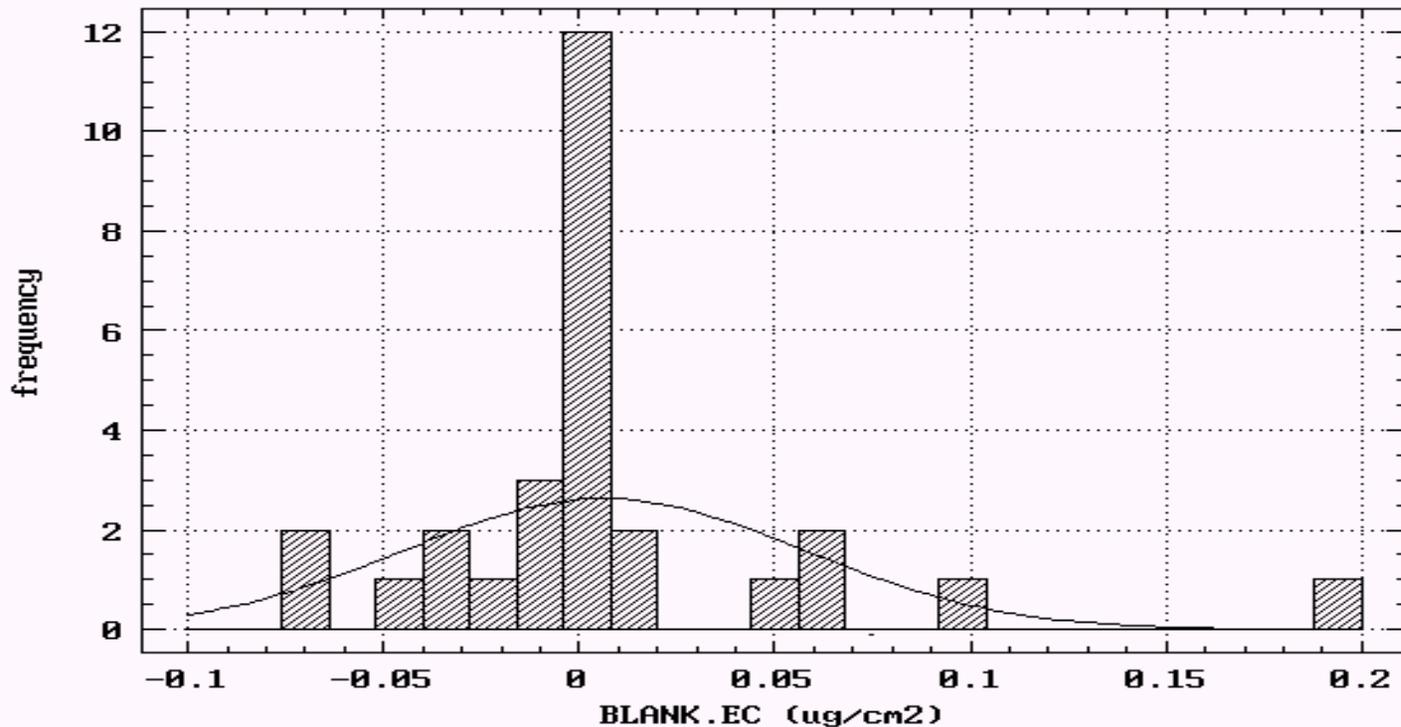
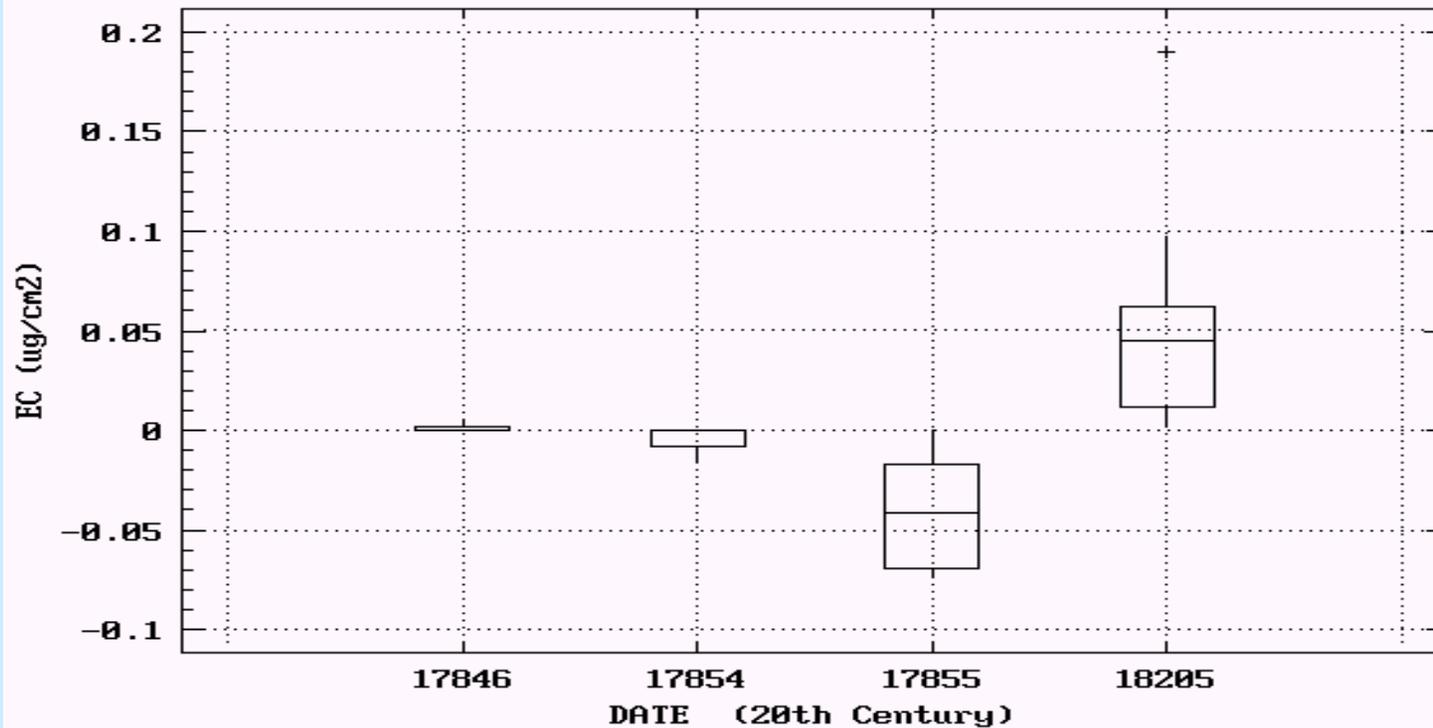$$L_C \text{ (paired)} = t_{27,0.05} \, s_B \sqrt{2} = 0.12 \ \mu g/cm^2$$

EC Field Filter Blank -- time series

<ASSUMPTION INVALIDITY: Not Stationary!>

Some Bottom Lines

- *Real* blanks, and df are expensive
  - paired measurements vital when small df

- Empirical B-distributions having abnormal variance (meson BG) or abnormal shape (skew, kurtotic) may signal non-random (exogenous) artifacts

- Bi(+) variate isotopic blanks:
  - may carry blank-source information
  - yield non-linear correction surfaces

- Valid detection rests totally on Distrib(B_i - B_j)

Virtual Reality

(reporting of low-level data)
L.A. Currie, October 2002

◆ EPA/NBS intercomparisons - 1970's (info-loss and bias)

◆ Virtual presence (storage of low-level radioactive waste)

◆ Virtual absence (emissions from ordnance use & disposal)

Table 25.1 Reporting Practices (Intercomparison Results)

Hg (μg/g) in SRM 1577 (bovine liver)

0.055 ± 0.014	0.016 ± 0.002
0.070 ± 0.015	0.012 ± 0.005
$\leqslant 0.2$	0.021
0.043 ± 0.024	0.09
	0.006 ± 0.0006

SRM 1633 (coal fly ash)

As (μg/g, lab 11):	$<100, <100, <100, <100, <100$
S (%, lab 9):	$<5.5, <6.7, <6.0, <5.0, <6.0$

*L. Currie, Ch. 25 in T. Dzubay, Ed., *X-ray fluorescence analysis of environmental samples* (1977)

Virtual Radioactivity (case study - 1)

"Nuclear waste storage sites filling up with virtual radioactivity"

Issue-1:

Inadequate measurement capability (LSC, ^{14}C)

Issue-2:

Inadequate low-level data reporting (info. loss and bias)

(e.g., 500±800 kBq $\rightarrow$ <1300 kBq $\rightarrow$ 1300 kBq)

Workshop on Standards … for Low-level and Environmental Radionuclide
Mass Spectrometry and Atom Counting (NIST, April 1999).

Virtual Absence (case study - 2)

COUNTER - EXAMPLE:

Emissions Database filled with zeroes!

- Small scale field studies of emissions from ordnance disposal
  resulted in over 100,000 data, of which 80% were "ND, NS, or NA."

- NDs were set to zero, "to facilitate validation and statistical analysis …"

- "Validated database" to be used with sophisticated model
  to forecast emissions from large-scale open burning and detonation

DOD Workshop on Research Needs for Air Quality Compliance (June 1999)

Lloyd Currie