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Snow, D. D., Chakraborty, P., Uralbekov, B. et al. (6 more authors) (2020) Legacy and current pesticide residues in Syr Darya, Kazakhstan:Contamination status, seasonal variation and preliminary ecological risk assessment. Water research. 116141. ISSN 0043-1354

https://doi.org/10.1016/j.watres.2020.116141

Legacy and current pesticide residues in Syr Darya, Kazakhstan: Contamination status, seasonal variation and preliminary ecological risk assessment

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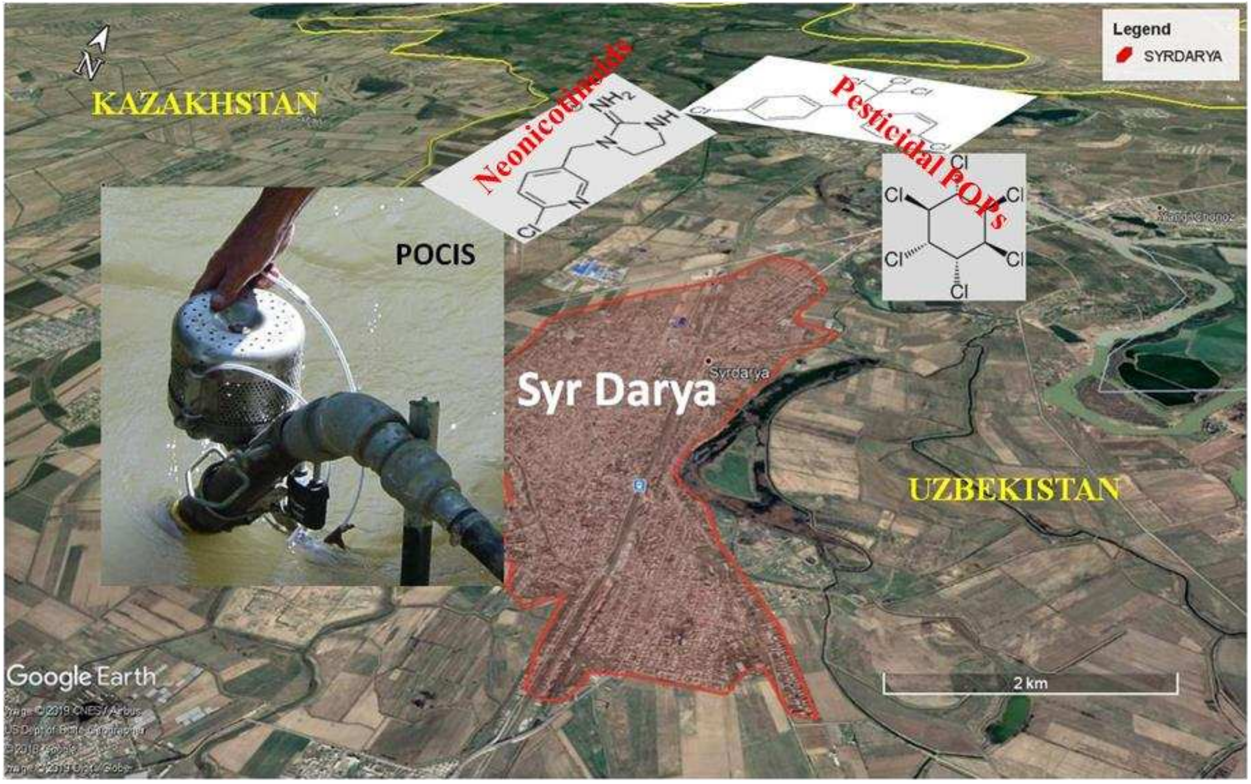
Highlights

- Modern and banned “legacy” pesticides are present in the Syr Darya
- Organochlorine contaminants occur throughout irrigation season
- Ecologic risks from exposure to aquatic organisms are likely
- Passive and grab sampling help monitor contaminants in remote watersheds

Graphical Abstract



Abstract

The Syr Darya is one of two major rivers in Central Asia supplying critical fresh water to the Aral Sea. In spite of the river’s importance and agriculturally intensive history, few studies have provided a modern evaluation of and the occurrence of pesticide residues and potential effects to aquatic life. The primary goal of this investigation was to determine seasonal variations in ambient concentrations of modern and legacy pesticides in bottom sediment and water of the Syr Darya in Kazakhstan downstream from an agriculturally intensive watershed in Uzbekistan. Grab samples and passive samplers used at five remote sampling stations during June 2015 to provide a baseline for ecotoxicological evaluation. Results were compared with samples collected during and after the agricultural growing season. Polar organic chemical integrative samplers (POCIS) were used in June and calibrated for time weighted average concentrations of current use pesticides. Among legacy chlorinated pesticides measured in grab samples from the river, lindane (γ-HCH) was detected most frequently with the highest concentrations occurring during June. For all the sampling events, residues of lindane (γ-HCH) ranged from 0.014 µg/L to 0.24 µg/L detected in grab samples are among the highest concentrations reported for rivers globally. Concentrations of *γ*-HCH, *p,p’*-DDE and dieldrin were highest in October when dieldrin concentrations approached 0.4 µg/L. Sources of legacy pesticides may be either illicit upstream use or evidence of previous atmospheric contamination of glacial meltwater. Chronic exposure to these residues may lead to ecological risk to lower order organisms in both the sediment and water column.

Key words: Syr Darya, γ-HCH, p,p’-DDE, risk assessment

1. Introduction

Large-scale diversion of water from the Aral Sea in central Asia is one of the most widely cited environmental disasters of the last century (Cai et al., 2002). During the 1960s, the government of the former Soviet republics promoted agricultural practices that led to substantial reduction in total discharge of the Amu Darya and the Syr Darya rivers (Figure 1), primarily to irrigate water-intensive crops including, rice, melons and cotton (Glantz, 2007). Diversion of the two major rivers feeding the Aral Sea had a globally visible impact, as the total surface area declined to less than 10% of its historical size and resulted in the near total loss of its commercial fishery (Hecht, 2014).

The southern Amu Darya no longer replenishes the Aral Sea and this part of the basin has substantially reduced in volume, increased in salinity, and has completely lost its fishery. The northern tributary of Syr Darya now provides limited freshwater replenishment to the northern basin of the Aral Sea, and this basin consequently has fared much better than its southern counterpart. The Kokaral Dam was built in 2005 as an effort to raise the water level in the north basin of the Aral Sea and restore the local fishery (Hecht, 2014). The north basin derives its freshwater from the Syr Darya. This dam has helped to partially fill the Aral Sea with enough water so that commercial fishing, seeded by fish species that have taken refuge in the lower regions of the Syr Darya, is returning to the region.

Despite the importance of the Syr Darya inflow to the revival of the north basin of the Aral Sea, few recent water quality studies have been conducted on the Syr Darya. Because of the difficulty in regulating use in developing countries, organochlorine pesticides, such as dichlorodiphenyltrichloroethane (DDT) and lindane ($\gamma -$HCH), may continue to be used upstream (Ali et al., 2014). These persistent, bio-accumulative pesticides were heavily used on irrigated agricultural fields that lie within the Syr Darya watershed (Li, 1999). Consequently, the Syr Darya may carry a significant load of legacy pesticides as well as modern pesticide residues, such as neonicotinoid insecticides into the north basin of the Aral Sea. Legacy pesticides can be highly significant contributors to exposure of stream biota (Rasmussen et al., 2015), and it is increasingly clear that both modern and legacy toxins be considered in risk assessment. This paper provides a novel and recent assessment of pesticide concentrations in a remote Central Asian region. Few studies have examined the occurrence and ecological risk of a mixture of legacy and modern pesticides in Central Asia. The goal of this study was to characterize the concentrations of a wide variety of potentially toxic chemicals in an important freshwater supply for the Aral Sea, and provide a baseline for ecotoxicological evaluation of these effects. Samples were collected during three reconnaissance trips to the Syr Darya during the months of June, August, and October 2015. Passive, *in-situ* and grab sampling techniques were tested to evaluate the suitability of alternative means for sampling collection in remote regions such as south Kazakhstan. A suite of different sampling techniques was employed to evaluate how newer technologies may be adapted to monitoring in remote areas. Results from this study provides a snapshot of chemical contaminant concentrations from samples collected over a single growing season.

2. Materials and methods

2.1 Site selection and general sampling

Preliminary reconnaissance by local researchers identified six accessible locations for sampling and collection of fish tissues along a stretch of the Syr Darya from where it enters Kazakhstan (KZ) to a point upstream from the Arys River south of Turkistan, KZ (Figure 1). Sampling trips were scheduled to coincide with the beginning, middle, and end of the irrigation season. June sampling results provided a baseline of water quality, while samples collected in August and October coincided with conditions during and at the end of the irrigation season (Frenken, 2013) when increased inputs of persistent pesticide residues from irrigation return flows may be expected. The timing of sampling allowed for an evaluation of changes in contaminant loading from irrigation return flows during a single crop growing season.

Figure 1. Map showing the six sample locations (numbers in red) along the Syr Darya, Kazakhstan. River flow is from south to north. All six in-stream locations were sampled in June and October. Coordinates are provided in supplementary material. The Shardara Reservoir is located in the bottom center and site 2X on the eastern shore.

The Shardara multi-purpose reservoir (Figure 1), constructed between 1964 and 1967 on the Syr Darya in Shardara City, KZ, provides storage for both irrigation water and hydroelectric power generation and lies immediately downstream of a boundary with the country of Uzbekistan. The reservoir capacity is approximately 5.2x10^9 m^3 and, depending on upstream precipitation amounts, its volume may be turned over several times annually. Sampling locations were chosen to evaluate the chemical composition of river water as it crossed the border into

Kazakhstan and helped characterize changes in water quality downstream from the reservoir through a region of highly irrigated cotton production. The total distance between the Shardara Reservoir and the final sampling point above the confluence with the Ayrs River, is approximately 250 km. Six sites were chosen selected for repeated sampling in the river and reservoir and three additional sites for grab samples during the growing season (Figure 1). Site 1 is the most upstream sampling location, is immediately adjacent to the Uzbekistan border and receives inflow only during the spring and summer months. Sites 2 and 2X are located on the shores of the Shardara Reservoir near inflow and outflow respectively prior to controlled release to downstream Sites 3, 4, and 5 (Figure 1).

A suite of sampling techniques were employed to assess occurrence of pesticides in the Syr Darya. Water and sediment grab samples, along with *in-situ* sampling devices, including polar organic chemical integrative samplers (POCIS, Environmental Sampling Technologies, St. Joseph, MO), and continuous low-level aquatic monitoring (C.L.A.M., C.I. Agent Solutions, Louisville, KY) samplers permitted a broad range of sampling methods and sensitivity. POCIS and C.L.A.M. samplers were only used in June. Table 1 summarizes the types of samples collected during each event.

Table 1. Sampling regime utilized to assess the presence of pesticide residues in the Syr Darya. August samples were collected primarily to account for ephemeral irrigation canal inputs.

Dates	Sites (Fig 1)	Samples Types Collected
5-6 June 2015	1,2, 2X, 3, 4, 5	Water and river sediment grab samples
	1, 2X, 5	POCIS, C.L.A.M.
23 August 2015	1, 2X	Water grab samples only
	Irrigation ditches	Water grab samples only – 4 sites draining into reservoir
12-13 October 2015	1,2, 2X, 3, 4, 5	Water and river sediment grab samples
	2X, 5	

Samples from all locations were obtained in June and October 2015, though very little water was present in the river channel upstream (Site 1, Figure 1) of the reservoir in October. In August, four additional grab samples of surface water were collected from intermittently filled irrigation ditches upstream of the Shardara Reservoir (*Gulistan Area* and *Zhetisay District*) to help characterize local irrigation canal inflow water quality.

2.2. Collection and processing of water samples

Water samples for pesticide analysis were collected in 1-liter square amber glass bottles and transported in a cooler filled with frozen ice packs and transported to Al-Farabi Kazakh National University (KazNU) where they were stored at 4ºC. Each 1-liter water sample was extracted within three days of collection and was divided into three 300 mL portions by weight for solid phase extraction (SPE) and subsequent analysis by three instrumental methods. Two of these portions were spiked and equilibrated with 2,000 ng terbuthylazine and butachlor surrogates to account for losses during extraction, and immediately extracted using preconditioned 1 g trifunctional tC18 bonded silica SPE cartridges (Waters Corporation, Milford, MA USA). The third 300 mL portion was extracted onto a 200 mg HLB SPE cartridge (Waters Corporation, Milford MA USA). Reverse phase tC18 cartridges were preconditioned onsite by passing 5 mL of ethyl acetate, 5 mL of acetonitrile and 5 mL of purified (deionized distilled) reagent water, while the HLB cartridges were preconditioned using 5 mL acetonitrile followed by 5 mL of purified reagent water immediately prior to use.

During extraction, each sample portion was slowly aspirated under vacuum through 1/8" OD Teflon^{TM} tubing and a glass microfiber filter (Whatman GF/F, GF/F: 0.7 µm pore size, binderless) held in a 25 mm Teflon^{TM} filter holder connected using Leur adapter to each preconditioned cartridge mounted on a flow control valve and vacuum flask. The glass fiber filter was removed, and the holder rinsed with 100% ethanol and purified reagent (deionized distilled) water after each sample to minimize any cross contamination. Following extraction, each labelled SPE cartridge was air dried via vacuum aspiration at room temperature for 5 min, and then stored in sealed zipper bags at 4°C. Processed SPE cartridges containing extracted residues were transported to the University of Nebraska Water Sciences Laboratory (UN-WSL) and stored at -20°C until further processing. One of the two tC18 cartridges from each sample was utilized for the analysis of 22 non-organochlorine pesticides, while the other was utilized for the analysis of six organochlorine pesticides. The HLB cartridges were processed for the analysis of neonicotinoids and one organophosphate insecticide.

Table 2. Target compounds included in analysis SPE cartridge extracts, and extracts from sediment samples, polar organic chemical integrative samplers (POCIS), continuous low-level aquatic monitoring (C.L.A.M.) samplers.

Water			
tC18 cartridge 1 extracts			
Acetochlor	Alachlor	Atrazine	Butylate
Chlorthalonil	Cyanazine	Deethylatrazine	Deisopropylatrazine
Dimethenamid	EPTC	Metolachlor	Metribuzin
Norflorazon	Pendimethalin	Permethrin	Prometon
Propachlor	Propazine	Simazine	Tefluthrin
Terbufos	Trifluralin		
tC18 cartridge 2 extracts			
4,4-DDE	4,4-DDT	α-HCH	Aldrin
β-HCH	δ-HCH	Dieldrin	γ-HCH (Lindane)
Heptachlor			
HLB cartridge extracts			
Acetamiprid	Clothianidin	Imidacloprid	Metalaxyl
Dimethoate	Dinotefuran	Thiacloprid	Thiamethoxam
Sediment			
4,4-DDE	4,4-DDT	α-HCH	Aldrin
β-HCH	δ-HCH	Dieldrin	γ-HCH (Lindane)
Heptachlor			
POCIS			
Acetamiprid	Acetochlor	Atrazine	Bifenthrin
Boscalid	Carbofuran	Chlorpyrifos	Clothianidin

Cyhalothrin	Cyprodinil	Deltamethrin	Deethylatrazine
Deisopropylatrazine	Diazinon	Dimethoate	Dinotefuran
Fludioxonil	Imidacloprid	Malathion	Metalaxyl
Methidathion	Metolachlor	Metribuzin	Parathion ethyl
Parathion methyl	Pendimethalin	Permethrin	Pyrimethanil
Quinoxyfen	Tebuconazole	Thiacloprid	Triadimefon
Thiamethoxam			
C.L.A.M. Samplers			
Acetochlor	Atrazine	Boscalid	Carbofuran
Chlorpyrifos	Cyprodinil	Deethylatrazine	Deisopropylatrazine
Diazinon	Fludioxonil	Malathion	Methidathion
Metolachlor	Metribuzan	Parathion ethyl	Parathion methyl
Pendimethalin	Propazine	Pyrimethanil	Simazine

2.3. SPE Cartridge elution

The tC18 SPE cartridges used for non-organochlorine pesticide analysis (Table 2) were eluted with 6 mL of ethyl acetate, and eluate spiked with 5 µg each of $^{13}C_3$-labelled atrazine, deethylatrazine (DEA) and desisopropylatrazine (DIA) added and used as internal standards. Quantitation by isotope dilution was used for atrazine, DEA and DIA and other residues were quantified using $^{13}C_3$-atrazine. Ethyl acetate extracts were evaporated under nitrogen to ~1 mL and residual water was removed with the addition of anhydrous sodium sulfate, followed by quantitative transfer using 2 mL of ethyl acetate to a clean borosilicate culture tube. After vortexing, the solvent volume was then further reduced to 200 µL under dry nitrogen. Concentrated extracts were transferred to autosampler vials outfitted with 300 µL silane-treated glass inserts. Extracts were analyzed for the compounds listed in Table 2 by gas chromatography-mass spectrometry (GC/MS) with selected ion monitoring as described previously (Cassada et al., 1994). Further details of the analytical method and results of a validation study are provided in supplementary materials.

The second set of tC18 SPE cartridges, used for preconcentration of chlorinated pesticides, were eluted with 3 mL of acetone, followed by 3 mL of hexane, and 3 mL of ethyl acetate. Solvent eluate was spiked with 5 µg of labelled internal standards ($^{13}C_3$-atrazine, $^{13}C_3$-deethylatrazine, and $^{13}C_3$-deisopropylatrazine (Merck Sharp & Dohme/Isotopes, St. Louis, MO USA), and slowly evaporated under dry nitrogen. Residual water was removed with anhydrous sodium sulfate during the concentration process and quantitatively transferred to clean borosilicate culture tubes using additional ethyl acetate. Each extract was evaporated completely, residues dissolved in 200 µL ethyl acetate, and finally transferred to a 300 µL silane-treated glass insert for analysis of chlorinated insecticides (Table 2) by full scan GC/MS. Method detection limits were determined by extraction and analysis of eight (8) replicate samples of purified reagent water fortified at 0.3 µg/L, and range from 0.007 µg/L for 4-DDE to 0.053 µg/L for aldrin (Table S7).

Compounds retained on polymeric HLB SPE cartridges were eluted and analyzed for polar neonicotinoid and organophosphorus insecticides (Table 2) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). Full details of the extraction, elution and instrumental method is included in the supplemental materials. Standards for each of the target analytes, as well as isotopically-labelled standards (d4-Imidacloprid, d3-Thiamethoxam and d6-Metalaxyl), were obtained from Sigma Aldrich (St. Louis, MO). Each HLB SPE cartridge was eluted under vacuum with 6 mL of high purity methanol (Optima, Fisher Scientific, St. Louis, MO), the eluate was spiked with 50µL of 1.0 ng/µL internal standard mix, and completely evaporated under dry nitrogen in borosilicate culture tubes. The residue was dissolved in 50 µL high purity methanol and mixed with 200 µL purified (distilled deionized, organic free) reagent water prior to LC-MS/MS analysis. A well end-capped 250 x 2 mm x 5 µm BetaBasic C18 reverse phase HPLC column (ThermoFisher, St. Louis, MO USA) was used for the gradient separation with 0.15% formic acid in methanol/water (97:3) and 0.15% formic acid in water/methanol (97:3) at a constant temperature of 50°C and a flow rate of 0.3 mL/min. Analysis run time was 30 minutes, with positive ion mode atmospheric pressure chemical ionization (APCI) on a Waters Quattro Micro triple quadrupole mass spectrometer (Waters Corporation, Milford, MA USA). A pseudo-molecular ion $[M+H]^+$ for each compound was selected as the parent ion for fragmentation, and corresponding fragment ion(s) selected for identification and quantitation (Table S7). Method detection limits ranged from 0.005 and 0.025 µg/L.

Compound recovery and method detection limits, determined through 8 to 10 replicate analyses of low-level fortified blanks (USEPA, 1986), are presented in Table S10. Quality controls processed in Kazakhstan included laboratory duplicates and method blanks prepared from distilled deionized water. Additional quality controls processed in the U.S. are laboratory fortified blank and method blanks. Results of quality controls, together with analysis of certified reference material samples, is included in the supplemental section.

2.3. Collection and chemical analysis of sediment grab samples

Sediment samples (~200 g) were collected in 250 mL amber jars, held on ice and then transferred to a freezer for subsequent extraction using microwave assisted solvent extraction with analysis by GC/MS. Briefly, five (5.00) grams of wet sample was weighed into a 10 milliliter (mL) Teflon^{TM} microwave digestion vessel, spiked with 200 ng surrogate compounds, and thoroughly mixed with 6 mL of acetonitrile. Batches of up to 40 samples are then subjected to microwave irradiation (400W) for 10 minutes at 90ºC using a MARS Xpress microwave digestion system (CEM, Matthews, NC USA). After cooling and decanting solvent, sediment was mixed with an additional 6 mL of acetonitrile, allowed to settle and then solvent combined with the first portion. Extract volume is then reduced to near 1-2 mL under dry nitrogen and spiked with 500 ng of isotope-labelled internal standards. The acetonitrile was mixed with 100 mL of water, and extracts purified by reverse phase (tC18) solid phase extraction (SPE) cartridges used in water extraction. Absorbed compounds were then eluted with ethyl acetate and analyzed by GC/MS as described above. Method detection limits, determined from extraction and analysis of eight replicates of 5 grams of clean sand spiked at 4.0 ng/g, ranged from 0.4 ng/g for trifluralin to 5.0 ng/g for dieldrin (Table S5).

2.4. Deployment, calibration and chemical analysis of POCIS

Polar organic chemical integrative samplers (POCIS) is an effective passive water sampling of polar organic compounds at spatial and temporal scale. We have therefore estimated the sampling rates for neonicotinoids in the laboratory before deploying those in the field. Nine POCIS were obtained from Environmental Sampling Technologies (St. Joseph, MO USA) were placed in three stainless-steel deployment canisters and deployed at three of the sampling sites for seven days during the June sampling campaign. One POCIS canister, deployed at location 2X (Figure 1) was missing and presumed lost at the conclusion of the deployment. Upon retrieval, each POCIS deployment canister was placed in a plastic bag and put in a cooler containing ice packs until transport to the laboratory at Al-Farabi KazNU. Within three days of retrieval, the HLB sorbent from each POCIS was removed and quantitatively transferred to glass chromatography columns containing a plug of glass wool by gently rinsing the polymer with purified deionized water. After draining the water, three 20 mL portions of reagent grade acetonitrile were used to slowly extract and elute compounds from the sorbent. The POCIS extracts were evaporated under dry nitrogen to ~30 mL, stored in glass vials with Teflon^{TM}-lined caps and transported to the Water Sciences Laboratory, University of Nebraska, USA for elution and analysis of pesticide residues. After spiking the extract with internal standards listed in the method for water samples, the extracts were evaporated to dryness, spiked with 50 µL of 1.0 ng/µL internal standard mix, and completely evaporated under dry nitrogen in borosilicate culture tubes. The residue was dissolved in 50 µL high purity methanol and mixed with 200 µL purified (distilled deionized, organic free) reagent water and analyzed for neonicotinoid insecticides and organophosphate insecticides (Table 2).

Uptake rates for the neonicotinoids and dimethoate using POCIS were determined in the laboratory using procedures detailed previously (Bartelt-Hunt et al., 2011). Briefly three POCIS were suspended in stirred 2-liter aqueous solutions spiked with 5 µg/L of all compounds in pH=7.0 buffered reagent water. A fourth stirred solution without POCIS was stirred and used a control. Fifty milliliter portions of each solution were removed at the beginning of the uptake experiment and after 1 day, 3 days, 7 days and 14-days of exposure to the POCIS device. The aqueous concentration was measured in each solution and the observed decrease in the aqueous concentration of neonicotinoids over time was modeled by using first-order kinetics based on the following equation:

$$\mathbf{C_w(t)= C_w(0) \exp[-kt]} \qquad (1)$$

where $C_w(t)$ is the aqueous concentration at time t; $C_w(0)$ is the aqueous concentration at time 0; and k is the rate constant. The value of k was determined from the natural logarithm of the slope of the change in water concentration over the exposure time. The POCIS uptake rate (R_s) was calculated as:

$$\mathbf{R_s=k_U V_T} \qquad \mathbf{(2)}$$

where V_T was the total volume of the water in the container. Volume changes in the beakers due to sampling during the sampling events were considered by adjusting the values of V_T. Uptake rates were calculated using all data created over the 14 days exposure (Table S9).

2.4. Use and processing of continuous low-level aquatic monitoring (C.L.A.M.) samplers

The C.L.A.M. sampler devices were outfitted with HLB-H Disks (#A50-HLB-H) and used as described by the manufacturer (C.I. Agent StormWater Solutions, Louisville, KY USA). Total sample volumes at each location were calculated by estimating total flow through the C.L.A.M. over the extraction period per manufacturer recommendation. The C.L.A.M. (#HLB-H Disk A50-HLB-H) samplers were processed for the analytes listed in Table 2. Elution followed modified manufacturer protocols by slowly passing 50 mL of methanol through the disk followed by 50 mL of methylene chloride directly into a 150 mL RapidVap N2 glass vial (Labconco Corp, Kansas City, MO USA). The resultant mixture was spiked with 5,000 ng each of $^{13}C_3$- atrazine, $^{13}C_3$-deethylatrazine (DEA) and $^{13}C_3$-deisopropylatrazine (DIA), and 2000 ng of terbuthylazine and butachlor surrogates, and then evaporated completely at 40°C under nitrogen. The concentrated residue was dissolved in hexane, transferred to 300 µL silane-treated glass insert for analysis of pesticides by full scan GC/MS (Cassada et al., 1994). Instrumental conditions are the same as those listed for herbicide and organophosphorus insecticides determined in grab samples.

2.7. Risk Assessment

A preliminary ecotoxicological risk assessment for DDT and γ-HCH concentrations in river water samples was calculated using the hazard quotient (HQ) equation (3), based on USEPA guidelines (USEPA, 1998):

$$\boldsymbol{HQ} = \frac{\boldsymbol{MEC}}{\boldsymbol{PNEC}} \qquad \textbf{(3)}$$

where MEC = maximum reported environmental concentration, and PNEC = predicted no-effect concentration. The PNEC values were obtained from previously published methods (Chakraborty et al., 2016; Chen et al., 2020; Zeng et al., 2018) for five species in five groups in different trophic levels -. zooplankton, phytoplankton, mollusc, insects, and fishes. HQs were determined for each sampling site to characterize risk throughout this stretch of river.

Potential risk from organochlorine pesticide exposure in sediments to ecological integrities was evaluated by comparing the mean concentrations of detected pesticides in the sediment with the threshold effect level (TEL) and probable effect level (PEL) given by the Canadian Council of Ministry of the Environment Guidelines (CCME, 2006.) and effect range of low (ERL) level mentioned in other studies (Long et al., 1998; Yang et al., 2013). Potential toxicity in the mixture was estimated in terms of sediment quality guideline quotient (SQGQ) reported in several papers (Long and MacDonald, 1998; Wang et al., 2017).

$$\mathrm{SQGQ} = \sum_{x=1}^{n} \frac{PELQx}{n} \qquad \textbf{(4)}$$

$$\text{where, } PELQx = \frac{\mathrm{Cx}}{PEL} \qquad \textbf{(5)}$$

where, *PEL* is the guideline value for contaminant “x”, C_x is the measured concentration of the same contaminant, and “n” is the number of contaminants for which sediment guidelines are available. SQGQ values < 0.1 indicates no effects; $0.1 \leq \mathrm{SQGQ} < 1$ indicates moderate effects and $\mathrm{SQGQ} \geq 1$, high adverse biological effects (Costa et al., 2011).

3. Results and discussion

A summary of pesticide residues detected is presented in Table 4. Even with the large number of target compounds measured, the number of detections and relative concentrations is remarkably low given the agriculturally intensive history of this region. Residues of current use and legacy chlorinated pesticides were detected in grab samples, bottom sediment and passive sampling devices. The highest concentrations were found among legacy pesticide residues in both the water column and sediment samples. Monthly recorded precipitation was highest Zhetysay, KZ located 10 km south of Shardara reservoir (Figure 1) in May ~24 mm and dropped to 1 mm or less for June through October. Discharge at Site 1 was highest in May and averaged 167 m^3/sec during this period (Supplemental Information). Based on recorded precipitation and discharge measurements, June samples should correspond periods when instream concentrations are from precipitation triggered run-off, while August and October samples would be more characteristic of irrigation water supplied pesticides (Figure S1).

3.1. Legacy pollutants in the Syr Darya

Lindane were detected in nearly all of the surface water grab samples at concentrations ranging from 0.014 µg/L to 0.24 µg/L. The average (±SD) lindane concentration across all sampling dates was 0.130±0.06 µg/L and the highest concentrations were measured in the June samples (Table 4). The organochloride insecticide aldrin and its metabolite dieldrin were detected in grab samples collected in August and October at concentrations ranging up to 0.37 µg/L. Sediment samples contained residues of *p,p'*-DDE at concentrations ranging from 0.18 to 2.45 ng/g upstream and downstream (give the sampling locations) of the Shardara Reservoir, and trifluralin at 0.20 ng/g upstream of the reservoir (Site 1) and at 0.14 ng/g in the reservoir grab sample (Site 2), both collected in June (Table 4). Other chlorinated pesticides, including heptachlor and p,p'-DDT, as well as the hexachlorohexane isomers (α-HCH and β-HCH) typically found as manufacturing impurities were not detected in any grab samples.

Table 4. Detected pesticide concentrations measured from the Syr Darya sampling sites. POCIS concentrations represent time-weighted average concentration determined from the mass (± standard deviation) of three POCIS deployed at each site. "ND" = "Not Detected".

Pesticide	**Month**	**Site 1**	**Site 2**	**Site 2X**	**Site 3**	**Site 4**	**Site 5**
Grab Samples - Water (µg/L)							
Lindane	June 2015	0.16	0.17	0.24	0.18	0.21	0.17
	Aug 2015	0.09	ND	ND	ND	ND	ND

	Oct 2015	0.18	0.10	0.014	0.09	0.06	0.08
Dieldrin	June 2015	ND	ND	ND	ND	ND	ND
	Aug 2015	ND	ND	0.07	ND	ND	ND
	Oct 2015	0.14	0.27	ND	0.37	ND	0.23
Aldrin	June 2015	ND	ND	ND	ND	ND	ND
	Aug 2015	ND	ND	ND	ND	ND	ND
	Oct 2015	ND	ND	0.10	ND	ND	ND
Imidacloprid	June 2015	ND	ND	ND	ND	ND	ND
	Aug 2015	ND	ND	0.008	ND	ND	ND
	Oct 2015	0.013	ND	ND	ND	ND	ND
Dimethoate	June 2015	ND	ND	ND	ND	ND	ND
	Aug 2015	ND	ND	ND	ND	ND	ND
	Oct 2015	0.006	ND	ND	ND	ND	ND
Grab Samples - Bottom Sediment (ng/g)							
p,p'-DDE	June 2015	2.45	ND	ND	0.52	ND	ND
	Oct 2015	1.49	ND	0.19	0.18	ND	ND
Trifluralin	June 2015	0.20	0.14	ND	ND	ND	ND
	Oct 2015	ND	ND	ND	ND	ND	ND
POCIS - time-weighted average concentrations (ng/L)							
Atrazine	June 2015	1.11±0.7					1.19 ±0.8
Acetamiprid	June 2015	0.18±0.1					ND
Dimethoate	June 2015	0.74±0.1					0.36±0.1
Imidacloprid	June 2015	1.15±0.1					ND
Metolachlor	June 2015	0.476 (J)					0.722 ±0.5

3.2. Current-use neonicotinoid and organophosphorus pesticides

Imidacloprid was detected in the upstream grab samples at sites 1 and 2X in October and August, respectively, while dimethoate was detected at site 1 in October (Table 4). These insecticides are comparatively polar and mobile with relatively short half-lives, suggesting that they were used in close proximity (temporally and spatially) to the sites where they were detected.

3.3. Residues in POCIS and C.L.A.M. sampler extracts

The C.L.A.M. samplers used in the June sampling contained trace levels (~0.05 μg/L) of atrazine at Site 1 and cyprodinil at Site 2, but all other compounds were below detection limits. The absence of residue detections was potentially due to variability in volume of water extracted at each location, ranging from ~0.5 to 3.8 liters primarily due to the high levels of suspended solids. The volume extracted is estimated based on the field-measured flowrate and time elapsed between sampler submersion and removal and this flow rate varies considerably depending on the battery condition and time until the extraction disk filter frit became plugged. Differences in concentrations and frequency of detections between C.L.A.M. sampler and other devices or grab samples has been previously reported (Coes et al., 2014; Ensminger et al., 2017). Generally, frequency of detection is reported to be higher than those measured from grab samples but concentrations may be lower. The C.L.A.M. sampler may be very effective for surface water with low levels of suspended solid but likely has limited application in turbid river water.

Of ~33 pesticide residues monitored, POCIS extracts contained detectable levels of two neonicotinoid insecticides (acetamiprid and imidacloprid), an organophosphorous insecticide (dimethoate), atrazine and metolachlor at Site 1 (Table 4). Three of these compounds (atrazine, dimethoate and metolachlor) were also detected at Site 5 in June. POCIS have been extensively used to quantify the levels of polar organic pollutants like pharmaceuticals, pesticides, and hormones in water as reported elsewhere (Alvarez et al., 2007; Arditsoglou and Voutsa, 2008; MacLeod et al., 2007; Sellin et al., 2009).

Passive sampling provides low detection limits and ability to integrate over long sampling times which is good incentive for their use in toxicological studies (Alvarez et al., 2008; Kolok et al., 2014; Sellin et al., 2009). The results of the POCIS uptake rate experiments, provided in the supplemental materials (Table S9), were used to convert pesticide mass recovered to time weighted average concentrations during the 7-day exposure period in June 2015 (Table 4). Sampling uptake rates for neonicotinoids were found to vary between 0.24 to 0.76 L/day excluding dinotefuran, which showed almost negligible uptake to the POCIS. Low uptake for this compound is likely due to the fact that this compound is a weak base (pKa= 12.6) and high water solubility (54,300 mg/L). Linear rates of uptake rates (r^2 between 0.6 to 0.9), observed for acetamiprid, chothianidin, imidacloprid, metalaxyl, thiacloprid and thiamethoxam (Table S9), permitted estimation of average concentrations in the river where residues were detected in POCIS. Estimated time weighted average (TWA) concentrations were below 0.005 µg/L. Higher TWA levels were measured in the POCIS deployed upstream from the Shardara Reservoir (Figure 1). None of the herbicides, pyrethroids, traditional organophosphorous insecticides, or fungicides were detected in the grab samples.

3.4 Occurrence and Potential Sources of Legacy Pesticides

Lindane was detected in the water column but was not measurable in sediment samples, suggesting that this pesticide may have entered the water upstream via irrigation return flow. Over 80% of the total land area upstream of the Shardara Reservoir is located in the Ferghana Valley of Uzbekistan and is devoted to intensive cotton agriculture. It has been reported that banned pesticides may continue to be used in these remote intensively agricultural areas (Wegerich et al., 2015). Estimated flux at Site 1 near the border between Uzbekistan and Kazakhstan of lindane is similar in June and October 2015, while dieldrin and imidacloprid is higher in October (Table S10). The concentrations of lindane and dimethoate in the water column are remarkably similar to those reported in the 1990s (Kimstach et al., 1998) and the chronic occurrence of lindane is a concern for both aquatic organisms and human health, particularly given that lindane has been classified as a Group I carcinogen (Loomis et al., 2015). Food crops such as potatoes and melons are produced in irrigated fields downstream of the Shardara Reservoir and presumably use water diverted from the Syr Darya (Figure 1). Occurrence of legacy pesticides in irrigation water may also affect food quality, as a recent study of pesticide residues in crops from northern Kazakhstan reported detectable levels of pesticides including DDT, γ-HCH, aldrin, and diazinon (Lozowicka et al., 2013).

The ranges of lindane concentrations in samples from the Syr Darya are comparable to those previously reported in other agriculturally contaminated rivers around the world (Table 5).

Table 5: Reported lindane concentrations in river samples from in Asia and Africa.

River	Country	Range (µg/L)	Mean (µg/L)	Reference
Syr Darya	Kazakhstan	0.014 - 0.240	0.187	This study
Chenab	Pakistan	0.0011 - 0.08	0.025	(Eqani et al., 2012)
Kucuk Menderes	Turkey	ND-0.398	0.198	(Turgut, 2003)
Huihe	China	0.0002 - 0.00377	0.002	(Feng et al., 2011)
Beijing	China	0.0002 - 0.00371	0.007	(Jiawei et al., 2008)
Niger	Africa	0.015–0.0468	0.029	(Unyimadu et al., 2017)
Gomti	India	ND- 0.0634	0.008	(Malik et al., 2009)
Yamuna	India	0.0001 - 0.165	0.120	(Kumar et al., 2012)
Ghaggar	India	ND - 0.0487	0.005	(Kaushik et al., 2008)
Hooghly	India	0.003-0.5	0.123	(Khuman and Chakraborty, 2019)
Brahmaputra	India	ND -0.014	0.006	(Chakraborty et al., 2016)

Mean lindane concentrations in Syr Darya are among the highest reported for rivers of China, Pakistan, India, and Africa (Table 5). Comparable γ-HCH concentrations have been reported in the Kucuk Menderes River in Turkey (Turgut, 2003) and the Yamuna (Kumar et al., 2012) and Brahmaputra (Chakraborty et al., 2016) in India. Banned organochlorine pesticide residues have also been reported in surface water from a national park in Turkey (Turgut et al., 2010). The elevated concentrations in the Syr Darya suggests that despite the ban on legacy POPs some of these organochlorine pesticides may continue to occur in the riverine environment of Kazakhstan. Recent reviews suggests that residues of these persistent organochlorine pesticides are widespread throughout Asia (Ali et al., 2014) and there is also growing evidence for continued use of banned pesticides as well as atmospheric recirculation throughout areas of high use in the south Asian riverine environment (Chakraborty et al., 2016). In addition to replenishment form irrigation return flow from fields with previously contaminated soils, a possible mechanism for delivering these compounds in the Syr Darya could be from long range atmospheric recirculation and deposition (Ali et al., 2014).

Snowmelt has been found to contain substantial quantitaties of lindane in the Russian Arctic and is thought to contribute substantially to dissolved pesticide loading in these nonagricultural regions (Hoferkamp et al., 2010). As in other areas of Central and southern Asia (Ali et al., 2014), snow accumulation in the Tian Shen mountains facilitates deposition of a wide variety of semi-volatile organochlorine chemicals in this region including γ-HCH. Significant concentrations of these chemicals are often released from melting snowpack (Meyer et al., 2011) and concentrations have been previously reported to peak during snowmelt in late spring, as observed in this study. Similarly, measurable concentrations of both legacy and current-use pesticides have also been reported in snowmelt from the western U.S. (Hageman et al., 2006). It seems increasingly apparent that studies of residual contamination of surface water must consider atmospheric deposition as potential source. Repeated detection of dieldrin in the Syr Darya water column in October is consistent with its greater persistence in soils compared to aldrin (Chakraborty et al., 2016) and likely attributed to inputs from irrigation return flows.

3.5 From chemical concentration to risk assessment.

The relative risk for aquatic organisms can be estimated from the detected chemical concentrations using the hazard quotient (equation 3), or “HQ” discussed previously. Using literature values, it is likely that phytoplankton and zooplankton are at a greatest risk from measured concentrations of lindane and DDT (Figure 2) than are other organisms, including fish and other vertebrates. This observation is consistent with the reports from the lower stretch of Ganga (Khuman and Chakraborty, 2019) and Brahmaputra (Chakraborty et al., 2016) rivers in

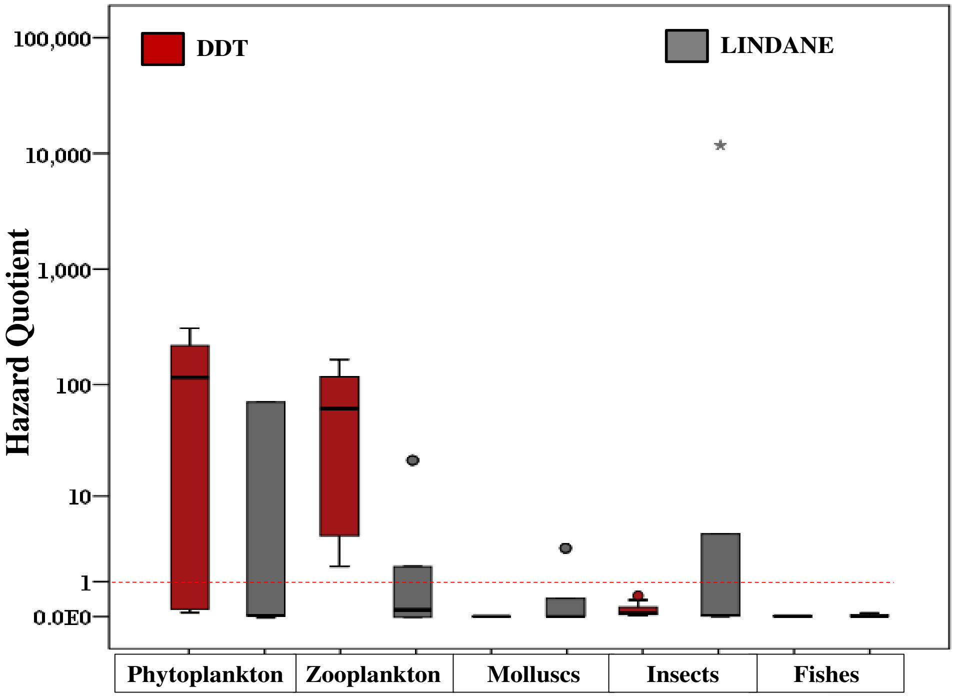


Figure 2. Box and whisker plot showing the ranges of Hazard Quotient values based on measured DDT and lindane concentrations in the Syr Darya.

India and in Pakistan (Ali et al., 2014) in south Asia where these organochlorine pesticides have been extensively used not only for agricultural purpose but also for vector control. Similarly, central Asia has a history of heavy usage of these pesticides leading to accumulations in upstream soils and glacier snowmelt that feed the Syr Darya.

Most measured pesticide concentrations were below the detection limits in sediment samples, and this observation is surprising considering that the legacy chlorinated pesticides are hydrophobic. However, the occurrence of measurable concentrations of *p,p'*-DDE in samples collected from Site 1 during June and October, might pose some risk to the ambient biota. SQGQ ranged between 0.1-1 for Site 1 during June and October 2016, indicating moderate biological effects. At 2X, the SQGQ value during October is less than 0.1. At Site 3, the June SQGQ values were between 0.1-1 indicating moderate biological effects but during October month, the SQGQ was less than 0.1 indicating no effects.

3.6 Regulatory framework---POPs convention in Central Asia

The collapse of the former Soviet Union in 1991 led to widespread abandonment of agricultural land use and crop production in Central Asia. In some areas of northern Kazakhstan, for example almost 45% of the intensive cropland reverted to grassland by the year 2001 (Kraemer et al., 2015). Since then, cropland area is slowly increasing throughout much of Central Asia mostly in previously intensive regions like the Syr Darya basin. According to the Food and Agriculture Organization statistics, pesticide use in Asia has almost doubled since 1992 and averaged between 3.5 and 4.0 kg/ha of cropland as of 2014 (WHO, 2020). Asia and the Americas lead the world in global use of pesticides for crop production. Pesticide use in some regions of Central Asia may still include application of persistent organic pollutants (POPs) banned under the Stockholm Convention. Stockpiles, and potentially illegally manufactured pesticide have undoubtably been used in many parts of Central Asia and some use may continue to be as long as supplies exist or are maintained (Ali et al., 2014; Chakraborty et al., 2016).

During an inventory of obsolete pesticides carried out in 2001 prior to Kazakhstan signing the Stockholm Convention, the country estimated that it had on hand approximately 621 tons of unusable products. Currently, pesticide stockpiles and waste materials from manufacturing may be stored unsecured in many remote areas. In the 1990s the government of Kazakhstan has banned the sale of many pesticides including lindane and DDT (Kraemer et al., 2015). Accumulated stockpiles of POPs in the Republic of Kazakhstan at the time of the report was estimated at 15.5 tons, including ~0.5 tons of DDT (East Kazakhstan oblast). In 2002, 105 tons of unwanted pesticides were disposed (buried) in the East Kazakhstan oblast (Kazakhstan, 2009), including 0.5 tons of DDT. Mixtures of pesticides of unknown composition constitute 72.0% of the total number. HCH isomers and lindane were reportedly not manufactured in Kazakhstan, but likely included among imported pesticides and stockpiles. According to the Ministry of Agriculture, HCH was not used in the territory of Kazakhstan, however a recent study reported high concentrations of organochlorine pesticides, including residues of DDT and HCH, in soils around a former storage facility in eastern Kazkahstan (Sailaukhanuly et al., 2016). These results suggest at the very least that lindane has been used or accumulated in soils upstream. Regular monitoring of POPs is not conducted in Kazakhstan or Uzbekistan and upstream use or run-off of previous use may impact water quality across its border. A lack of resources will likely inhibit the monitoring of POPs in the environment as well improving our understanding of the impact of POPs on the local environment and the health of the local residents.

4.0 Conclusions

The Aral Sea remains one of the most noteworthy hydrological and ecological case studies in the world, yet little has been published about its current condition and future prospects. Passive and grab sampling can help provide a snapshot of modern and legacy pesticide residue concentrations and risks to aquatic organisms in remote watersheds such as the Sy Darya. This study provides some insight into the occurrence and concentrations of pesticides in the Syr Darya. Low concentrations of legacy pesticides, such as lindane and DDT residues occur and could be the result of upstream use but could also be from recycled legacy contamination either through atmospheric deposition or runoff via current irrigation practices. Low concentrations of modern pesticides, such as imidacloprid, also occur early in the irrigation season and may affect suitability of river water for other purposes.

This work illustrates the possibilities and difficulties of working in remote environments, and while environmental contamination can be readily assessed by analyzing grab and integrated samples, the toxicological impacts of those chemicals may be difficult to ascertain. Many indices that may better convey the significance of concentration measurements, such as the HQ, incorrectly imply that it is relatively simple to assess toxicity across trophic levels. The robustness of those estimates, as well as the associated risk assessment, are in question and still remain to be empirically demonstrated. Future studies of current surface water quality, and the toxicological impacts of chemicals from past and present agriculture in this region is needed to ensure long term sustainable development. Finally, contamination from past and present use of banned pesticides should be considered in any ecotoxicological assessment of this region.

Acknowledgements. This study was funded through a National Science Foundation's Catalyzing New International Collaborations (CNIC) Program grant (#1427834) awarded to D. Snow., A. Kolok, S. Bartelt-Hunt and M.K. Sellin-Jefferies. Additional funding was provided through a Kazakhstan Ministry of Education and Science grant (#1547/GF4) to B. Uralbekov. Thanks to Emily Shafto, Maria Rakestraw, Nurbek Nurpesov, Zhandos Shalabayev and Ilona Matveyeva for assistance in sample collection and processing in Kazakhstan.

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