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

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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

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42   <u>**Graphical Abstract**</u>

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Abstract

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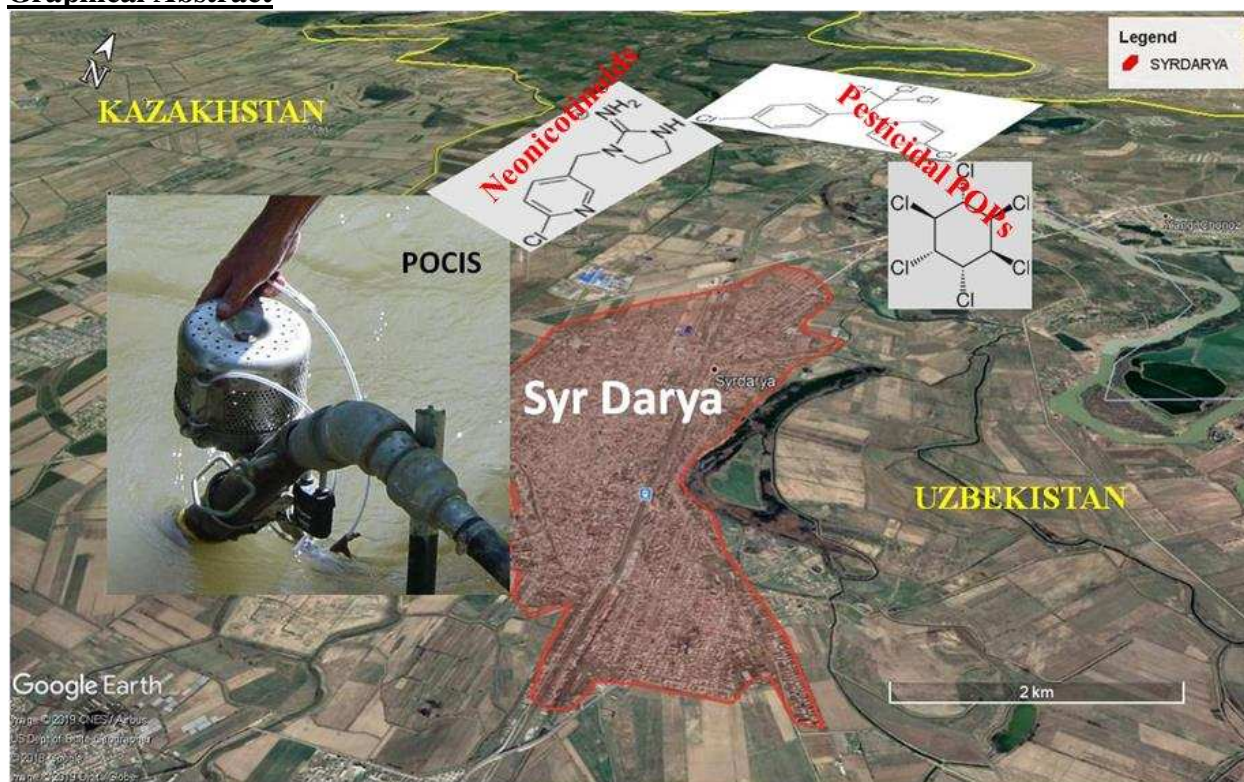
45   The Syr Darya is one of two major rivers in Central Asia supplying critical fresh water to

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 µg/L to

58 0.24 µg/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 µg/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

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

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
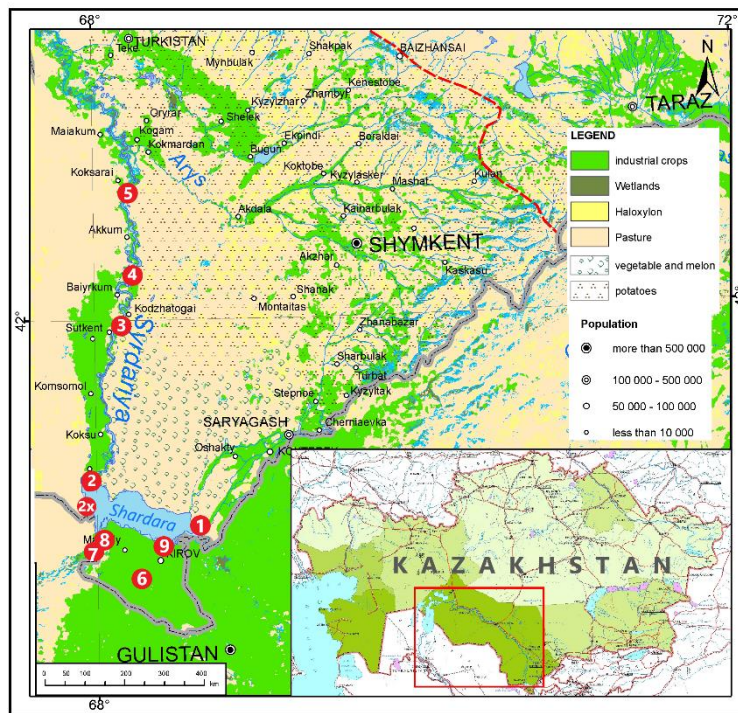
Figure 1. Map showing the six sample locations (numbers in red) along the Syr Darya, Kazakhstan. River flow is from south to north. All six in-stream locations were sampled in June and October. Coordinates are provided in supplementary material. The Shardara Reservoir is located in the bottom center 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 5.2×10^9 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 4ºC. 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^{TM} tubing and a glass microfiber filter (Whatman GF/F, GF/F: 0.7 μm pore size,

164 binderless) held in a 25 mm Teflon^{TM} 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			
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

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 $^{13}C_3$-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 $^{13}C_3$-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 ($^{13}C_3$-atrazine, $^{13}C_3$-

196   deethylatrazine, and $^{13}C_3$-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 µg/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) Teflon^{TM} 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 Teflon[TM]-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 ng/µL 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 µg/L of all compounds in

271 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 $$C_w(t)= C_w(0) \exp[-kt] \qquad (1)$$

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 $$R_s = k_U V_T \qquad (2)$$

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 $^{13}C_3$- atrazine, $^{13}C_3$-deethylatrazine (DEA) and $^{13}C_3$-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
$$HQ = \frac{MEC}{PNEC} \qquad (3)$$

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

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

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; $0.1 \le SQGQ < 1$ indicates moderate effects and

323    $SQGQ \ge 1$, 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
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

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; Arditsoglou and Voutsa, 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 (pKa= 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, chothianidin, 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 form 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 quantitaties 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
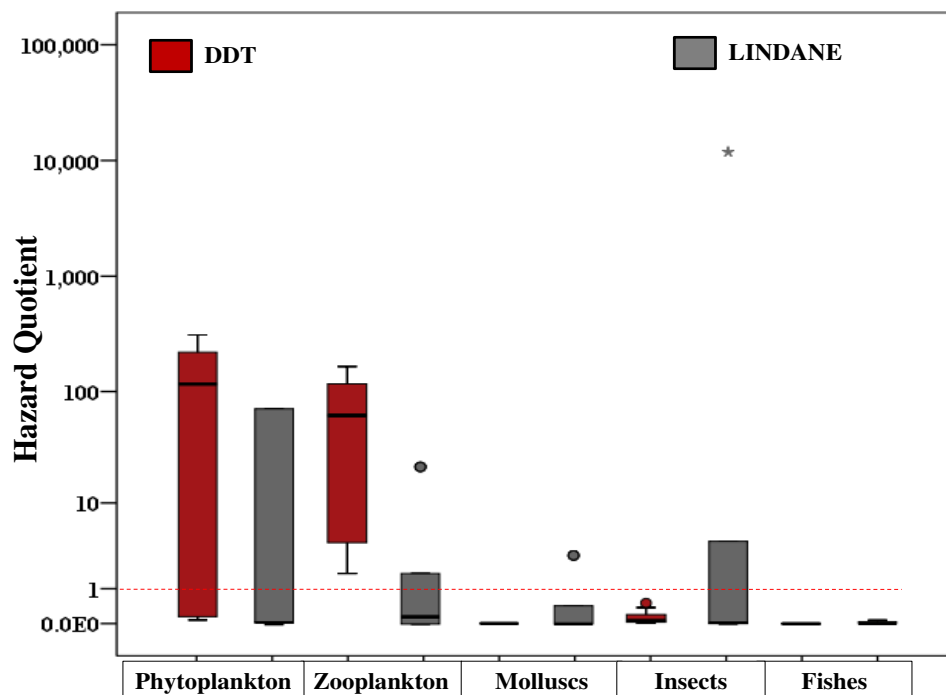
Figure 2. Box and whisker plot showing the ranges of Hazard Quotient values based on measured DDT and lindane concentrations in the Syr Darya.

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

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,

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 Kazkahstan (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.

523
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