ADEQ Arizona Department of Environmental Quality

TECHNICAL SUPPORT DOCUMENT

Opportunity Statement: Evaluate Contaminant Fate and Transport in Biosolids

Background: Biosolids are a byproduct of domestic wastewater treatment. Following physical separation from the liquid phase solids undergo physical and chemical treatment resulting in a semisolid, nutrient-rich product with applications for beneficial use. The Arizona Department of Environmental Quality (ADEQ) regulates the generation, disposal, and application of domestic biosolids through the Arizona Pollutant Discharge Elimination System (AZPDES) permitting program. Biosolids are derived from wastewater treatment plants that treat domestic wastewater, industrial wastewater treatment plants may not produce biosolids.

Biosolids must meet federal and state requirements specified in the Arizona Administrative application to agricultural land, parks, and reclamation sites (e.g. mining sites). When applied to land at the appropriate agronomic rate, biosolids provide a number of benefits including nutrient addition, improved soil structure, and water reuse. Land application of biosolids also can have economic and waste management benefits (e.g., conservation of landfill space; decreased demand on non-renewable nutrient sources like phosphorus; and a decreased demand for synthetic fertilizers). Biosolids may be disposed of by landfilling or other forms of surface disposal. Currently, in Arizona we have a biosolids General Permit (2022) that conforms to EPA standards for biosolids generation and disposal. For example, Arizona requires producers of biosolids to test for 8 metals, 24 volatile and semi-volatiles, and 9 herbicides or pesticides pollutants at a frequency dependent on dry metric tons produced. This list of regulated pollutants is based on a risk assessment conducted by EPA in 1995 on 200 potential pollutants (EPA, 1995).

Recent research findings suggest that further risk assessment of pollutants in biosolids is needed to protect human health and the environment (De Bhowmick & Sarmah 2022, Pritchard et al. 2010, Wolters et al. 2022). Emerging contaminants, microplastics, pharmaceuticals, and PFAS are just some of the pollutants of growing concern. An ADEQ preliminary screening of PFAS compounds in 2022 revealed the presence of PFAS in Arizona biosolids (Figure 1). A Pima County study of PFAS fate and transport in biosolids found no transport past 6 feet in a hydrogeologic environment where on average the water table is 120 feet below ground surface (Pima County Wastewater Reclamation, 2020). It is unknown whether these findings would be the same in other regions of Arizona. PFAS are persistent in the environment and have been shown to bioaccumulate. At present, compliance testing for PFAS is not required for biosolids in Arizona.

Opportunity Statement: ADEQ would like to better understand how numerous potential contaminants may be impacting the safe use and disposal of biosolids. Are there alternative best practices for monitoring and regulating biosolids in Arizona? Biosolids generated by domestic wastewater treatment plants are disposed of in landfills, stored on-site, or applied to agriculture or public spaces. For all of these biosolids, whether they are in the landfill or on agricultural or public lands, we need a better understanding of what pollutants of concern they contain and assess the chronic and acute impact they may have. Additionally, other states ship biosolids to Arizona for land application without providing monitoring information. States that send biosolids to Arizona for application or disposal do so because of limited capacity and possibly because they have more stringent biosolids standards than those in Arizona.

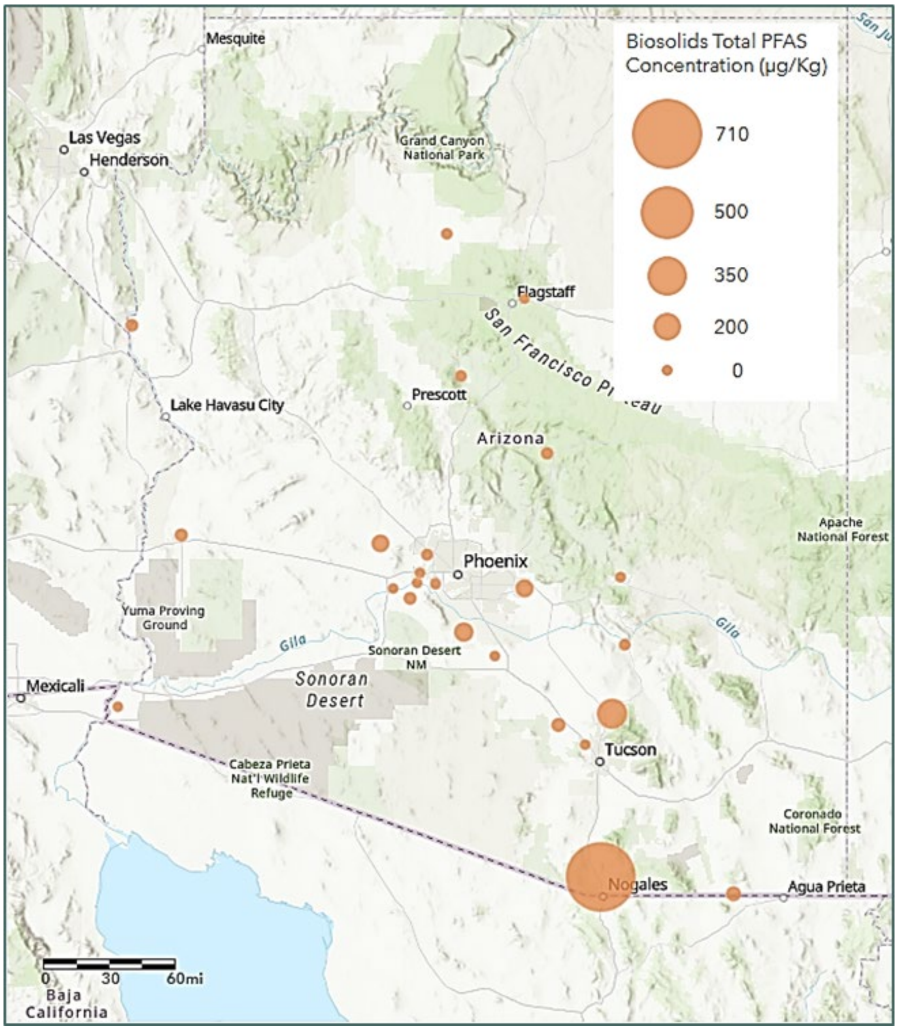

Figure 1. Preliminary assessment of PFAS concentrations in biosolids across Arizona.

Arizona needs a risk assessment of the many emerging contaminants, pharmaceuticals, and perfluoroalkyl substances (PFAS) with known health risks but are currently unregulated. These and other pollutants move readily through soil and have been found in groundwater wells, some used for drinking water. However, there is no clear picture of how these chemicals, contained in biosolids, are cycled through the environment. Biosolids are applied to the land

and taken up by plants and animals that are then consumed by humans. Additionally, biosolids are applied to areas exposed to rain which is known to collect pollutants and mobilize them in stormwater which flows, untreated, into our rivers and streams which are precious resources in which Arizonans and tourists swim and fish. We do not know where these chemicals end up in out ecosystems, which ones we should be concerned about and which ones we need to regulate.

A few of the questions that we need to answer to be protective while enjoying the benefits of biosolids in Arizona:

- Are current rules and regs protective? (our current rules and regs only allow us to protect against regulated pollutants and we are not monitoring outside of those)
- What chemicals are typically found in biosolids and is there a connection to groundwater? (we only know the roughly 40 pollutants that generators are required to test for but no others aside from what has been sampled for during specific and largely unrepresentative studies)
- How much PFAS is accumulating biosolids and is it leaching from biosolids to groundwater?
- How does the transport of pollutants through the ecosystem vary across the state with differing climates, soils, etc.
- What emerging contaminants are already in biosolids that ADEQ should be concerned about?

Mission Impact: Ensuring the safe use and disposal of biosolids protects human health and the environment by ensuring the biosolids are not impairing our aquifers, contaminating our crops, or endangering our citizens on public lands. ADEQ needs to stay current in assessing emerging risks and concerns to continue to protect the environment and the people of Arizona.

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ADEQ Opportunity Statement: Evaluate Contaminant Fate and Transport in Biosolids

Team: Arizona State University (ASU): Kerry Hamilton (PI), Erin Driver, Rolf Halden, Otak Conroy-Ben with collaboration from Clinton Williams (USDA); **University of Arizona (UA):** Amanda Wilson, Chuck Gerba; **Northern Arizona University** (**NAU):** Catherine Propper, Matthew Salanga

Background. Biosolids are a nutrient-rich byproduct of domestic wastewater treatment with the potential for beneficial reuse. However, contaminants present in biosolids and their impact on human and environmental health drive concerns for their generation, disposal, and land application. Biosolids are regulated by the Arizona Department of Environmental Quality (ADEQ) and must meet specific requirements depending on their intended end use. While several biosolids risk assessments have been performed at the national level and in Arizona (Gerba et al., 2002; Brooks et al., 2005; Brooks et al., 2012), additional concerns remain regarding emerging contaminants such as per-and polyfluoroalkyl substances (PFAS) (Pepper et al., 2021; Stoker et al., 2023; Villeneuve et al., 2023; Venkatesan and Halden, 2014). Additionally, other contaminants known to be present in biosolids such as endocrine disruptors, antibiotics, pathogens (e.g., enteric viruses), and antibiotic resistance determinants (antibiotic resistance genes, antibiotic resistant bacteria) have not been evaluated in a holistic context for their combined contributions to potential risks and are under consideration for regulation at the national level. Existing risk assessments and tools (e.g., Water Research Foundation Biosolids Site Specific Risk Assessment Tools for Land Applied Biosolids [SMART] tool, USEPA Part 503) have not updated their risk evaluations for a full suite of modern contaminants (including potentially additive and synergistic effects) and are only site-specific for pathogens, constraining their utility for Arizona decision-making.

Proposal goal. This proposal aims to address the fate and transport, potential risks, and data-driven best practices for monitoring and regulating biosolids in Arizona (**Figure 1**). This work will leverage over 40 years of research experience on Arizona biosolids contributed by an integrated, tri-university research team (Arizona State University, University of Arizona, and Northern Arizona University) to: (1) survey past, current, and potential future uses of biosolids in Arizona; (2) quantify high-priority contaminants of concern (PFAS, endocrine disruptors, organic toxicants, adenovirus, enteroviruses, and antibiotic resistance genes) in Arizona biosolids; (3) evaluate the toxicity of both individual compounds and real-world complex mixtures present in biosolids; (4) holistically assess microbial and chemical risks; (5) and apply science-based approaches to inform management practices, anticipate forthcoming regulatory initiatives, and identify information gaps specific to Arizona.

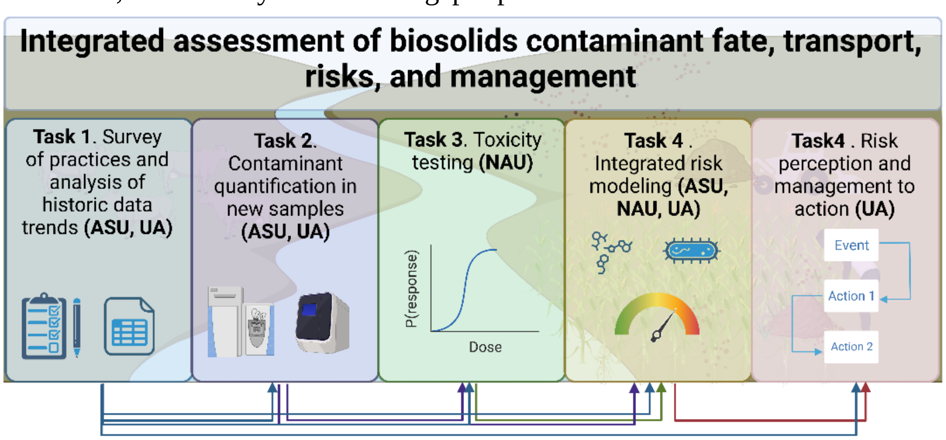

Figure 1. Proposed plan for integrated biosolids risk assessment and management in Arizona.

The team will engage multiple stakeholders, regions, and communities of Arizona, including tribal nations. The team has unique, deep interdisciplinary expertise in biosolids analysis and evidence of success from community-engaged research, improving management practices and public health policy as well as risk assessment.

Task 1. Survey past, current, and potential future uses of biosolids in Arizona and leverage historical databases. ***Aim 1.1. survey of biosolids practices:*** The Gerba lab team (UA) will lead a survey and assessment of biosolids uses in Arizona, including how they are treated, and historic as well as planned uses. The team will examine Class B permitting records and draw upon previously conducted surveys performed by the Gerba team on uses and locations of Class A biosolids. Questions to be addressed include: (i) biosolids disposal locations, (ii) management practices (e.g., treatment), and (iii) location of disposal and potential concerns (e.g., proximity to groundwater or communities) (**Table 1**).

Table 1. An abridged list of illustrative examples of treatment considerations in Arizona to be evaluated in this survey.

AZ-relevant examples of treatment interventions	Populations of interest for risk evaluation	Stakeholders	Exposure pathways / routes	Management considerations
Solar drying Drying beds Composting Biodegradation Emerging technologies (e.g., nanotechnology)	Agricultural workers Residential communities (adults, children)	ADEQ Biosolids industry Agriculture industry AZDHS General public Tribal communities Researchers	Contaminated groundwater, non-potable and potable waters Inhalation of water aerosols Irrigation contamination Ingestion of crops Inhalation of dust, soil Ingestion of deposited aerosols Surfaces/ dermal or ingestion Ecological receptor considerations	Regulatory (Class A, B, or other requirements) Administrative controls (setback distances, personal protective equipment for workers) Biosolids application timing restrictions, duration between application and harvest Treatment technology requirements

Aim 1.2. Statistical meta-analysis of rich historical datasets: The team will leverage ongoing systematic literature review databases curated by the Hamilton lab team on determinants of antibiotic resistance in biosolids, as well as a newly initiated review of PFAS occurrence and impact of management practices on PFAS in partnership with the US Department of Agriculture (USDA). The Gerba team also has maintained large databases of the long-term (>40 year) occurrence of contaminants in biosolids.

The Halden lab has compiled the U.S. National Sewage Sludge Repository (NSSR) (Venkatesan and Halden, 2014; Steele et al. 2022; Venkatesan and Halden, 2020) containing archived biosolids and contamination data, including on PFAS, from hundreds of samples collected in the U.S. and AZ starting in 2001. In the 2010s, the NSSR was absorbed into the Human Health Observatory at ASU, which harbors additional samples and contaminant profiles of a spectrum of sludge types from across the U.S. The Halden lab team will perform *in silico* analyses of data from samples previously analyzed and archived in the NSSR to determine the profile of contaminants that have been applied as biosolids, and specifically on Arizona lands (Walters et al., 2010; Venkatesan and Halden, 2014). **Work products (Table 2):**

WP1: inventory of AZ biosolids practices, land application maps, applied tonnages, etc.
WP2: inventory and statistical analysis of chem-bio threats in AZ vs. US biosolids.

Task 2. Quantify high-priority contaminants of concern (PFAS, endocrine disruptors, organics, odor-causing compounds, adenovirus, enteroviruses, and antibiotic resistance genes) in Arizona biosolids. ***Aim 2.1. Selection of archived samples and collection of new samples:*** Both the Gerba and Halden teams have extensive libraries of archived samples to inform the current work and will also collect new samples. Data on archived samples (see Task 1) will be supplemented by a strategic collection of soil and groundwater samples (UA team) reflective of biosolids generated in different cities in Arizona and those imported and land applied in Arizona. Newly collected samples will also reflect the impact of different treatment processes on contaminant reduction (e.g., Class A vs. Class B), impact on groundwater, and aerosol generation during application. For a relative risk assessment, control samples from agriculture and non-agricultural land on which biosolids have never been applied will also be tested.

Aim 2.2. Analysis of samples for multiple contaminants of concern: Multiple team members (UA-Gerba, ASU- Conroy-Ben, Hamilton, Halden, Driver) will quantify contaminants of concern in samples originating from both biosolids-associated and non-associated agricultural/soil sites to evaluate differences between "background" and biosolids-associated pollutant loads. A coordinated sampling plan will be developed among the various teams. The sampling plan will be designed to answer questions on the presence of contaminants in contemporary biosolids originating in or destined for Arizona, and on any adverse impacts on groundwater, soil or air quality from land application. Samples to be analyzed will be representative of AZ biosolids treatment approaches, methods of disposal, climate differences representative of the state (rainfall, temperature), agricultural practices, location of disposal (agricultural vs. mine reclamation sites), depth to groundwater, length of time biosolids have been applied to a given site, and other factors upon review of disposal practices in Arizona. At a minimum, the team will analyze 100 biosolids samples and 40 groundwater samples each year for the first two years of the project.

The Gerba lab will lead culture-based and quantitative polymerase chain reaction (digital or qPCR) analysis of enteroviruses and adenoviruses to inform risk assessment. Adenoviruses are not regulated, but recent risk assessments indicate they occur in greater numbers in treated biosolids and pose aerosol risks (Carducci et al., 2016). The Hamilton team will quantify antibiotic resistance genes (ARG) using digital PCR and Hamilton/Halden will supervise a postdoctoral scientist who will perform PFAS analysis on a Waters Xevo triple quadrupole mass spectrometer (TQMS) in laboratories of the Department of Agriculture, Maricopa County, AZ (see collaborator: Clinton Williams, USDA, ALARC).

The Conroy-Ben team will prepare samples for bioassays and perform extractions in conjunction with the Halden group for downstream ecotoxicology and chemical analyses. Sample extracts for bioassays will be processed through microwave-assisted extraction (MAE) with ethanol, a method developed by Co-PI Conroy-Ben to test for estrogenicity and androgenicity of land-applied biosolids. Solutes will be filtered with a pre-ashed glass fiber filter and tested on multiple bioassays, with concurrent analysis with LC-MS/MS analysis in the Halden group. Extracts of biosolids contaminant mixtures will be provided to NAU for testing on *in vivo* and *in vitro* endocrine disrupting and cancer-linked activity.

Dr. Conroy-Ben (Oglala-Lakota) will also engage with Tribal communities in Arizona, building upon long-standing relationships. Tribal wastewater facilities' sludge processing from conventional wastewater treatment often is limited to lagoons and drying beds only. To obtain data and samples from Tribal facilities, we will document AZ Tribal facilities, their secondary treatment, biosolids processing, and terminal use, building upon a Tribal wastewater database developed by ASU and the InterTribal Council of Arizona's Tribal Water Systems Department. Tribal consultation will be led by ASU (Jacob Moore, Vice-President for Tribal Relations) and co-PI Dr. Conroy-Ben, who have initiated agreements and projects with the Hopi Tribe and Navajo Nation.

WP3: database of contemporary contaminant concentrations in biosolids and groundwater.

Task 3. Evaluate the toxicity of both targeted compounds and non-targeted complex mixtures present in biosolids. The NAU team (Catherine Propper, Matthew Salanga) will lead the evaluation of ecotoxicity of key PFAS, other identified chemical targets, and chemical mixtures present in biosolids by performing three aims in experiments and appropriate controls.

Aim 3.1. Systematic literature review of dose-response data: A review will be performed for the contaminants of concern found in biosolids (PFAS, endocrine disruptors, organics). ***Aim 3.2. Developmental Disruption:*** The team will conduct *in vivo* fish and/or amphibian assays commonly used as models for toxicity and endocrine disruption associated with long-term health outcomes during early development (Searcy et al., 2012; Park et al, 2021; Smith et al., 2022). ***Aim 3.3. In vitro assays:*** Estrogen-, androgen-, and thyroid hormone-sensitive cancer cell lines will be used to determine changes in metabolism, DNA damage, and endocrine-signaling disruption that can lead to risks associated with cancer development and progression. The scoping review and lab testing will inform a narrowing down of the pathways of concern to be considered in chemical risk assessment. The team will generate new dose-response curves for PFAS of concern noted in the literature and found through the ASU/USDA and UA lab work. The results will provide a standardized approach for low-dose extrapolation for risk assessment by the ASU team with development of reference doses (RfD) and potency factors. The team will also test complex mixtures that are representative of biosolids using whole organic extractions to further provide information about exposure to contaminant mixtures present in biosolids. The non-targeted approach will fill data gaps in the scientific literature regarding simultaneous exposures to multiple toxicants and thus inform risk assessment aims. Based on specific PFAS identified as key to human and environmental health concerns in AZ, specific compounds will be identified for focus with a fractionated sample analysis approach (see Aim 2). Results from the combined research of the three teams will be used to identify ecological models in AZ for future testing of exposure outcomes and risk assessment to human populations in a real-world setting.

WP4: Inventory of existing toxicology studies for PFAS.

WP5: Expanded database with new dose-response relationships.

Task 4. Holistically assess microbial and chemical risks for contaminants in biosolids. ***Aim 4.1. Prioritize biosolids contaminants***: Hazards will be ranked based on occurrence and dose-response or toxicity reference values for humans and ecological receptors (e.g., cancer potency factors and reference doses from USEPA IRIS and USEPA Ecotox; pathogen dose-response relationships found in the quantitative microbial risk assessment wiki) (Hamilton team). For targeted contaminants mentioned above (PFAS, enterovirus, adenovirus, ARB and ARG), dose-response data from proposed experiments (NAU Team) and available literature will inform chemical and microbial risk assessments.

Aim 4.2. Fate and transport modeling: The Halden and Conroy-Ben teams will apply peer-reviewed models to evaluate leaching, migration propensity, potential impact on groundwater, and persistence to inform the risk models and enable spatial mapping of occurrence and risk. Maximum application rates based on acceptable risk targets will be computed to inform policies. ***Aim 4.3. Health risk assessment:*** Hamilton (ASU) and Wilson (UA) will lead human health chemical and microbial risk assessments for occupational and residential populations using estimates of ingested or inhaled aerosols during biosolid applications. Task-specific behaviors will be modeled using methods previously utilized by Wilson (UA) (Wilson et al. 2021). Aerosol size distributions will be used to determine the efficiency at which different size aerosols will be inhaled vs. ingested, using methods previously used and developed by Hamilton (ASU) (Hamilton et al. 2017, 2019). Residential risks will include consumption of groundwater influenced by land application of biosolids and inhalation of aerosols and setback distances for communities nearby biosolid applications.

A literature review will be conducted to gather current data regarding aerosol transport from biosolid applications, concentrations of aerosols or airborne contaminants at setback distances, groundwater contamination concentrations from biosolid application, and aerosol size distributions generated from land applications. Aerosol scenarios will be explored using literature data to scope future data collection efforts as part of a "what-if" sensitivity analysis. Using the proposed models, the interventions specified in **Table 1,** augmented with stakeholder input, will be tested to rank the relative benefits of different approaches (e.g., to what extent does changing the biosolids application timing or method of incorporation reduce risks compared to implementing a new treatment technology?). Maps of hazards and risks will be developed in Geographic Information Systems (GIS) (Gerba team).

WP6: Ranked priority list of biosolids-borne hazards.

WP7: Spatial maps of hazards and risks from past and current practices.

Task 5. Use science-based approaches to inform management practices, anticipate forthcoming regulatory approaches, and identify gaps specific to Arizona. ***Aim 5.1. Risk perception survey:*** A survey will elucidate public and occupational acceptance of biosolid applications. The Knowledge-Attitudes-Behaviors (KABs) framework (Xu et al., 2010) will be used by Wilson (UA) to design survey questions. This framework is used to explain how knowledge and attitudes drive behaviors. KABs outputs can then inform the design and evaluation of subsequent outreach efforts (Paul et al., 2020, Teo et al., 2023, Xu et al., 2010). The first portion of the survey will include measuring current knowledge regarding biosolid applications, how biosolids are regulated, and potential hazards associated with direct or indirect exposure to biosolids. Measured attitude questions will relate to feelings regarding biosolid technologies, perceived risks (in comparison to risk assessment outputs) applications, and exposures. Behavior questions will inquire about measures workers or the public use to reduce potential exposures, if near sites where biosolids are applied. Recruitment of participants for this will occur through online communications with communities through partnership with water utilities that serve those areas.

WP8: Annotated inventory of biosolids risk perception findings & policy recommendations.

Education, dissemination, and communication of findings. Our team will participate in education efforts by training graduate students, postdoctoral students, and undergraduate students in lab methods for quantifying emerging contaminants. The team will attend the Arizona Water Biosolids Conference and will engage with stakeholders through survey efforts. Regular quarterly meetings will be held with ADEQ to inform the trajectory of the work, including a kickoff meeting to obtain additional feedback on the project plan, integrate ADEQ perspectives, and connect with relevant stakeholders. A workshop will be held to facilitate interaction between ADEQ and the regulatory community, AZDHS, and biosolids stakeholders and to identify potential outreach opportunities, led by the Gerba team. The broader team will leverage existing partnerships with Pima County (Gerba), tribal communities (Conroy-Ben), the City of Flagstaff (Propper) and Payson plant (Propper) to examine the implications of management practices and obtain input on key aspects of the research plan throughout the project.

Impacts for Arizona. The 8 impactful new work products generated here will benefit AZ regulators, policymakers, and the public at large. Work products will prepare the state to better anticipate and manage constituents of still emerging regulatory import. By incorporating new tox data on hazards and mixtures in AZ biosolids into integrated risk models, findings will inform cost-effective ways to protect public health. Transparency in decision-making will promote responsible material reuse and land management. Engaging with AZ stakeholders will encourage communication and coordinated interventions to reduce biosolids risks, while fully leveraging nutrient sources in the state.

Timeline

Table 2. Research and dissemination timeline with dates of work product (WP) deliverables.

Task	Location	Research Activity	Year 1				Year 2				Year 3			
			Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	UA	Survey of past and present disposal practices		**WP 1**										
		Occurrence and removal of emerging viral pathogens										**WP2**		
2	UA, ASU	Chemical, biological and statistical analysis of contaminant profiles in AZ biosolids/wastewater												**WP3**
3	NAU	Systematic Review for endocrine disruption			**WP 4**									
		In vitro and in vivo assays for known PFAS in Arizona Biosolids												
		In vitro and in vivo assays for complex mixes identified in Aim 2												**WP5**
4	UA, ASU	Literature review for model parameters												
		Occup. risk assessment model development & finalization									**WP6**			
		Residential pop. risk assessment model development & finalization												**WP7**
5	UA	Letters of support from utilities												
		IRB approval; Survey finalization												
		Participant recruitment												
		Survey analysis											**WP 8**	

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