PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN CENTRAL ASIA: ENVIRONMENTAL OCCURRENCE, INDUSTRIAL POINT SOURCES, BIOLOGICAL EFFECTS AND ADVANCED ANALYTICAL WORKFLOWS

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Abstract. Per- and polyfluoroalkyl substances (PFAS) are persistent synthetic organofluorine compounds linked to liver toxicity, immunotoxicity, endocrine disruption, developmental impairment and some cancers, yet Central Asia remains almost unstudied. This short review brings together the evidence on probable PFAS sources in Uzbekistan, Kazakhstan and Tajikistan, namely textile wet processing, fluorinated surfactants in enhanced oil recovery and aluminum smelting, and on two regional factors that may spread them, microplastics and saline dust from the dried Aral Sea bed. We follow the exposure chain into biology: uptake in wheat and cotton, oxidative stress, disturbed soil microbial communities and the toxicological endpoints known from other regions. We also outline solid-phase extraction on weak anion exchange sorbents, matrix suppression in saline samples, and the added value of high-resolution mass spectrometry and cyclic ion mobility. Much of the evidence is indirect, and we mark where regional data are needed.

Keywords: PFAS; Central Asia; Aral Sea; microplastics; fluorotelomer biotransformation; bioaccumulation; ecotoxicity; non-targeted screening; cyclic ion mobility mass spectrometry

Annotatsiya. Per- va poliftoralkil moddalar (PFAS) barqaror sintetik ftororganik birikmalar bo‘lib, jigar toksikligi, immunotoksiklik, endokrin tizim buzilishi, rivojlanishning susayishi va ba’zi saraton turlari bilan bog‘liq, biroq Markaziy

Osiyo deyarli o‘rganilmagan. Ushbu qisqa sharhda O‘zbekiston, Qozog‘iston va Tojikistonda PFAS ning ehtimoliy manbalari, ya’ni to‘qimachilikda nam ishlov berish, neftni oshirilgan usulda qazib olishda ishlatiladigan ftorli sirt faol moddalar va alyuminiy eritish, shuningdek ularning tarqalishiga yordam berishi mumkin bo‘lgan ikki mintaqaviy omil, ya’ni mikroplastiklar va qurigan Orol dengizi tubidan ko‘tariladigan sho‘r chang haqidagi ma’lumotlar jamlangan. Biz ta’sir zanjirini biologiyagacha kuzatamiz: bug‘doy va paxtada to‘planish, oksidlovchi stress, tuproq mikrob jamoalarining buzilishi hamda boshqa hududlarda ma’lum bo‘lgan toksikologik oqibatlar. Shuningdek, kuchsiz anion almashinuvchi sorbentlarda qattiq fazali ekstraksiya, sho‘r namunalarda matritsa ta’sirida signalning susayishi hamda yuqori aniqlikdagi mass-spektrometriya va siklik ion harakatchanligining afzalliklari bayon etilgan. Ma’lumotlarning aksariyati bilvosita bo‘lib, mintaqaviy ma’lumotlar zarur bo‘lgan o‘rinlar ko‘rsatib o‘tilgan.

Kalit so‘zlar: PFAS; Markaziy Osiyo; Orol dengizi; mikroplastiklar; ftortelomerlar biotransformatsiyasi; bioakkumulyatsiya; ekotoksiklik; maqsadsiz skrining; siklik ion harakatchanligi mass-spektrometriyasi

Аннотация. Пер- и полифторалкильные вещества (PFAS) представляют собой устойчивые синтетические фторорганические соединения, связанные с токсическим действием на печень, иммунотоксичностью, нарушением работы эндокринной системы, нарушениями развития и некоторыми видами рака, однако Центральная Азия остаётся почти не изученной. В данном кратком обзоре обобщены данные о вероятных источниках PFAS в Узбекистане, Казахстане и Таджикистане, а именно мокрой обработке текстиля, фторированных поверхностно-активных веществах при повышении нефтеотдачи и выплавке алюминия, а также о двух региональных факторах, которые могут способствовать их распространению, микропластике и засолённой пыли с осушенного дна Аральского моря. Мы прослеживаем цепь воздействия вплоть до биологических эффектов: накопление в пшенице и хлопчатнике, окислительный стресс, нарушение почвенных микробных сообществ и токсикологические эффекты, известные из других регионов. Также описаны твердофазная экстракция на слабых анионообменных сорбентах, матричное подавление сигнала в засолённых образцах и преимущества масс-спектрометрии высокого разрешения и циклической ионной подвижности. Значительная часть данных носит косвенный характер, и мы указываем, где необходимы региональные данные.

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Ключевые слова: PFAS; Центральная Азия; Аральское море; микропластик; биотрансформация фторteломеров; биоаккумуляция; экотоксичность; нецелевой скрининг; масс-спектрометрия с циклической ионной подвижностью

INTRODUCTION.

Per- and polyfluoroalkyl substances (PFAS) are a family of more than 14,000 synthetic organofluorine compounds whose carbon backbone is fully or partly fluorinated [1]. The carbon-fluorine bond, one of the strongest single bonds in organic chemistry, makes them thermally stable and chemically resistant, and their amphiphilic character lets them repel both water and oil [1]. These properties have kept PFAS in wide use for about eight decades, for example in water-repellent textile finishes, aqueous film-forming foams (AFFF) and petrochemical extraction [2]. They resist degradation, have spread across the globe on air and ocean currents [3], and accumulate in food webs. Long-term exposure has been associated with hepatotoxicity, immunotoxicity, endocrine disruption, developmental impairment and a higher risk of renal and testicular carcinomas [4].

Long-chain compounds such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) and perfluorohexane sulfonic acid (PFHxS) have been restricted, most prominently through listing under the Stockholm Convention on Persistent Organic Pollutants (POPs), and manufacturers have moved toward fluorinated alternatives [5]. Central Asia, here Uzbekistan, Kazakhstan and Tajikistan, is one of the largest gaps in global PFAS research, although North America and the European Union have carried out extensive biomonitoring [4]. The region has industrialized quickly since the Soviet period, its agriculture depends on transboundary rivers, and it must deal with the desiccation of the Aral Sea [6]. It also hosts industries that are recognized PFAS sources elsewhere: large textile and cotton processing complexes in Uzbekistan, enhanced oil recovery (EOR) in Kazakhstan, and non-ferrous metallurgy in Tajikistan.

This review examines the occurrence, probable industrial sources and ecological consequences of PFAS in the region, with particular attention to biological effects along the chain from sources to crops, soil organisms, livestock and people, and compares targeted and non-targeted analysis of saline samples (Figure 1).

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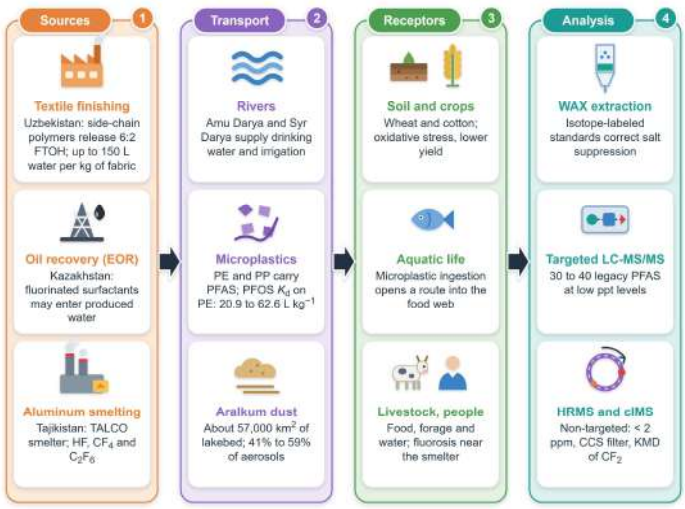


Figure 1. Conceptual overview of the pathway from regional PFAS sources through rivers, microplastics and Aralkum dust to receptors, and the analytical tools used to detect them. The diagram is conceptual and shows no measured regional data.

THE DATA GAP AND THE "DOUBLE BURDEN" OF CONTAMINATION.

Environmental monitoring of persistent organic pollutants in Central Asia has mostly addressed legacy contaminants, such as organochlorine pesticides and polychlorinated biphenyls. In Kazakhstan, for example, measurements in the water bodies of the Aral Sea and Syrdarya basin have so far covered these compounds [7]. The regulation of PFAS differs widely between countries and is still developing [8]. Missing PFAS data should not be read as evidence that contamination is absent. It is a blind spot in surveillance, particularly because millions of people depend on the Amu Darya and Syr Darya basins for drinking water and irrigation [6]. We call the meeting of newly recognized pollutants such as PFAS with existing ecological crises a "double burden": two abundant solid phases, aquatic microplastics and wind-blown dust, are likely to control how PFAS move, persist and become available to organisms in the region.

Microplastics can act as vehicles for hydrophobic and amphiphilic contaminants, PFAS included, especially aged secondary particles formed from fragmenting debris [9]. Because of their high surface-area-to-volume ratio and persistence, they can concentrate dilute aqueous PFAS and may help PFAS enter the food web when benthic and pelagic organisms ingest them [9]. Sorption is spontaneous and driven by hydrophobic, electrostatic and van der Waals forces, and on polyethylene (PE) and polypropylene (PP), which dominate in Uzbek rivers [6], it points to partitioning into the polymer [9]. Reported solid-water distribution coefficients (K_d) for PFOS on PE range from 20.9 to 62.6 L kg^{-1} [10], and PFOS sorbs much more strongly than carboxylates such as PFOA [11]. The Aral Sea basin and irrigated areas are saline [11]. Hypersaline waters may therefore

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increase PFAS loading onto microplastics, although this is an inference from mechanistic studies and not a regional measurement (Figure 4A).

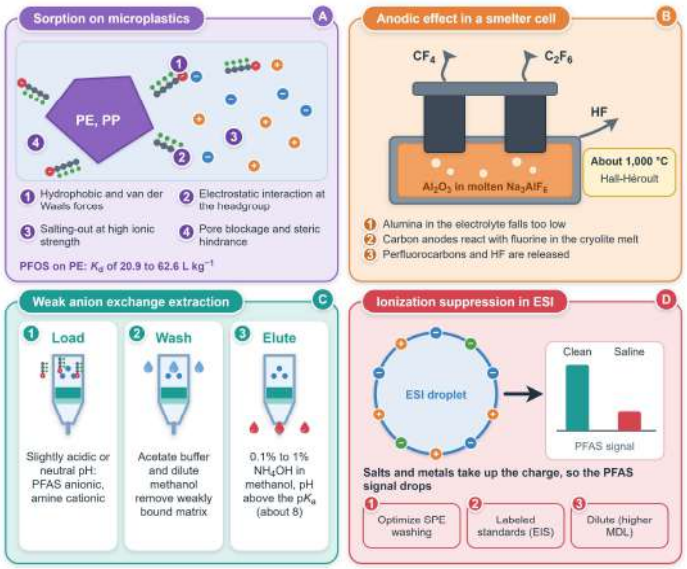


Figure 4. Mechanisms discussed in this review: (A) PFAS sorption onto microplastics; (B) CF_4 and C_2F_6 formation in a Hall-Héroult cell; (C) retention and elution on a weak anion exchange sorbent; (D) ionization suppression in electrospray and corrective measures.

The atmosphere is a second pathway. Decades of irrigation diversions have almost completely dried the Aral Sea, and about 57,000 km^2 of hypersaline lakebed are now exposed as the Aralkum Desert [12], a large source of salt-alkali dust storms [13]. Aralkum aerosols carry salts, heavy metals and persistent organic pollutants and make up 41% to 59% of measured aerosols in the basin, depending on the season [13]. Because PFAS are strong surfactants, they partition onto mineral surfaces, clay and organic matter carried in dust [11], so dust storms could move PFAS through the air and deposit them on agricultural soils, cities and mountain glaciers. No PFAS measurements in Aralkum dust are cited in the literature reviewed here, so this pathway remains a hypothesis (Figure 2).

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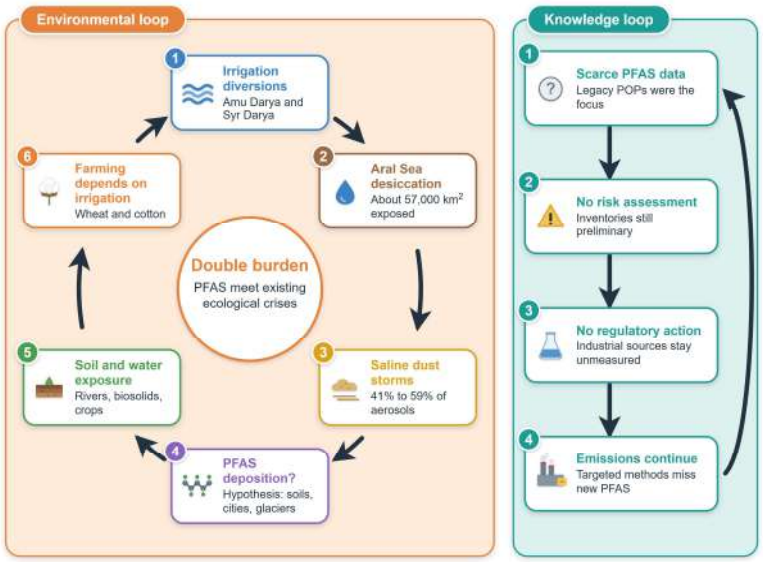


Figure 2. Proposed feedback loops behind the double burden of contamination: the exposed Aralkum emits saline dust that may deposit PFAS on irrigated soils (environmental loop), and scarce data keep emissions unmeasured (knowledge loop). Both loops are conceptual.

INDUSTRIAL POINT SOURCES.

In Uzbekistan, textile wet processing is widely recognized as one of the largest sources of PFAS emissions, because the chemicals are applied in large quantities to give fabrics water-, oil- and stain-resistant finishes [14]. After the global phase-outs, finishes moved to side-chain fluorinated polymers that carry short-chain perfluoroalkyl groups ($\leq C_6$) [15]. Wet processing of 1 kg of fabric is estimated to need up to 150 liters of water and produces wastewater that is difficult to treat, and untreated effluent is frequently discharged to surface waters or used for irrigation [16]. Treatment may lack the tertiary steps, such as granular activated carbon (GAC) filtration or reverse osmosis, that are needed to capture PFAS [2].

Weathering, washing and enzymatic activity slowly break the ester linkages that hold the fluorinated side chains to the polymer, which releases volatile fluorotelomer alcohols, especially 6:2 FTOH [17]. It is oxidized by soil and sludge microbes to 6:2 FTCA, which loses hydrogen fluoride to form 6:2 FTUCA, and further β-oxidation and decarboxylation yield 5:3 acid, a stable intermediate that is often the dominant metabolite in soil and has an elimination half-life of 20 to 30 days [18] (Figure 3). Degradation ends in persistent short-chain carboxylic acids (PFHxA, PFPeA and PFBA) [19] that dissolve readily in water, sorb weakly to soil organic matter, can leach into groundwater and are taken up quickly by crops [20].

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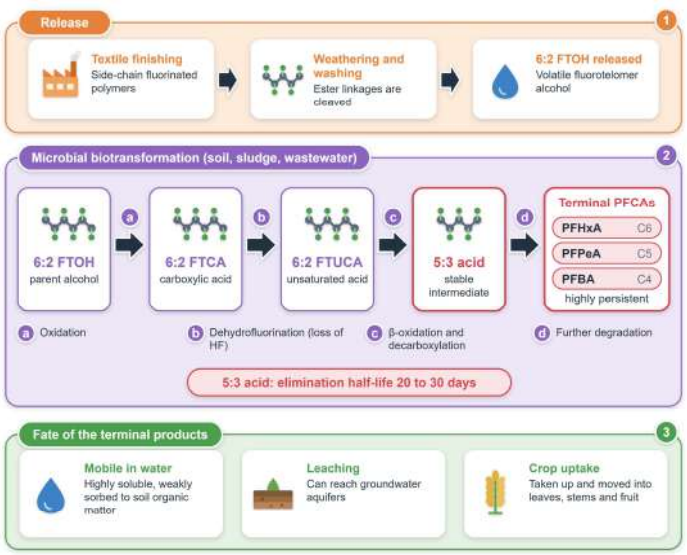


Figure 3. Aerobic biotransformation of 6:2 FTOH released from textile finishing: oxidation to 6:2 FTCA, dehydrofluorination to 6:2 FTUCA, and β-oxidation with decarboxylation to 5:3 acid (half-life 20 to 30 days), ending in mobile short-chain PFCAs (PFHxA, PFPeA and PFBA).

Kazakhstan's economy rests on hydrocarbon extraction in the mature Caspian oilfields, where operators increasingly turn to EOR [21]. Among the injected chemicals, fluorinated surfactants are described as high-performance oil displacement agents that remain stable under deep reservoir conditions [22]. Injected fluids generate large volumes of "produced water" that can contain unreacted fluorinated surfactants and breakdown products [23], and if it is not adequately treated it could carry complex PFAS into the aquifers and surface waters of Kazakhstan [24]. Many EOR surfactants are proprietary, so standard targeted methods may not detect them. None of the sources cited here shows that fluorinated surfactants are actually used in Kazakhstan.

The Tajik Aluminium Company (TALCO) runs one of the largest primary aluminum smelters in the region [25]. It is a major point source of inorganic fluoride and a suspected source of polyfluorinated organic emissions [26], and its industrial waste has been linked to negative effects on soil, groundwater and air quality around the plant [25]. During the "anodic effect" in the Hall-Héroult process, when the alumina in the molten cryolite electrolyte runs low, the carbon anodes react with the fluorine in the melt and produce the perfluorocarbons CF_4 and C_2F_6, which are powerful greenhouse gases and extremely stable fluorinated compounds [27]. Fluoride from aluminum smelters accumulates in vegetation and soil near the plant [28]. Local reports describe defoliated orchards, lower yields and fluorosis in livestock and people downwind in Uzbekistan, but the peer-reviewed sources cited here do not document these effects for this region, and they would be

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effects of inorganic fluoride, not of PFAS. Whether complex organofluorine by-products are co-emitted has not, to our knowledge, been investigated.

SAMPLE PREPARATION AND MASS SPECTROMETRY.

Saline, metal-rich samples such as those from the Aral Sea basin demand careful preparation. Solid-phase extraction (SPE) on mixed-mode weak anion exchange (WAX) sorbents is the standard way to isolate and concentrate ultra-trace PFAS while limiting interferences [29]. A WAX sorbent retains PFAS by reversed-phase interaction with the fluorinated tail and by electrostatic attraction between its amine groups (pK_a of about 8) and the anionic headgroup [30]. Because this binding is strong, elution needs a basic solvent, typically 0.1% to 1% ammonium hydroxide in methanol, which raises the pH above the sorbent pK_a and breaks the ionic bond [31]. High concentrations of dissolved salts and heavy metals co-extract with the PFAS [32]. In electrospray ionization (ESI) they compete with PFAS for charge on the droplet surface, which suppresses ionization [29]. Isotopically labeled internal standards correct for losses and suppression [30], and very saline samples may need dilution before loading, at the cost of higher detection limits (Figure 4C and 4D).

Regulatory monitoring relies almost entirely on targeted liquid chromatography-tandem mass spectrometry (LC-MS/MS) on triple quadrupole instruments in negative-ion ESI, in which a precursor ion is fragmented and two transitions, a quantifier and a qualifier, confirm the identity of the analyte [31, 33]. The method is very sensitive but is blind to anything that is not on the target list, typically 30 to 40 legacy PFAS. Short-chain fluorotelomers and proprietary EOR surfactants could therefore be missed. High-resolution mass spectrometry (HRMS) records exact masses with an accuracy typically better than 2 ppm and supports suspect and non-targeted screening [34]. The Kendrick mass defect (KMD) approach rescales the mass scale to the difluoromethylene unit (CF_2, 49.9968 Da), so that homologous PFAS series line up horizontally and non-fluorinated features can be filtered out, which helps to reveal novel PFAS classes, precursor degradation products and branched industrial by-products [35].

Even HRMS cannot separate isobaric and isomeric interferences [36]. Ion mobility spectrometry (IMS) adds a gas-phase separation by size, shape and charge before mass analysis, and the collision cross section (CCS) is an intrinsic property of the ion [36]. In cyclic IMS (cIMS) the ions travel around a closed loop several times, and a mobility resolving power of about 750 has been demonstrated for 100 passes [37]. Branched PFAS isomers from electrochemical fluorination fold into more compact shapes with smaller CCS values than linear isomers, and cIMS can separate them, which is important because isomers differ in toxicokinetics, bioaccumulation and mobility [38-39]. In addition, PFAS fall along a narrow

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trendline in CCS versus *m/z* space, so predicted CCS databases and tight CCS tolerances (±2%) can discard matrix ions and lower false-positive rates [40]. Figure 5 shows the proposed tiered workflow.

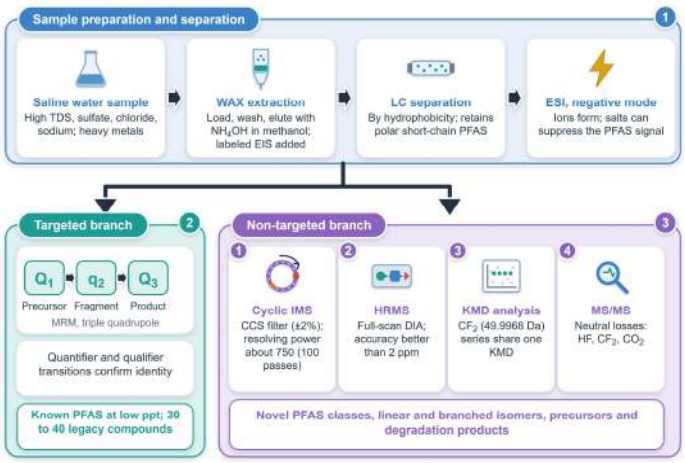


Figure 5. Proposed tiered analytical workflow for PFAS in saline Central Asian samples: weak anion exchange extraction with labeled standards, LC separation and negative-mode electrospray, then a targeted branch (QqQ, MRM) for known PFAS and a non-targeted branch (cIMS, HRMS, KMD analysis, MS/MS) for novel PFAS, isomers and degradation products.

BIOLOGICAL EFFECTS AND HEALTH IMPLICATIONS.

The evidence for biological effects in Central Asia itself is indirect. Large irrigation networks draw on potentially contaminated rivers (the Amu Darya, Syr Darya and Zerafshan) and municipal biosolids are applied to arid soils, so transfer of PFAS into the soil-plant continuum is likely [41]. Uptake depends on carbon chain length and headgroup [42]. Short-chain PFAS, the terminal products of 6:2 FTOH from textiles, cross the root endodermis, travel in the transpiration stream and accumulate in leaves, stems and fruit [42]. Long-chain PFAS (PFOS and PFOA), from historical use, AFFF or fallout from facilities such as TALCO, stay mainly in roots, with bioaccumulation factors highest in root, then straw, then grain [43].

Such accumulation could threaten the safety of food and livestock forage. High PFAS concentrations in soil can also be phytotoxic: they induce oxidative stress, disturb the microbial communities that drive nutrient cycling and can lower crop yields [44]. Cotton and wheat are central to regional economies, so PFAS entry into agricultural soils is a potential threat to economic output and food security [41]. At the base of the aquatic food web, microplastics that carry sorbed PFAS can be ingested by benthic and pelagic organisms [9], and PFAS accumulate through food webs up to people, in whom exposure has been associated with hepatotoxicity, immunotoxicity, endocrine disruption, developmental impairment and a higher risk of renal and testicular carcinomas [4]. PFAS have been measured

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in human breast milk from several Asian countries [45], although to our knowledge not from Central Asia (Figure 6).

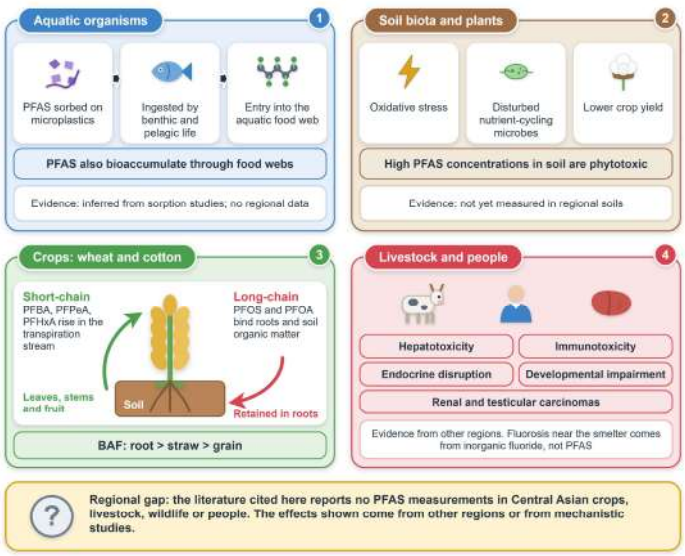


Figure 6. Biological effects along the PFAS exposure chain as described in the reviewed literature. The evidence comes from studies outside Central Asia or from mechanistic work; fluorosis near the smelter is attributed to inorganic fluoride, not PFAS.

Two points follow for the interpretation of future data. First, chain length decides where in a plant PFAS accumulate, so edible above-ground parts may carry more short-chain PFAS [42-43]. Second, the fluorosis, orchard damage and yield losses reported near the smelter come from inorganic fluoride [28] and should not be attributed to PFAS unless organofluorine data are collected. The literature cited here reports no PFAS concentrations in Central Asian crops, livestock, wildlife or people, so linking measured regional exposure to biological response is the largest open question.

PERSPECTIVES AND CONCLUSION.

Baseline monitoring should come first: PFAS could be added to the sites and samples of the microplastic surveys in Uzbek rivers, covering surface water, sediment, groundwater, agricultural soils, biosolids, textile and smelter effluents, EOR produced water and Aralkum dust. Matched sampling of water, soil and crops would allow chain-length-specific bioconcentration factors to be measured for regional conditions. A tiered strategy suits these samples: targeted LC-MS/MS on WAX extracts for quantification, then HRMS with KMD analysis and cIMS for precursors, short-chain products, proprietary surfactants and isomers. Biological studies should run alongside the chemistry, including PFAS in wheat and cotton, effects on soil enzymes and microbial communities in saline arid soils, and separate measurement of inorganic fluoride and organofluorine compounds near the smelter.

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Uzbekistan, Kazakhstan and Tajikistan form a large and largely uncharacterized frontier for PFAS contamination. Baseline data are scarce, but active industrial sources suggest a burden that has not yet been recognized, although this remains to be confirmed by measurement. Side-chain fluorinated polymers in Uzbek textiles, fluorinated surfactants that may be used in Kazakh EOR and the fluorinated emissions of aluminum smelting in Tajikistan are plausible release routes, and Aralkum dust and microplastics in saline rivers may amplify them. Both are mechanistic expectations and not yet regional measurements. Their possible biological consequences, uptake by wheat and cotton, oxidative stress, disturbed soil microbial communities and the toxic effects known from other regions, make the data gap relevant to food safety and health. Closing it will require a move from targeted monitoring to high-resolution approaches such as cIMS-HRMS.

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