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

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4
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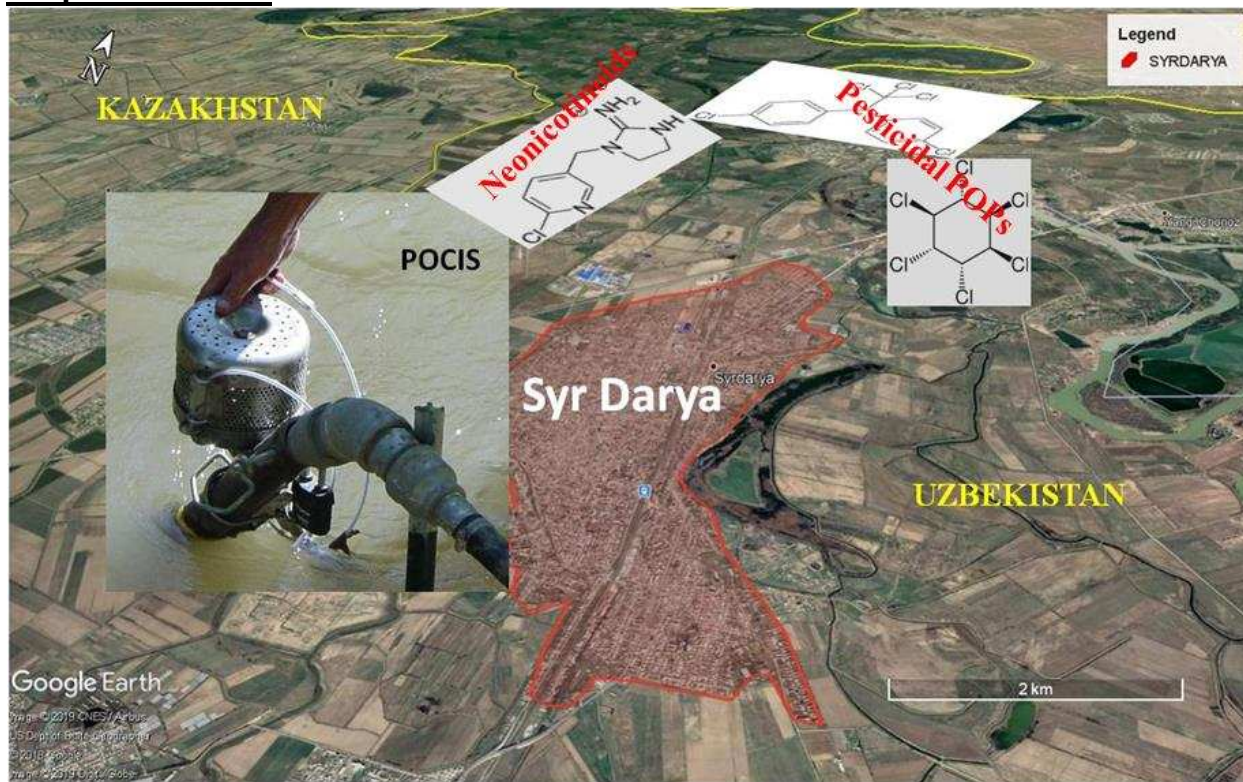
35 **Highlights**

- 36
- Modern and banned “legacy” pesticides are present in the Syr Darya
- 37
- Organochlorine contaminants occur throughout irrigation season
- 38
- Ecologic risks from exposure to aquatic organisms are likely
- 39
- Passive and grab sampling help monitor contaminants in remote watersheds

40

41

42 **Graphical Abstract**



44 **Abstract**

45 The Syr Darya is one of two major rivers in Central Asia supplying critical fresh water to
46 the Aral Sea. In spite of the river's importance and agriculturally intensive history, few studies
47 have provided a modern evaluation of and the occurrence of pesticide residues and potential
48 effects to aquatic life. The primary goal of this investigation was to determine seasonal variations
49 in ambient concentrations of modern and legacy pesticides in bottom sediment and water of the
50 Syr Darya in Kazakhstan downstream from an agriculturally intensive watershed in Uzbekistan.
51 Grab samples and passive samplers used at five remote sampling stations during June 2015 to
52 provide a baseline for ecotoxicological evaluation. Results were compared with samples
53 collected during and after the agricultural growing season. Polar organic chemical integrative
54 samplers (POCIS) were used in June and calibrated for time weighted average concentrations of
55 current use pesticides. Among legacy chlorinated pesticides measured in grab samples from the
56 river, lindane (γ -HCH) was detected most frequently with the highest concentrations occurring
57 during June. For all the sampling events, residues of lindane (γ -HCH) ranged from 0.014 $\mu\text{g/L}$ to
58 0.24 $\mu\text{g/L}$ detected in grab samples are among the highest concentrations reported for rivers
59 globally. Concentrations of γ -HCH, *p,p'*-DDE and dieldrin were highest in October when
60 dieldrin concentrations approached 0.4 $\mu\text{g/L}$. Sources of legacy pesticides may be either illicit
61 upstream use or evidence of previous atmospheric contamination of glacial meltwater. Chronic
62 exposure to these residues may lead to ecological risk to lower order organisms in both the
63 sediment and water column.

64

65 **Key words:** Syr Darya, γ -HCH, *p,p'*-DDE, risk assessment

66

67 **1. Introduction**

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

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

85 Despite the importance of the Syr Darya inflow to the revival of the north basin of the
86 Aral Sea, few recent water quality studies have been conducted on the Syr Darya. Because of the
87 difficulty in regulating use in developing countries, organochlorine pesticides, such as
88 dichlorodiphenyltrichloroethane (DDT) and lindane (γ -HCH), may continue to be used
89 upstream (Ali et al., 2014). These persistent, bio-accumulative pesticides were heavily used on

90 irrigated agricultural fields that lie within the Syr Darya watershed (Li, 1999). Consequently, the
91 Syr Darya may carry a significant load of legacy pesticides as well as modern pesticide residues,
92 such as neonicotinoid insecticides into the north basin of the Aral Sea. Legacy pesticides can be
93 highly significant contributors to exposure of stream biota (Rasmussen et al., 2015), and it is
94 increasingly clear that both modern and legacy toxins be considered in risk assessment. This
95 paper provides a novel and recent assessment of pesticide concentrations in a remote Central
96 Asian region. Few studies have examined the occurrence and ecological risk of a mixture of
97 legacy and modern pesticides in Central Asia. The goal of this study was to characterize the
98 concentrations of a wide variety of potentially toxic chemicals in an important freshwater supply
99 for the Aral Sea, and provide a baseline for ecotoxicological evaluation of these effects. Samples
100 were collected during three reconnaissance trips to the Syr Darya during the months of June,
101 August, and October 2015. Passive, *in-situ* and grab sampling techniques were tested to evaluate
102 the suitability of alternative means for sampling collection in remote regions such as south
103 Kazakhstan. A suite of different sampling techniques was employed to evaluate how newer
104 technologies may be adapted to monitoring in remote areas. Results from this study provides a
105 snapshot of chemical contaminant concentrations from samples collected over a single growing
106 season.

107 **2. Materials and methods**

108 *2.1 Site selection and general sampling*

109 Preliminary reconnaissance by local researchers identified six accessible locations for
110 sampling and collection of fish tissues along a stretch of the Syr Darya from where it enters
111 Kazakhstan (KZ) to a point upstream from the Arys River south of Turkistan, KZ (Figure 1).
112 Sampling trips were scheduled to coincide with the beginning, middle, and end of the irrigation

113 season. June sampling results provided a baseline of water quality, while samples collected in
114 August and October coincided with conditions during and at the end of the irrigation season

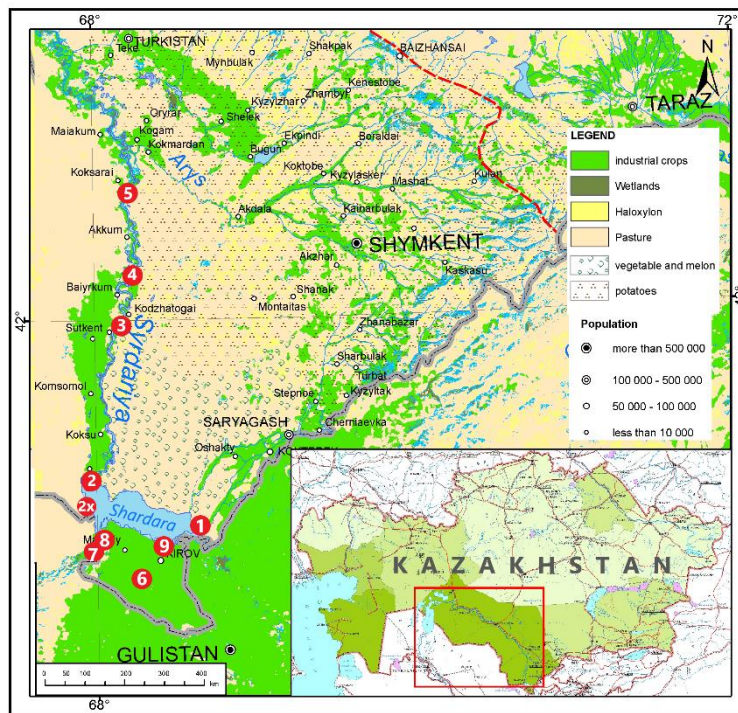


Figure 1. Map showing the six sample locations (numbers in red) along the Syr Darya, Kazakhstan. River flow is from south to north. All six in-stream locations were sampled in June and October. Coordinates are provided in supplementary material. The Shardara Reservoir is located in the bottom center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

115 (Frenken, 2013) when increased inputs of persistent pesticide residues from irrigation return
116 flows may be expected. The timing of sampling allowed for an evaluation of changes in
117 contaminant loading from irrigation return flows during a single crop growing season.

118 The Shardara multi-purpose reservoir (Figure 1), constructed between 1964 and 1967 on
119 the Syr Darya in Shardara City, KZ, provides storage for both irrigation water and hydroelectric
120 power generation and lies immediately downstream of a boundary with the country of
121 Uzbekistan. The reservoir capacity is approximately $5.2 \times 10^9 \text{ m}^3$ and, depending on upstream
122 precipitation amounts, its volume may be turned over several times annually. Sampling locations
123 were chosen to evaluate the chemical composition of river water as it crossed the border into

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

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

140 **Table 1.** Sampling regime utilized to assess the presence of pesticide residues in the Syr Darya.
 141 August samples were collected primarily to account for ephemeral irrigation canal inputs.
 142

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	

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

148 2.2. *Collection and processing of water samples*

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

162 During extraction, each sample portion was slowly aspirated under vacuum through 1/8”
163 OD Teflon™ tubing and a glass microfiber filter (Whatman GF/F, GF/F: 0.7 µm pore size,
164 binderless) held in a 25 mm Teflon™ filter holder connected using Leur adapter to each
165 preconditioned cartridge mounted on a flow control valve and vacuum flask. The glass fiber

166 filter was removed, and the holder rinsed with 100% ethanol and purified reagent (deionized
 167 distilled) water after each sample to minimize any cross contamination. Following extraction,
 168 each labelled SPE cartridge was air dried via vacuum aspiration at room temperature for 5 min,
 169 and then stored in sealed zipper bags at 4°C. Processed SPE cartridges containing extracted
 170 residues were transported to the University of Nebraska Water Sciences Laboratory (UN-WSL)
 171 and stored at -20°C until further processing. One of the two tC18 cartridges from each sample
 172 was utilized for the analysis of 22 non-organochlorine pesticides, while the other was utilized for
 173 the analysis of six organochlorine pesticides. The HLB cartridges were processed for the analysis
 174 of neonicotinoids and one organophosphate insecticide.

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

Water			
<i>tC18 cartridge 1 extracts</i>			
Acetochlor	Alachlor	Atrazine	Butylate
Chlorthalonil	Cyanazine	Deethylatrazine	Deisopropylatrazine
Dimethenamid	EPTC	Metolachlor	Metribuzin
Norflorazon	Pendimethalin	Permethrin	Prometon
Propachlor	Propazine	Simazine	Tefluthrin
Terbufos	Trifluralin		
<i>tC18 cartridge 2 extracts</i>			
4,4-DDE	4,4-DDT	α -HCH	Aldrin
β -HCH	δ -HCH	Dieldrin	γ -HCH (Lindane)
Heptachlor			
<i>HLB cartridge extracts</i>			
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
Quinoxifen	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

178

179 *2.3. SPE Cartridge elution*

180 The tC18 SPE cartridges used for non-organochlorine pesticide analysis (Table 2) were

181 eluted with 6 mL of ethyl acetate, and eluate spiked with 5 µg each of ¹³C₃-labelled atrazine,

182 deethylatrazine (DEA) and desisopropylatrazine (DIA) added and used as internal standards.

183 Quantitation by isotope dilution was used for atrazine, DEA and DIA and other residues were

184 quantified using ¹³C₃-atrazine. Ethyl acetate extracts were evaporated under nitrogen to ~1 mL

185 and residual water was removed with the addition of anhydrous sodium sulfate, followed by

186 quantitative transfer using 2 mL of ethyl acetate to a clean borosilicate culture tube. After

187 vortexing, the solvent volume was then further reduced to 200 µL under dry nitrogen.

188 Concentrated extracts were transferred to autosampler vials outfitted with 300 µL silane-treated

189 glass inserts. Extracts were analyzed for the compounds listed in Table 2 by gas

190 chromatography-mass spectrometry (GC/MS) with selected ion monitoring as described

191 previously (Cassada et al., 1994). Further details of the analytical method and results of a

192 validation study are provided in supplementary materials.

193 The second set of tC18 SPE cartridges, used for preconcentration of chlorinated
194 pesticides, were eluted with 3 mL of acetone, followed by 3 mL of hexane, and 3 mL of ethyl
195 acetate. Solvent eluate was spiked with 5 µg of labelled internal standards (¹³C₃-atrazine, ¹³C₃-
196 deethylatrazine, and ¹³C₃-deisopropylatrazine (Merck Sharp & Dohme/Isotopes, St. Louis, MO
197 USA), and slowly evaporated under dry nitrogen. Residual water was removed with anhydrous
198 sodium sulfate during the concentration process and quantitatively transferred to clean
199 borosilicate culture tubes using additional ethyl acetate. Each extract was evaporated completely,
200 residues dissolved in 200 µL ethyl acetate, and finally transferred to a 300 µL silane-treated glass
201 insert for analysis of chlorinated insecticides (Table 2) by full scan GC/MS. Method detection
202 limits were determined by extraction and analysis of eight (8) replicate samples of purified
203 reagent water fortified at 0.3 µg/L, and range from 0.007 µg/L for 4-DDE to 0.053 µg/L for
204 aldrin (Table S7).

205 Compounds retained on polymeric HLB SPE cartridges were eluted and analyzed for
206 polar neonicotinoid and organophosphorus insecticides (Table 2) using liquid chromatography-
207 tandem mass spectrometry (LC-MS/MS). Full details of the extraction, elution and instrumental
208 method is included in the supplemental materials. Standards for each of the target analytes, as
209 well as isotopically-labelled standards (d4-Imidacloprid, d3-Thiamethoxam and d6-Metalaxyl),
210 were obtained from Sigma Aldrich (St. Louis, MO). Each HLB SPE cartridge was eluted under
211 vacuum with 6 mL of high purity methanol (Optima, Fisher Scientific, St. Louis, MO), the eluate
212 was spiked with 50µL of 1.0 ng/µL internal standard mix, and completely evaporated under dry
213 nitrogen in borosilicate culture tubes. The residue was dissolved in 50 µL high purity methanol
214 and mixed with 200 µL purified (distilled deionized, organic free) reagent water prior to LC-
215 MS/MS analysis. A well end-capped 250 x 2 mm x 5 µm BetaBasic C18 reverse phase HPLC

216 column (ThermoFisher, St. Louis, MO USA) was used for the gradient separation with 0.15%
217 formic acid in methanol/water (97:3) and 0.15% formic acid in water/methanol (97:3) at a
218 constant temperature of 50°C and a flow rate of 0.3 mL/min. Analysis run time was 30 minutes,
219 with positive ion mode atmospheric pressure chemical ionization (APCI) on a Waters Quattro
220 Micro triple quadrupole mass spectrometer (Waters Corporation, Milford, MA USA). A pseudo-
221 molecular ion $[M+H]^+$ for each compound was selected as the parent ion for fragmentation, and
222 corresponding fragment ion(s) selected for identification and quantitation (Table S7). Method
223 detection limits ranged from 0.005 and 0.025 $\mu\text{g/L}$.

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

230 *2.3. Collection and chemical analysis of sediment grab samples*

231 Sediment samples (~200 g) were collected in 250 mL amber jars, held on ice and then
232 transferred to a freezer for subsequent extraction using microwave assisted solvent extraction
233 with analysis by GC/MS. Briefly, five (5.00) grams of wet sample was weighed into a 10
234 milliliter (mL) TeflonTM microwave digestion vessel, spiked with 200 ng surrogate compounds,
235 and thoroughly mixed with 6 mL of acetonitrile. Batches of up to 40 samples are then subjected
236 to microwave irradiation (400W) for 10 minutes at 90°C using a MARS Xpress microwave
237 digestion system (CEM, Matthews, NC USA). After cooling and decanting solvent, sediment
238 was mixed with an additional 6 mL of acetonitrile, allowed to settle and then solvent combined

239 with the first portion. Extract volume is then reduced to near 1-2 mL under dry nitrogen and
240 spiked with 500 ng of isotope-labelled internal standards. The acetonitrile was mixed with 100
241 mL of water, and extracts purified by reverse phase (tC18) solid phase extraction (SPE)
242 cartridges used in water extraction. Absorbed compounds were then eluted with ethyl acetate and
243 analyzed by GC/MS as described above. Method detection limits, determined from extraction
244 and analysis of eight replicates of 5 grams of clean sand spiked at 4.0 ng/g, ranged from 0.4 ng/g
245 for trifluralin to 5.0 ng/g for dieldrin (Table S5).

246 *2.4. Deployment, calibration and chemical analysis of POCIS*

247 Polar organic chemical integrative samplers (POCIS) is an effective passive water
248 sampling of polar organic compounds at spatial and temporal scale. We have therefore estimated
249 the sampling rates for neonicotinoids in the laboratory before deploying those in the field. Nine
250 POCIS were obtained from Environmental Sampling Technologies (St. Joseph, MO USA) were
251 placed in three stainless-steel deployment canisters and deployed at three of the sampling sites
252 for seven days during the June sampling campaign. One POCIS canister, deployed at location 2X
253 (Figure 1) was missing and presumed lost at the conclusion of the deployment. Upon retrieval,
254 each POCIS deployment canister was placed in a plastic bag and put in a cooler containing ice
255 packs until transport to the laboratory at Al-Farabi KazNU. Within three days of retrieval, the
256 HLB sorbent from each POCIS was removed and quantitatively transferred to glass
257 chromatography columns containing a plug of glass wool by gently rinsing the polymer with
258 purified deionized water. After draining the water, three 20 mL portions of reagent grade
259 acetonitrile were used to slowly extract and elute compounds from the sorbent. The POCIS
260 extracts were evaporated under dry nitrogen to ~30 mL, stored in glass vials with TeflonTM-lined
261 caps and transported to the Water Sciences Laboratory, University of Nebraska, USA for elution

262 and analysis of pesticide residues. After spiking the extract with internal standards listed in the
263 method for water samples, the extracts were evaporated to dryness, spiked with 50 μL of 1.0
264 $\text{ng}/\mu\text{L}$ internal standard mix, and completely evaporated under dry nitrogen in borosilicate
265 culture tubes. The residue was dissolved in 50 μL high purity methanol and mixed with 200 μL
266 purified (distilled deionized, organic free) reagent water and analyzed for neonicotinoid
267 insecticides and organophosphate insecticides (Table 2).

268 Uptake rates for the neonicotinoids and dimethoate using POCIS were determined in the
269 laboratory using procedures detailed previously (Bartelt-Hunt et al., 2011). Briefly three POCIS
270 were suspended in stirred 2-liter aqueous solutions spiked with 5 $\mu\text{g}/\text{L}$ of all compounds in
271 $\text{pH}=7.0$ buffered reagent water. A fourth stirred solution without POCIS was stirred and used a
272 control. Fifty milliliter portions of each solution were removed at the beginning of the uptake
273 experiment and after 1 day, 3 days, 7 days and 14-days of exposure to the POCIS device. The
274 aqueous concentration was measured in each solution and the observed decrease in the aqueous
275 concentration of neonicotinoids over time was modeled by using first-order kinetics based on the
276 following equation:

$$277 \quad C_w(t) = C_w(0) \exp[-kt] \quad (1)$$

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

$$282 \quad R_s = kU V_T \quad (2)$$

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

286 *2.4. Use and processing of continuous low-level aquatic monitoring (C.L.A.M.) samplers*

287 The C.L.A.M. sampler devices were outfitted with HLB-H Disks (#A50-HLB-H) and
288 used as described by the manufacturer (C.I. Agent StormWater Solutions, Louisville, KY USA).
289 Total sample volumes at each location were calculated by estimating total flow through the
290 C.L.A.M. over the extraction period per manufacturer recommendation. The C.L.A.M. (#HLB-H
291 Disk A50-HLB-H) samplers were processed for the analytes listed in Table 2. Elution followed
292 modified manufacturer protocols by slowly passing 50 mL of methanol through the disk
293 followed by 50 mL of methylene chloride directly into a 150 mL RapidVap N2 glass vial
294 (Labconco Corp, Kansas City, MO USA). The resultant mixture was spiked with 5,000 ng each
295 of $^{13}\text{C}_3$ - atrazine, $^{13}\text{C}_3$ -deethylatrazine (DEA) and $^{13}\text{C}_3$ -deisopropylatrazine (DIA), and 2000 ng
296 of terbuthylazine and butachlor surrogates, and then evaporated completely at 40°C under
297 nitrogen. The concentrated residue was dissolved in hexane, transferred to 300 μL silane-treated
298 glass insert for analysis of pesticides by full scan GC/MS (Cassada et al., 1994). Instrumental
299 conditions are the same as those listed for herbicide and organophosphorus insecticides
300 determined in grab samples.

301 *2.7. Risk Assessment*

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

$$305 \quad \mathbf{HQ} = \frac{\mathbf{MEC}}{\mathbf{PNEC}} \quad \mathbf{(3)}$$

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

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

$$318 \quad \text{SQGQ} = \sum_{x=1}^n \frac{PELQx}{n} \quad (4)$$

$$319 \quad \text{where, } PELQx = \frac{Cx}{PEL} \quad (5)$$

320 where, *PEL* is the guideline value for contaminant “x”, *C_x* is the measured concentration of the
321 same contaminant, and “n” is the number of contaminants for which sediment guidelines are
322 available. SQGQ values < 0.1 indicates no effects; 0.1 ≤ SQGQ < 1 indicates moderate effects and
323 SQGQ ≥ 1, high adverse biological effects (Costa et al., 2011).

324 **3. Results and discussion**

325 A summary of pesticide residues detected is presented in Table 4. Even with the large
326 number of target compounds measured, the number of detections and relative concentrations is
327 remarkably low given the agriculturally intensive history of this region. Residues of current use
328 and legacy chlorinated pesticides were detected in grab samples, bottom sediment and passive

329 sampling devices. The highest concentrations were found among legacy pesticide residues in
 330 both the water column and sediment samples. Monthly recorded precipitation was highest
 331 Zhetysay, KZ located 10 km south of Shardara reservoir (Figure 1) in May ~24 mm and dropped
 332 to 1 mm or less for June through October. Discharge at Site 1 was highest in May and averaged
 333 167 m³/sec during this period (Supplemental Information). Based on recorded precipitation and
 334 discharge measurements, June samples should correspond periods when instream concentrations
 335 are from precipitation triggered run-off, while August and October samples would be more
 336 characteristic of irrigation water supplied pesticides (Figure S1).

337 3.1. Legacy pollutants in the Syr Darya

338 Lindane were detected in nearly all of the surface water grab samples at concentrations
 339 ranging from 0.014 µg/L to 0.24 µg/L. The average (±SD) lindane concentration across all
 340 sampling dates was 0.130±0.06 µg/L and the highest concentrations were measured in the June
 341 samples (Table 4). The organochloride insecticide aldrin and its metabolite dieldrin were
 342 detected in grab samples collected in August and October at concentrations ranging up to 0.37
 343 µg/L. Sediment samples contained residues of *p,p'*-DDE at concentrations ranging from 0.18 to
 344 2.45 ng/g upstream and downstream (give the sampling locations) of the Shardara Reservoir,
 345 and trifluralin at 0.20 ng/g upstream of the reservoir (Site 1) and at 0.14 ng/g in the reservoir
 346 grab sample (Site 2), both collected in June (Table 4). Other chlorinated pesticides, including
 347 heptachlor and *p,p'*-DDT, as well as the hexachlorohexane isomers (α -HCH and β -HCH)
 348 typically found as manufacturing impurities were not detected in any grab samples.

349 **Table 4.** Detected pesticide concentrations measured from the Syr Darya sampling sites. POCIS
 350 concentrations represent time-weighted average concentration determined from the mass (±
 351 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
<i>Grab Samples - Water (µg/L)</i>							
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)							
<i>p,p'</i> -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

352

353 3.2. Current-use neonicotinoid and organophosphorus pesticides

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

359 3.3. Residues in POCIS and C.L.A.M. sampler extracts

360 The C.L.A.M. samplers used in the June sampling contained trace levels (~0.05 µg/L) of
361 atrazine at Site 1 and cyprodinil at Site 2, but all other compounds were below detection limits.
362 The absence of residue detections was potentially due to variability in volume of water extracted
363 at each location, ranging from ~0.5 to 3.8 liters primarily due to the high levels of suspended
364 solids. The volume extracted is estimated based on the field-measured flowrate and time elapsed

365 between sampler submersion and removal and this flow rate varies considerably depending on
366 the battery condition and time until the extraction disk filter frit became plugged. Differences in
367 concentrations and frequency of detections between C.L.A.M. sampler and other devices or grab
368 samples has been previously reported (Coes et al., 2014; Ensminger et al., 2017). Generally,
369 frequency of detection is reported to be higher than those measured from grab samples but
370 concentrations may be lower. The C.L.A.M. sampler may be very effective for surface water
371 with low levels of suspended solid but likely has limited application in turbid river water.

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

379 Passive sampling provides low detection limits and ability to integrate over long
380 sampling times which is good incentive for their use in toxicological studies (Alvarez et al.,
381 2008; Kolok et al., 2014; Sellin et al., 2009). The results of the POCIS uptake rate experiments,
382 provided in the supplemental materials (Table S9), were used to convert pesticide mass
383 recovered to time weighted average concentrations during the 7-day exposure period in June
384 2015 (Table 4). Sampling uptake rates for neonicotinoids were found to vary between 0.24 to
385 0.76 L/day excluding dinotefuran, which showed almost negligible uptake to the POCIS. Low
386 uptake for this compound is likely due to the fact that this compound is a weak base ($pK_a = 12.6$)
387 and high water solubility (54,300 mg/L). Linear rates of uptake rates (r^2 between 0.6 to 0.9),

388 observed for acetamiprid, clothianidin, imidacloprid, metalaxyl, thiacloprid and thiamethoxam
389 (Table S9), permitted estimation of average concentrations in the river where residues were
390 detected in POCIS. Estimated time weighted average (TWA) concentrations were below 0.005
391 µg/L. Higher TWA levels were measured in the POCIS deployed upstream from the Shardara
392 Reservoir (Figure 1). None of the herbicides, pyrethroids, traditional organophosphorous
393 insecticides, or fungicides were detected in the grab samples.

394 *3.4 Occurrence and Potential Sources of Legacy Pesticides*

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

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

413 **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)

414
415 Mean lindane concentrations in Syr Darya are among the highest reported for rivers of
416 China, Pakistan, India, and Africa (Table 5). Comparable γ -HCH concentrations have been
417 reported in the Kucuk Menderes River in Turkey (Turgut, 2003) and the Yamuna (Kumar et al.,
418 2012) and Brahmaputra (Chakraborty et al., 2016) in India. Banned organochlorine pesticide
419 residues have also been reported in surface water from a national park in Turkey (Turgut et al.,
420 2010). The elevated concentrations in the Syr Darya suggests that despite the ban on legacy
421 POPs some of these organochlorine pesticides may continue to occur in the riverine environment
422 of Kazakhstan. Recent reviews suggests that residues of these persistent organochlorine
423 pesticides are widespread throughout Asia (Ali et al., 2014) and there is also growing evidence
424 for continued use of banned pesticides as well as atmospheric recirculation throughout areas of
425 high use in the south Asian riverine environment (Chakraborty et al., 2016). In addition to
426 replenishment from irrigation return flow from fields with previously contaminated soils, a
427 possible mechanism for delivering these compounds in the Syr Darya could be from long range
428 atmospheric recirculation and deposition (Ali et al., 2014).

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

442 *3.5 From chemical concentration to risk assessment.*

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

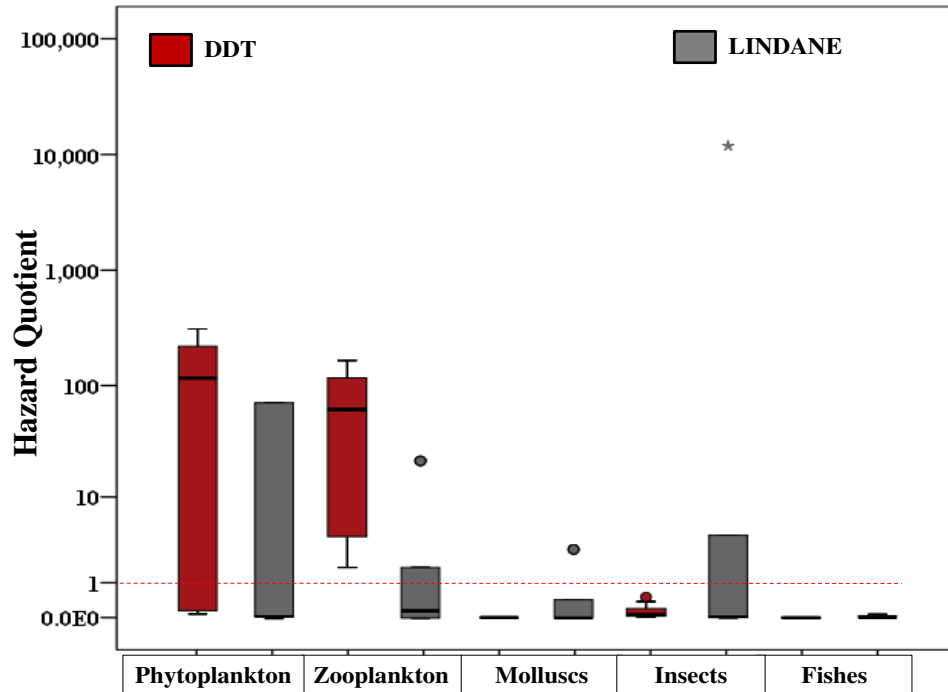


Figure 2. Box and whisker plot showing the ranges of Hazard Quotient values based on measured DDT and lindane concentrations in the Syr Darya.

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

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

461

462 *3.6 Regulatory framework---POPs convention in Central Asia*

463 The collapse of the former Soviet Union in 1991 led to widespread abandonment of
464 agricultural land use and crop production in Central Asia. In some areas of northern Kazakhstan,
465 for example almost 45% of the intensive cropland reverted to grassland by the year 2001
466 (Kraemer et al., 2015). Since then, cropland area is slowly increasing throughout much of
467 Central Asia mostly in previously intensive regions like the Syr Darya basin. According to the
468 Food and Agriculture Organization statistics, pesticide use in Asia has almost doubled since
469 1992 and averaged between 3.5 and 4.0 kg/ha of cropland as of 2014 (WHO, 2020). Asia and
470 the Americas lead the world in global use of pesticides for crop production. Pesticide use in
471 some regions of Central Asia may still include application of persistent organic pollutants
472 (POPs) banned under the Stockholm Convention. Stockpiles, and potentially illegally
473 manufactured pesticide have undoubtedly been used in many parts of Central Asia and some use
474 may continue to be as long as supplies exist or are maintained (Ali et al., 2014; Chakraborty et
475 al., 2016).

476 During an inventory of obsolete pesticides carried out in 2001 prior to Kazakhstan
477 signing the Stockholm Convention, the country estimated that it had on hand approximately 621
478 tons of unusable products. Currently, pesticide stockpiles and waste materials from
479 manufacturing may be stored unsecured in many remote areas. In the 1990s the government of
480 Kazakhstan has banned the sale of many pesticides including lindane and DDT (Kraemer et al.,
481 2015). Accumulated stockpiles of POPs in the Republic of Kazakhstan at the time of the report
482 was estimated at 15.5 tons, including ~0.5 tons of DDT (East Kazakhstan oblast). In 2002, 105
483 tons of unwanted pesticides were disposed (buried) in the East Kazakhstan oblast (Kazakhstan,

484 2009), including 0.5 tons of DDT. Mixtures of pesticides of unknown composition constitute
485 72.0% of the total number. HCH isomers and lindane were reportedly not manufactured in
486 Kazakhstan, but likely included among imported pesticides and stockpiles. According to the
487 Ministry of Agriculture, HCH was not used in the territory of Kazakhstan, however a recent
488 study reported high concentrations of organochlorine pesticides, including residues of DDT and
489 HCH, in soils around a former storage facility in eastern Kazakhstan (Sailaukhanuly et al., 2016).
490 These results suggest at the very least that lindane has been used or accumulated in soils
491 upstream. Regular monitoring of POPs is not conducted in Kazakhstan or Uzbekistan and
492 upstream use or run-off of previous use may impact water quality across its border. A lack of
493 resources will likely inhibit the monitoring of POPs in the environment as well improving our
494 understanding of the impact of POPs on the local environment and the health of the local
495 residents.

496 **4.0 Conclusions**

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

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

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