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Chapter

Considerations for Stability of Environmental Samples in Storage for Long-Term Studies

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Abstract

It is often advantageous to store collected environmental samples for future retrospective analyses. However, information about sample stability is necessary to determine if there will be analyte loss or gain or degradation under the specified storage conditions and storage period. Failure to evaluate stability could result in inaccurate results and biased exposure assessments. As part of the National Children's Study pilot, we considered which types of environmental samples could be stored for extended periods of time. We conducted an extensive literature review and considered the conduct of long-term stability studies for environmental samples. We present our findings and experience below as guidance for consideration by the environmental research community.

Keywords: Sample stability, Sample storage, Environmental samples, Long-term studies

1. Introduction

For long-term environmental studies, such as for prospective epidemiology studies, it is often advantageous to store collected environmental samples for future retrospective analyses. Traditionally, stored environmental samples have included human tissue and fluids, animal and plant tissues, soils, sediments, and ice cores [1]. Such samples can be used to evaluate results of government policies, health of an animal population, or temporal trends in ecosystems or exposures [2]. In longitudinal studies, this also permits spreading costs of analyses over time – an important consideration as analysis for environmental contaminants can be expensive. Additionally, it provides more flexibility to analyze subsets of samples in nested case–control studies for specific health outcomes or for inclusion of new target analytes or analysis methods. For instance, concern about the presence of pesticides, pharmaceuticals and personal care products (PPCPs) has heightened over the past several years due to the presence of these chemicals in wastewater, groundwater, surface water and drinking water [3–10].

Information about sample stability in long-term studies is critical to determine, if there will be analyte loss or gain or degradation under specified storage conditions and storage period. Failure to evaluate stability could result in inaccurate results and biased exposure assessments due to partial or complete analyte decomposition, chemical transformation, or loss/gain.

The National Children's Study (NCS) was a longitudinal cohort study that aimed to follow 100,000 children from birth until 21 years of age to evaluate the health effects of environmental exposures, including chemical, physical, biological, and psychosocial factors. A variety of different types of samples were collected during the NCS pilot study including environmental samples and biospecimens. The environmental samples that could not be stored because of known instability (e.g., badge samples for air oxidants) were analyzed immediately after collection. Other samples and biospecimens were stored in the NCS repository. The plan was to store the other environmental samples (e.g., water, soil, and dust) and biospecimens (e.g., blood, urine) until children aged, analyzing only samples as requisitioned for children included in subsequent case–control studies.

As part of the NCS pilot, we considered which types of environmental samples could be stored for extended periods of time. Many factors can affect stability of chemical compounds in stored environmental samples over time, such as temperature, humidity, pH, and microbial enzymatic activity of the sample matrix, physicochemical properties of the analytes themselves and their reactions with the matrix, container materials, and other analytes present in the sample [11].

2. Literature survey

The literature was surveyed through 2020 in PubMed, Web of Science and other commercial sources to identify published sample preparation and storage information of contaminants in any environmental matrix. Stability of analytes in analytical standards and in stored biospecimens were not included in this review.

Table 1 summarizes the 63 peer-reviewed articles and 8 reports and book chapters selected after initial screening that discussed stability of anthropogenic chemical compounds in environmental matrices. The most common analytes studied were pesticides and trace elements. Various environmental matrices were considered, including air, water, soil/sediment, dust, and food (plant and animal tissue).

Two major scopes for stability studies were identified: (1) long-term stability in storage (retained samples, environmental specimen banking), and (2) short-term stability of samples in transport conditions. There was no generally accepted procedure for performing a stability study. Stability samples were sometimes prepared and stored all at the same time with some samples removed for analysis at various time periods. Alternatively, samples were prepared and stored at different time points and analyzed all at the same time. The former procedure is subject to day-to-day and longer term variability and changes in analysis procedures; the latter is subject to variability and changes in the preparation and analysis procedures when the time points are far apart.

Another sample stability test procedure, generally used for reference standards and sample transport, is isochronous testing, where samples are prepared at the same time and stored in conditions that offer the best stability, or the least degradation, until they are moved to the storage conditions to be tested for the specified time periods [43]. At the end of the testing period, each sample set is moved back to the original storage until all samples are removed for analysis at the same time. This procedure avoids the challenges of varying sample preparation and analysis conditions.

The determination of stability of an analyte in a sample is measured as the ratio of the concentration measured at time point t, compared to that measured at time point 0. The sample size required to make a decision with specified confidence for each analyte depends on the precision of the analysis method at each concentration level and the amount of change at which samples are considered to have degraded.

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
Air	Endotoxin on PM filters and filter extracts	LAL	4 °C filters, −20°C extracts	3 y		Stored well both in extract and on filter	[12]
	Endotoxin on PM filters and in extracts	LAL	−20°C, 4°C	14 d filters, 24 h extracts	Filter, dessicant	Store both filters and extracts frozen	[13]
	Cat (Fel d 1), dog (Can f 1), mouse (Mus m 1), and mite (DM, Der p 1, TP) allergens	Antigen-specific immunoassay	RT EDC, −20°C and − 80°C extracts	1.5 y	Buffer	EDC 4.8% loss Can f 1 every 30 d, extracts −20°C 1.2% loss DM every 30 d, extract with Tween	[14]
	Ammonia	Indophenol spectrophotometry	RT	0, 1, 2, 4, 6 d	Concentration	Loss 10–17% at 1 d, 40–64% at 6 d, depending on concentration	[15]
	15 volatile organic chemicals (VOC) in SUMMA canister and sorbent tubes	GC-FID, GC-ECD	Not specified	7 d, 30 d		Suitable for compounds tested	[16, 17]
	2,3,3,3-tetrafluoropropene on sorbent	GC-FID	RT, frozen, refrigerated	3, 7, 14, 30 d	sorbent	30 d is acceptable, analysis within 14 d due to migration	[18]
	Formaldehyde, acetaldehyde on sorbent	HPLC	4 °C	4, 12 d		Stable on sorbent for at least 12 d	[19]
	Ortho-phthalaldehyde (OPA) on sorbent	HPLC-MS	Extract refrigerated	5 d		Extract stable for at least 5 d	[20]
	1,2-Dibromo-3-chloropropane (DBCP), 1,3-diClpropene (DCP) on charcoal	GC-ECD	RT, 5.6,-14°C	2, 3, 11 d		Unstable 2 d at RT Stable 1 wk. at −14°C	[21]
	Volatile aliphatic and aromatic solvents on sorbents	GC (detector not specified)	RT, −22°C	7, 14, 28 d	Sorbent	Stable at RT for Chromosorb (except cyclohexanone), better at −22°C for all sorbents	[22]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	Ketones on carbon sorbents	GC (detector not specified)	RT, 4°C	1, 7, 30 d	Sorbent, water vapor	Stable 7 days on Anasorb, 30 d on Carboxen 564, except cyclohexanone	[23]
	4-vinyl-1-cyclohexene on charcoal	GC-FID	RT (27–29 °C), 4–6 °C	21 d		Stable 7 days at RT, 21 days refrigerated	[24]
	94 VOC (including terpenes, aromatic, halogenated, and aliphatic compounds) on Tenax GR sorbent	TD/GC–MS-SIM	4°C	1 mo		Stable 1 mo: 87 compounds	[25]
	Hazardous air pollutants (HAPs) in canisters – review of literature	Varied: GC-FID, GC-ECD	RT	Varied: generally 7–14 d, up to 35 d		Stable: 52 HAPs Likely stable: 9 HAPs Likely unstable: 17 HAPs Unknown: 19 HAPs	[26]
(applicable to other matrices)	56 SVOCs (amines, halo ethers, nitrobenzenes, phenols, phthalate esters, polycyclic aromatic hydrocarbons and chlorinated compounds)	GC–MS	Extract purified for analysis: −20°C, 4°C, 22°C	53 days	Vial color (light), fluctuating temperature	SVOCs stable in amber vials, PAHs mostly stable (mon-substituted phenols more affected by temperature), Half-life in clear vials 28–31 d, Constant temperature more important than absolute temperature	[27]
	Polycyclic aromatic hydrocarbons (PAH) on sorbents (XAD2, PYF) and quartz fiber filter	Ref provided	Room temperature, −20°C	10, 20, 30 d	Sorbent, filter	Stable: All at −20°C Stable PUF, RT: PAH Unstable PUF, RT: naphthalene, anthracene, benzo-a-pyrene Stable quartz filter, RT: All but cyclopenta[c,d] pyrene Stable XAD2, RT: All but 2,3-nitrofluoranthrene	[28]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	Benzo[a]pyrene on quartz filter	HPLC	−20°C, 20°C	0.5,1,2,4,12 yr	In air, argon	−20°C: Stable for 6 mo, 12% loss at 12 yr. 20°C: Unstable, 50% loss at 12 yr. No effect air vs. argon	[29]
	25 PAHs on PM filters and in extracts	GC–MS-SIM	4°C	7, 30 d filters, 1,5,6 mo extracts		Filters can be stored for 1 mo, extracts for 1 mo, hopanes and steranes for 5 mo	[30]
	Organic solvents on charcoal (ketones, esters, alcohols, aromatic hydrocarbons)	GC-FID/MS	20 °C	1, 2, 4 wk	Carbon sorbent, water, hydroquinone rinse	Unstable: Esters, alcohols, cyclic & aliphatic ketones loss dramatic, more pronounced on one carbon Stable: Toluene, butanol, DMF, styrene, 111-TCA, ethyl acetate Water adsorption affected recovery differently on two carbons Hydroquinone rinse partly effective in improving recovery	[31]
	Cyclic volatile methylsiloxanes (cVMS)	GC–MS	−20°C	14 d	Sorbent type	Stable on ABN Express sorbent, 367–62% loss on ENV+ sorbent	[32]
	30 pharmaceuticals, pesticides on organic-diffusive gradients in thin-films (o-DGT) passive sampler and the polar organic chemical integrative sampler (POCIS)	Not specified	Freezer	o-DGT 18 mo POCIS 6 yr	Sampler type	Average loss 9–14%	[33]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	14 Personal care products	GC–MS	4°C	3, 7, 14 d	On sorbent cartridges	Stable 7 d at 4°C	[34]
Water	As(III), As(V)	ICP-MS	6°C	3, 18 mo	pH	Storage in dark, pH < 2, 3 mo	[35]
	As(III), As(V)	ICP-MS	−18°C, 6°C, 20°C	9 d	pH	Storage in dark, 7 d at 6°C	[36]
	As, Se, Sb, Te	HPLC/ICP-MS	−20°C, 3°C, 20°C	30 d	speciation	Stable at 3°C in dark	[37]
	Inorganic Hg, labeled with ^{197}Hg	HPGe	5 °C, 20°C	1, 3, 6, 7, 10 d	Partitioning into particulate, containers	Stable at least for 10 d when acidified and stored in Teflon or glass	[38]
	Perchlorate	IC, LC–MS/MS	4°C, 22°C	638 d		300 d ground water, 90 d surface water	[39]
	44 VOC in wastewater samples	GC–MS	4°C	2–5 wk	Glass vials	Stability varies by VOC: Methylene chloride 2 wks, Chloroform 4 wks.	[40]
	18 bisphenols in wastewater	Not specified	−20°C, 4°C	4 wk		Stable for 4 weeks at either temperature	[41]
	29 PFAS	LC–MS/MS	−20°C, 4°C, 20°C	180 d	Sample type (bottled, surface, effluent)	10 analytes increased or decreased over time, analyte conversion observed in surface and effluent waters	[42]
	Polar pharmaceuticals, pesticides, PFOS, PFOA, caffeine, PBA	LC–MS/MS	4°C, 20°C, 40°C	6 wk		Storage for 6 wk. at 4°C	[43]
	24 pharmaceuticals, pesticides	LC–MS/MS	−20°C	20 mo	In POCIS, in SPE	Small statistically significant losses, add labeled IS	[44]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	Pharmaceuticals and pesticides	LC–MS/MS-SRM	4°C	21 d		Steroidal hormones 3 d, others 21 d ok	[45]
	21 organochlorine pesticides on solid-phase extraction (SPE) disks	GC-ECD	−18°C, 4°C	3, 14. 30 d	Sodium azide addition	Stable for at least 30 days at both temperatures, slight improvement for some analytes with sodium azide addition	[46]
	12 pesticides	GC-ECD, HPLC-UV	−20°C, 4°C	3, 30, 90, 180 d	In SPE	Losses in storage for 90 and 180 d storage	[47]
	9 pesticides	GC-NPD	−18°C	119, 319 d	In SPE	119 d recovery 53–155%	[48]
	8 phenylurea pesticides	HPLC	6 °C	21 d	preservatives	21 day storage is ok	[49]
	10 pesticides	GC-MSD	6°C, RT	21 d	In SPE, pH, additives	14 d storage with additives	[50]
	9 organophosphate pesticides	GC-NPD	−20 °C, 4°C, 20°C	60 d	In SPE, drying	60 d at −20°C in dark	[51]
	10 pesticides, 3 atrazine metabolites	LC-APCI-MS, LC-DAD	−20°C, 4°C, RT	1 wk., 3 mo	In SPE	Recovery>90% after storage for 3 mo at −20°C	[52]
	Isoproturon, bentazone, terbuthylazine, alachlor	HPLC-UV	4 °C	14 d, 30 d		Variability due to complexity of matrix	[53]
	OP, OC pesticides, pyrethroids, carbamates	GC-ECD	−17°C, 3°C	2,5,8,14,21,28, 39 d	In SPE, pH	In SPE 6 wk. frozen, otherwise 5 d	[54]
	18 herbicides	LC-APCI-MS	−20°C, 4°C, 20°C	30 d, 60 d	In SPE	Best 60 d at −20°C in dark	[55]
	Phenoxyacid herbicides	LC-DAD-MS	20°C		Water type, bottle type	Half-life river water ~20 d in light, 34–50 d in dark storage; seawater has shorter half-life	[56]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	65 Pharmaceuticals and drugs	LC–MS/MS	−20°C	2, 4, 6 wk	In SPE, pH, sample prep	All analytes stored well	[57]
	Pharmaceuticals, PCPs, steroids, hormones	LC/MS/MS	−20°C, 4°C	7, 14, 28 d	Various co-contaminants	Stable 30 d < 6°C, with appropriate preservatives	[7]
	Drugs of abuse	GC–MS/MS	−20°C	1,3,5,7 d, 2,3,12 wk	Preservation, SPE	Stable in SPE at −20°C for at least 3 mo	[58]
	Cocaine	Capillary electrophoresis	8 °C, 25°C, 37°C	1 wk		Store at 8 °C	[59]
	3-mercaptopropionic acid, derivatized	HPLC	4°C	1, 2, 8, 52 wk	buffer	Derivatized samples can be stored at least for 1 y.	[60]
	RDX explosive transformation products	HPLC	4 °C, 23°C, 40°C	45 d	pH, salinity	Stable at 4 °C with 10% sea salts	[61]
Dust/ wipes	Cat (Fel d 1) and mite (Der p 1) allergens	ELISA	−80°C	6, 12, 18, 30 mo		Stable in dust stored in vials for 30 mo	[62]
	Cat (Fel d 1) and mite (Der p 1, Der f 1) allergens, β(1 → 3)-glucan, endotoxin	ELISA, LAL	−20°C	10 mo		Stable in dust stored on vacuum filters stored in plastic bags	[63]
	181 VOCs on activated charcoal cloth (ACC)	GC	−80°C	4 wk	Concentration	Majority stable, exception is n-pentane ~40% loss	[64]
Soil/ sediment	Organophosphate pesticides, organochlorine pesticides, pyrethroids, carbamates	GC-ECD	−17°C, 3°C	2,5,8,14,21,28, 39 d		1 mo frozen	[54]
	4 OP pesticides (diazinon, chlorpyrifos, malathion, fenamiphos) in spiked soil samples	GC	2 °C, Room temp	8 mo		Fenamiphos: Stable Diazinon, CPF, Malathion: Unstable, more so at RT. Store refrigerated or in deep freeze.	[65]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	Pesticides	GC–MS	–20°C, 4°C	7, 14, 28, 42, 84, 168 d		Storage for 299 d at –20°C	[66]
	As, Se, Sb, Te	HPLC/ICP-MS	–20°C, 3°C	30 d	speciation	Soil extracts storable 3 d at 3 °C	[37]
	As(III), As(V), monomethylarsonic acid, dimethylarsinic acid in reducing and oxidizing soil	HPLC/ICP-MS of extract	–20°C	1, 2, 3 mo	Extraction solvent	Extracts: MMA, DMA stable, AsIII oxidized to AsV	[67]
	As species in mineral and organic soils	HPLC/ICP-MS	–20°C, 2°C	1 mo	Drying	Storage and drying changes speciation Unstable, freeze-dried samples more stable than wet samples	[68]
	As, Cd, Cr, Cu, Ni, Pb, Zr	FAAS, ZETAAS (Zeeman single-beam AAS), ICP-AES	20 °C, 40°C	24 mo		Storage above 20 °C should be avoided	[69]
	As, Cu, Pb, Zn	ICP-MS	4 °C, RT	90, 183, 284, 392 d	Air drying	Storage at –20°C: 364 709 d	[16]
	Cr(VI)	AAS	–20°C, 4°C	14, 28, 56, 112, 224 d		Storage for 224 d at –20°C	[16]
	Cd, Cr, Cu, Ni, Pb, Zn in irrigation field soil	ICP-AES, ETAAS	–20°C, 4°C, 20°C, 40°C	3, 6, 12, 18 mo	Sterilization	Unstable above 20°C Sterilized samples more stable than non-sterilized	[70]
	C, P, S, Al, Ba, Ca, Mg, Mn, Sr., Zn in forest soil	ICP	–21°C, 3°C, 22°C	1842 d (5 yr)		Increase in all at 22°C due to decreased pH >50 d, store at –20°C or lower	[70]
	Hg	Cold vapor AAS	RT	10, 11, 12, 17 yr	Soil carbon content	Stable	[71]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	Methylmercury	Atomic fluorescence detection	30 °C	1 hr., 1 d, 4 d, 7 d	Drying method, soil type	Freeze sample immediately after collection and freeze-dry to prevent bacterial mercury methylation	[72]
	3 PCB, 7 congeners	GC-ECD	–20°C, 4°C	7, 14, 28, 42, 84, 168 d		Storage for 168 d at –20°C	[73]
	17 PAH	GC–MS	–20°C, 4°C	7, 14, 28, 42, 84, 168 d		Storage for 100 d at –20°C	[73]
	3-mercaptopropionic acid, derivatized	HPLC	4°C	1, 2, 8, 52 wk	Buffer	Derivatized samples can be stored at least for 1 y.	[58]
	13 PAH in contaminated soils	HPLC-FlD	–20°C, 4°C	6 wk. frozen, 8–10 mo	In dark, additives	Some stable for 8 mo, some only 2 wk. at 4°C (e.g., 3-ring PAH > degradation than 5-ring PAH) Sodium azide-contamination stabilized PAH degradation	[74]
	16 PAH	GC–MS	RT < 30°C	4, 8, 12, 16 mo		Stable in air-dried, ground sediment in shade for 16 mo	[75]
	2 PAH (phenanthrene, pyrene)	GC	Freeze–thaw cycle (–15°C 8 h, 25°C 8 h)	Extraction efficiency at 1, 4, 8, 13, 16, 30 and 120 d	Soil organic content	Competitive effect on extraction efficiency with soil organic content and freeze–thaw cycle	[76]
Plant	As species in needles and mosses	HPLC/ICP-MS	–20°C, 2°C	1 mo	Drying	Storage and drying changes speciation - Unstable, freeze-dried samples more stable than wet samples	[65]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	As(III), As(V), monomethylarsonic acid, dimethylarsinic acid in rice	HPLC/ICP-MS	−4°C	1, 2, 3 mo	Extraction solvent	Extracts stable at least for 3 mo.	[67]
	As species in algae	HPLC/ICP-MS	−80°C, −18°C, 4°C, RT	1 yr	Preprocessing	Lyophilization and cryogenic grinding and storage in RT, other temp ok	[77]
	Arsenic species in marine microalgae	LC-ICP-MS	−80°C, −18°C, 4°C, RT	1, 45 d	Processing	Store dried at RT, non-dried at 4°C, freezing results in loss of As	[78]
	19 pesticides in various vegetables, fruits, grains, seeds	HPLC, GC-NPD, GC-ECD	−20°C	1 yr	Hydrolysis, glass bottles	Storage stability referred from hydrolytic behavior: Half-life >10 d at 70°C - stable at least 1 y at −20°C. Half-life <1 d: Unstable	[79]
Animal tissue	As, Se, Sb, Te	HPLC/ICP-MS	−20°C, 3°C	30 d	Speciation	Should be analyzed immediately to avoid transformations	[37]
	Hg-total, Hg-org	CV-AAS	−150°C, −80°C, −30°C, 4°C, 25°C	1 yr		Biobanking: stable after first year	[80]
	As(III), As(V), monomethylarsonic acid, dimethylarsinic acid in fish and chicken	HPLC/ICP-MS	−20°C	3 mo	Speciation	Extracts: Stable for 2 mo, then AsB transformed to DMA	[68]

Matrix	Analytes	Analysis method(s)	Storage conditions			Results	References
			Temperature	Time	Other		
	N-methylcarbamates in beef, duck, chicken liver	HPLC	−4 °C	0.5, 1, 1.5, 2, 3, 4, 5, 6 mo		Store at cryogenic conditions for preparation and storage due to enzymatic activity. Some analytes stable for 6 mo, some not at all	[81]

AAS – Atomic absorption spectrometry, AES – Atomic emission spectrometry, APCI – Atmospheric pressure chemical ionization, DAD – Diode array detector, ECD – Electron capture detection, EDC - Electrostatic dust collector, ELISA - Enzyme-linked immunosorbent assay, FID – Flame ionization detection, GC – Gas chromatography, HPLC – High pressure liquid chromatography, ICP – Inductively coupled plasma, LAL – Limulus amoebocyte lysate, LC – Liquid chromatography, MS – Mass spectrometry, NPD - Nitrogen phosphorous detection, SIM - Selective ion monitoring, SRM – Selected reaction monitorin.

Table 1.
Summary of environmental sample stability studies identified in the literature by matrix and analytes.

The change in concentration over time that indicates significant degradation is often set to 5 or 10 percent, particularly for biological samples. This level is likely too stringent for environmental samples where, for instance, sample processing may itself introduce a reduction of 5 to 10 percent and, therefore, a decision criterion of 20 percent change is most often used.

Despite the widespread practice and numerous and strong benefits of long-term environmental sample storage, we found very little documentation to support preservation of analytes during long-term storage. The findings of the literature review were disappointing in that many questions went mostly unanswered for many sample matrices and analytes of interest, in particular:

- ***What are acceptable long term storage times for various sample types?*** Storage times in the identified studies varied from a few days up to five years. One study extended the storage study to 12 years for air samples [82]. For water, only a few published reports were found on storage stability over 6months, mostly on pesticide stability. These studies do not fully address the compounds or tap water matrix [4, 7, 28, 73, 83–86].

- ***What are acceptable long term storage conditions for various samples types?*** Storage conditions in the identified studies included ambient or room temperature (generally around 20°C), refrigerator (4°C), freezer (−20°C), and/or cryogenic temperatures (−60–80°C). Environmental specimen banks store samples for 50–100 years in cryogenic conditions [79, 80, 87], but do not document the rationale for sample stability under these conditions and time periods. For longer-term storage, some researchers have extracted water contaminants through solid phase extraction (SPE) cartridges and stored frozen for up to a year. Interestingly, colder storage does not always equate to less analyte degradation, as commonly assumed [74].

We also reviewed standard analysis methods for the samples and analytes of interest in the NCS. We found that standard methods are generally focused on regulatory compliance and do not consider long term storage. For example, for ambient vapor and gas sampling, updated storage studies of SUMMA and whole air canisters are needed (US EPA method allows storage of only 30days).

3. NCS stability study experience

The overall objective of the planned NCS storage studies was to determine the stability of target analytes in NCS environmental samples stored in collection containers at specific storage conditions, including reconstitution after thawing and re-freezing of samples, as applicable. For instance, the objective of the tap water study was to evaluate the effect of prolonged storage at −20°C on the stability of the pesticide and pharmaceutical target analytes spiked in analyte-free water. The results of this study were to be used to extrapolate the observed changes in the target analyte concentrations to the stability of those compounds in the NCS study samples.

3.1 Planning

The stability study plans included stability samples similar to environmental field samples, sample processing, analytes or classes of analytes of interest, and analysis methods. The in-depth literature review addressed the prevalence of

potential analytes and classes of analytes of interest in an indoor environment, concentrations measured, sampling and analytical methods, reaction or degradation products in these matrices, and storage conditions and stabilities. In addition, experts, agencies and groups with relevant experience, e.g., National Institute of Standards and Technology (NIST), the U.S. Environmental Protection Agency (EPA), the Children's Center Study, National Human Exposure Assessment Survey (NHEXAS), Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP), and New York State Department of Health/Love Canal project researchers, were contacted for information. This information was used to develop the plans for the preparation and analysis of the stability samples and archiving of both the field and stability samples.

Storage effects due to freeze–thaw cycles, sample pretreatment, and reconstitution were also considered. For example, freeze–thaw cycles can affect the volatile and semi-volatile compound concentrations on a filter or in bulk dust. The pretreatment of samples before storage is performed when metabolism or reaction after collection is known to be of concern. For example, water samples for metals analysis are usually acidified to pH < 2 [86], and dust samples are sometimes irradiated to stop microbial growth and metabolism.

3.2 Acquisition of samples

Stability study samples with known concentrations of analytes were planned to be acquired in similar matrices to the NCS samples, i.e., particulate filters, wipes, and vacuum filters. These samples were to include (1) newly-prepared samples that have been spiked with known concentrations of analytes, and (2) pre-tested 'real-world' samples.

Surface dust wipe and air diffusive samples could be made by spiking study sampling media and tap water samples by spiking analyte-free water with known amounts of the target analytes. These kind of samples can be purchased from reference material producers, proficiency testing sample providers, and/or accredited laboratories. To allow for a possible difference in reaction/degradation rate of analytes with their concentration in matrix, each matrix was to be spiked at environmentally relevant concentration levels, based on the literature review, and at concentrations that can be most reliably quantified by the analytical method employed, preferably at concentrations near the midpoint of the instrumental calibration range. Another benefit of this approach was that the concentration of the stability samples could be set to match the concentration used in the laboratory QC samples for increased comparability [7].

Some samples cannot be spiked onto matrices in a manner representative of the corresponding environmental samples, or it would be very difficult to do so. There may be a difference in behavior of analytes in environmental samples and in similar spiked matrices due to pH, microbial enzymatic activity of the sample matrix, physicochemical properties of the analytes themselves and their reactions with the matrix, and other analytes present in the environment. For example, for vacuum filter and deposition plate stability samples, dust from non-participant homes could be obtained, homogenized, and aliquoted before storage.

Each spiked and real-world sample should represent the environmental sample matrix as close as possible to account for inter-analyte and analyte-matrix interactions. If it is not possible to include all analytes of interest in one matrix sample, they can be classified into groups by their chemical characteristics, and include representative analytes of each group deemed most unstable. Because sample homogeneity is very important, for example, surface wipe and dust samples should be aliquoted before spiking and the whole sample used for analysis.

All samples were planned to be collected on exactly the same collection media using the same samplers and stored in the same containers as used in the field study and one manufacturer's lot of each media and containers used, whenever possible. Blank media was to be stored together with the samples for each sample type and analysis time point and unused sample media provided to the analysis laboratories, as required. There should be additional samples stored as back-up for sample loss due to, for instance, filter or container breakage, and for repeat analyses. Additional samples should also be stored to account for the possibility that laboratories or analysis methods may change during the study and simultaneous measurements are necessitated. For each sample type, to the extent possible, samples should be analyzed by one laboratory in order to minimize inter-laboratory bias. For NCS, standard laboratory methods were specified for each analysis, identical to those planned for the field sample analysis.

3.3 Number of samples and analysis time points

Samples are usually analyzed before storage (time point 0) to determine analysis method recovery, concentrations at the beginning of the study (time 0), and to verify the homogeneity of the aliquots. This will take into account any analyte losses during pre-analysis, such as extraction and processing. The frequency of future time points and the number of samples required for statistical significance at each point should be planned carefully before start of the study.

The frequency of time points is chosen to detect the instability of samples and analytes, such as VOC, as early as possible. It is assumed that in most cases, particularly for the organic analytes, the rate of degradation would be highest at the beginning, that is, first order kinetics; this corresponds to a linear change in the log transformed measurement over time [65, 82, 88]. In the NCS stability plans, at each test time t, it is tested statistically with a t-test if a specified percentile of the concentration measurements (the target percentile) will be greater than the specified limit of 80 percent at some future time, assuming stability decreases exponentially (or the log transformed stability decreases linearly) with time. For calculating sample size, it was assumed that the log transformed ratios have a normal distribution and the mean log transformed recovery decreases linearly over time.

As the study proceeds there will be accumulating data from prior test times that can also be used to get a more precise estimate of the slope or fit a nonlinear trend. Calculating samples size when using all prior data is more complicated than calculating sample size for a t-test. The calculations depend on the analysis that might be performed. The number of samples depends on: the alpha and target power for a slope of zero; the standard deviation of the measurement error; the standard deviation of the slope factor; the target percentile (80%); and, the timing of the time points. The test-wise alpha and power for no degradation were set to achieve an overall mean alpha of 5% and an overall power of 95%.

The standard deviation of the measurement error can be estimated from the variation among replicate samples or aliquots, typically measured as a relative standard deviation or, equivalently, a coefficient of variation (CV). The sample sizes were calculated using the error term calculated from the estimated coefficient of variation of the measurement methods. This model was assumed to be adequate for calculating sample sizes and for a variety of sample collection designs, analyses, and distributional or statistical model assumptions. The planned frequency of time points for the NCS was 0, 1, 2, 3, 5, 8, 13, 21, 32, 48, 72, 108, 160, and 240months, altogether 14 time points (or test times). The numbers of planned stability samples varied by sample type and were mostly around 300. The variation was due to the variation of the CV of different analysis methods.

4. Conclusions

Collection and analysis of environmental samples for various analytes in large-scale or longitudinal cohort studies is useful to investigate the contribution of the environment on health outcomes. Storing samples for long periods of time is necessary but expensive in these kinds of studies. Information about preserving sample quality and analyte stability in stored environmental samples is limited. Design and implementation of sample stability studies like those described here are recommended to ensure that samples are stored properly and generate reliable analytical results when required. Publication of environmental sample stability study results will likely provide valuable information to investigators who design and implement large-scale longitudinal environmental health studies.

5. Considerations for the environmental research community

Storage of environmental samples is an important component of large-scale and prospective studies. The environmental research community must address and document the answers to the questions above by conducting and providing data on stability of samples stored over long periods.

- If more stability data are available than presented here, these data should be provided in technical guidelines, study manuals, or published papers.
- Conduct and report on environmental sample storage stability studies, especially for new analytes of interest.
- In the interim, based on our research, a sample stability program should be integrated with sample collection as a part of the quality assurance procedures for the study.

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