THE IMPORTANCE OF APPLYING "CLEAN" AND VALIDATED QUANTIFICATION TECHNIQUES FOR STUDYING ENVIRONMENTAL LEVELS OF MATERIALS USED BY CONSUMERS

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Abstract

During the past two decades, a suite of organic compounds has been identified in the environment by various international research and monitoring programs. While these compounds, including industrial chemicals, softeners, flame-retardants, pharmaceuticals, fragrance materials and surfactants, are present in the environment, they are also present in the analytical laboratory where they are quantified because of their ubiquitous use by consumers. Implicit in this fact is the necessity to apply rigorous field sampling and analytical protocols to reduce and/or control, to the extent possible, sample contamination that would result ultimately in false positive confirmation of environmental concentrations. Several examples exist in the literature (e.g. trace metals, brominated flame retardants, fluorinated alkylated surfactants, phthalates, nitro musks and polycyclic musks) that highlight the importance of establishing these quality protocols for field work and laboratory treatment. Already in the 1980s and 1990s, it was recognized that errors caused by method contamination were present in the measurement of trace metals for regulatory purposes. Metals such as Cu, Ni and Zn have diffuse sources including natural emissions. Airborne concentrations, glassware, laboratory acids and regent water quality were found to impart contamination throughout the sampling, sample preparation and analytical processes. Application of "clean" analytical protocols to the collection and analysis of metals samples reduced, in general, the reported exposure by 2 to 3 orders of magnitude. A scheme is presented to develop appropriate methodologies for other compounds based on these examples.

Introduction

As researchers and regulatory authorities strive to address the assessment of the >20,000 organic chemicals used in commerce, attention needs to be paid to the very fundamental, and practical, importance of analytical chemistry in data collection. There are historical antecedents to these problems that may offer some insight into program development for sampling in the field and data collection in the laboratory, for these materials. Presented here are some examples of these historic antecedents, examples of other materials and some of the sampling and analytical concerns associated with them because of their pervasiveness in commerce, and methodological considerations for program development.

Historical Examples of the Effect of Sample Contamination on Data Quality

- Metals in the NY/NJ Harbor Estuary
- Environmental Measurements of Nitromusk and Polycyclic Musk Compounds

Metals

- Common contaminants with a wide range of potential sources for contamination of samples
  - Acids used in sample preservation and preparation
  - Glassware: from sample bottles to labware
  - Sampling personnel: trace levels of metals present on hands, clothing, etc.

Development of "Clean Techniques"

- Protocols designed to reduce or eliminate sample contamination and analytical interferences
- Derived from methods employed by geochemists and chemical oceanographers who had been aware of the problems associated with the sampling and analysis of metals in saline waters
- Examples of technique modifications
  - Use of twice distilled acids in the cleaning of glassware, preservation of samples, and sample digestion
  - Use of Teflon® sample bottles as an alternative to glass or plastic bottles
  - Two person sampling team ("clean hands/dirty hands") to control field contamination

NY/NJ Harbor Estuary

- Historic analytical data lead to the assumption that metals contamination was widespread throughout the region
- Significant compliance issues
  - Potential for high capital improvements for wastewater treatment throughout the estuary (municipal and industrial)
- "Clean Techniques" were employed as part of the approach to better assess the impact of dischargers on metal contamination within the estuary

Total Recoverable Metals in the NY/NJ Harbor Estuary
Historic Values vs. "Clean Techniques"
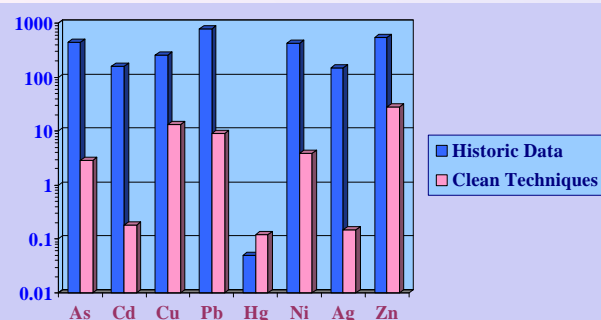
all values in ug/L
Data: Maximum reported values from Squibb, 1991 and Battelle, 1991

Results

- USEPA publishes 1600 Series methods for the sampling and analysis of trace metals using "clean" sampling and analytical methods
- Reassessment of aquatic impacts of estuary dischargers to metals contamination

Nitromusks and Polycyclic Musks

Material (CAS #)	Molecular Weight	log K_{ow}	C_w^{sat} (mg/L)	P_L^o (Pa)	K_H (Pa m³/mol)	Structure
Musk Xylene (81-15-2)	297.27	4.9	0.49	3×10^{-5}	1.82×10^{-2}	
Musk Ketone (81-14-1)	294.3	4.3	1.9	4×10^{-5}	6.2×10^{-3}	
AHTN (21145-77-7)	258.4	5.7	1.25	0.0608	12.6	
HHCB (1222-05-5)	258.4	5.9	1.75	0.0727	10.7	

Sample Contamination

Helbing et al. (1994) noted the commonplace occurrence of musk xylene and offered methods for the potential reduction of this contamination from biological samples. They identified contamination in the solvents used for sample clean-up, in materials used by the analyst, and on the hands of the analyst himself. They found up to 4.3 pg/mL musk xylene in acetone after 3 days of storage and nearly 9 ng rinsed off the hands of the analyst.

- To reduce contamination they recommended:
  - Solvents should be stored in small quantities to minimize exposure time in the laboratory
  - Paper tissues and latex gloves should not be used
  - The analyst should carefully avoid sample contact

Kallenborn et al. (1999) sought to identify the presence of musk xylene, HHCB, AHTN, moskene and 5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane (AITI, a polycyclic musk CAS# 68140-48-7) in ambient air at two Norwegian locations, Kjeller and Lista. In this paper they also cautioned against possible contamination of samples due to the ubiquitous nature of the nitromusks and polycyclic musks as evidenced by their indoor air samples. They noted the contamination found in laboratory samples during their attempts at developing a method to determine the concentration of nitromusks and polycyclic musk materials in the atmosphere simultaneously.

For example, in indoor air, using low resolution EI/MS, they found HHCB at 2470 pg/m3. They further recommend:

- Isolated storage of samples and solvents
  - Separate facilities and equipment for clean-up and sample prep
  - Special restrictions on the use of solvents

The Effects of Possible Contamination on Data Collection

Osemwengie et al. (2001) identified and quantified low volume of use and high volume of use polycyclic musks in Lake Mead, Nevada. The reported values for some of the materials are counterintuitive. The environmental behavior of the polycyclic musks AHTN and AITI are similar enough that it is unexpected to see AITI reported at equal to or greater than concentrations of AHTN. Concentrations were reported (85 L samples) for two samples collected downstream from one WWTP at day 0 and day 14. Insufficient information is presented to determine whether or not sample or laboratory contamination may have played a role in this set of data.

Material	AHTN	AITI
U.S. Volume of Use	~50 tons	< 0.5 tons
Reported Concentrations Day 0 (ng/L)	67.3	83.8
Reported Concentrations Day 14 (ng/L)	92.2	126

Data Problems

- The environmental behavior of the 2 structurally similar polycyclic musks AHTN and AITI is similar (e.g., neither are readily biodegradable)
- Volumes of use differ by 2 orders of magnitude
- It is unexpected that AHTN and AITI, based on use patterns, would result in similar aquatic concentrations
- Do these data make sense when the volume of use and their environmental behavior are considered?

Other Consumer Materials
◈ Phthalates ◈ Flame Retardants ◈ Pharmaceuticals

◈ Phthalates
- Use: Plasticizer
- Necessity for care in sampling and analysis identified as early as the late 1970's by Giam and colleagues
- Risk from contamination throughout sampling and analytical protocols:
  - Sample containers
  - Instrument valves, seals, connectors
  - Laboratory air

In Giam et al. (1975) pervasive phthalate contamination was identified. Di-2-ethylhexyl phthalate (DEHP) contamination ranged from 0.05 ppb in the Florisil used for sample clean-up to >1000 ppb levels identified as residues from various extracts from tubing and stoppers (e.g., polyethylene, Tygon, neoprene). Levels of DEHP present in glasswool and aluminum foil were in the range of 300 -1000 ppb. In addition to the obvious need to avoid contact with plastic and rubber materials, laboratory air was also found to be contaminated with appreciable levels. The air at the exit vent for laboratory air conditioning had levels as high as 35 ng/m3. Air monitoring within the laboratory was used to identify optimum working locations. They found the air over the work area was less contaminated if equipment was covered when not in use.

They were able to reduce procedural background levels for biota samples to as low as 25 ng for dibutyl phthalate and 50 ng for DEHP.

- Some recommended remedies:
  - Decontamination of glass equipment at 280°C (16h)
  - High purity solvent rinsing of equipment prior to use
  - Monitoring of laboratory air to identify source areas for contamiantion
  - Extensive use of blanks in sample schemes and laboratory analysis

◈ Flame Retardants
- Sources: Used pervasively in many product types including the electronic components of analytical instruments!

◈ Pharmaceuticals
- Growing research area for environmental monitoring
- Significant issues of concern:
  - Validation of exhaustive preparative and analytical procedures
  - Development of quality control procedures
  - Materials often degraded during high temperature injections (GC/MS)

Program Development

Sampling Procedures
- Are there sufficient field and trip blanks to determine sample and transport contamination?
- Are the field crew trained in methods to carefully handle samples (e.g., clean hands/dirty hands techniques)?
- What are possible sources of the materials under study from commerce?
- What materials are used in field sampling – are they a source of contamination?
- What are the quality of materials used in equipment decontamination?

Laboratory Concerns
- Are appropriate blanks used to validate the method quantification?
- Has the method (sample prep and instrumental) been validated between multiple laboratories (i.e., are the results reproducible)?
- Are the physical-chemical properties of the materials under study known? How does this affect analysis and sample preparation?
- Are standards available?

Program Imperatives

With an increasing demand on analytical technologies to identify and quantify more compounds with increased sensitivity coupled with the fact that many of these materials are ubiquitous in the environment from their use in commercial products, great care is necessary to assure the precision, accuracy and validity of the data generated. Data are fundamental to the regulatory decision-making process and, as demonstrated by the NY/NJ Harbor example regarding metals, the potential for very costly remedies are possible when using flawed data.

Field sampling and the laboratory both offer opportunity for contamination of samples from materials used in consumer products.

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