11TH FORUM OF THE INTERNATIONAL HCH AND PESTICIDE ASSOCIATION

The legacy of persistent organic pollutants in Azerbaijan: an assessment of past use and current contamination

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Received: 3 May 2012 / Accepted: 5 July 2012 / Published online: 24 July 2012 Springer-Verlag 2012

Abstract Azerbaijan has a history of production and heavy use of organochlorine pesticides (OCPs) with use focused in the main agricultural lowland region centred on the Kur River. Using a number of data sources, including archived reports from several government ministries, we attempt to construct production and use inventories for dichlorodiphenyltrichloroethane (DDT) and HCHs and compare these to scientific estimates of production and use of these chemicals in the 1960s to the 1980s. Notable discrepancies are evident particularly for DDT, with Azeri government records indicating much higher use (147-fold) than that estimated by the international scientific community. Soil and river sediment data from the 1980s and 2000s are also presented. While it is recognised that analytical uncertainties remain high for these older data (generated by GC-ECD), there is some evidence to show a decline in concentrations for some OCPs over this period. Extremely high concentrations of OCPs are

Responsible editor: Philippe Garrigues

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evident for soils sampled in the vicinity of obsolete pesticide storage sites (found in numerous locations around the agricultural lowlands) and these levels may pose a health risk to wildlife and humans. River sediment data indicate high levels of both OCPs and polychlorinated biphenyls (PCBs), particularly downstream of the confluence of the two main rivers, the Kur and Araz. Particle-bound annual fluxes from the Kur River into the Caspian Sea are estimated for PCBs and OCPs and these are likely to influence levels observed in local coastal sediments, with agreement between river sediment data generated in the early 2000s and coastal marine sediment data generated from separate studies. We recommend that monitoring efforts should focus on soils in agricultural areas and around pesticide storage and production facilities as these soils will continue to provide a source of POPs to the regional environment.

Keywords Organochlorine pesticides · Legacy contaminants · Chemical usage · Soils · Sediments

Introduction

Organochlorine pesticides (OCPs) were widely produced and applied in the Former Soviet Union (FSU) from the 1950s onwards as a result of extensive agricultural reforms undertaken as part of the Soviet era system of a planned economy (Fedorov and Yablokov 1999, 2004). There have been a number of studies on OCP pollution with particular focus on the production and use of these chemicals within the FSU (Bodo 1998; Voldner and Li 1995; Breivik et al. 1999; Fedorov and Yablokov 1999, 2004; Li et al. 2004, 2006a). Information on production quantities and usage, particularly in certain agricultural areas are difficult to obtain for the FSU, and in many cases, the available information is sparse or incomplete (Fedorov and Yablokov 1999). However, attempts to quantify these numbers are important with regards to understanding and estimating emissions, particularly at a regional scale, and for estimating concentrations of persistent organic pollutants (POPs) on a hemispheric or global scale. Recent studies now show that although production and use of many OCPs has ceased, their residues still persist in the environment, are subject to continued cycling between environmental compartments, undergo long-range transport and contribute to background levels of POPs at the hemispheric/global scale (Breivik et al. 2006; Iwata et al. 2002; Li et al. 1998; Li and Macdonald 2005; Lohmann et al. 2007; Wania and Mackay 1996).

Azerbaijan was a republic of the FSU which produced OCPs as a part of its chemical industry as well as used OCPs in its agricultural regions. To assess the legacy of OCP pollution, the Government of Azerbaijan, international organisations (UN Food and Agriculture Organisation, International HCH and Pesticide Association (www.ihpa.info) and a number of Azeri non-government organisations (NGOs) such as UNEP-ECORES NatCom, Ruzgar etc.) have been making efforts to implement various projects in the region to understand and tackle contamination issues as part of the requirements of the UNEP Stockholm Convention on Persistent Organic Pollutants (POPs; http://chm. pops.int/default.aspx). However, the issue of contamination in this region is complex, as Azerbaijan is one of five states that border the Caspian Sea, where high concentrations of these chemicals, particularly OCPs, have been observed in a variety of marine fauna (Kajiwara et al. 2003; 2008). The purpose of this review is to examine the use and levels of POPs in the environment of Azerbaijan over the last 50 years or so, using mainly unpublished and historical archives from Azeri government ministries. The intention is to reconcile these data with estimated usage numbers and contemporary measurements of POPs in soil, air and other matrices and also to examine the transfer of POPs between key environmental compartments, particularly the loading of OCPs to the Caspian Sea. In addition, this overview to POPs use in Azerbaijan will serve to place this country in the regional context and serve as a benchmark for the assessment of POPs use in other FSU countries.

Azerbaijan

Azerbaijan is located between 38°41'N and 44°50'E, on the western shore of the Caspian Sea with ~825 km of coastline. The country borders Russia's Dagestan Autonomous Republic to the north, Armenia and Georgia to the west and northwest, and Turkey and Iran to the southwest and south,

respectively, as illustrated in a later figure in this paper (see Fig. 5). Kazakhstan and Turkmenistan also border the Caspian Sea, to the northeast and east. The total area of Azerbaijan is ~86,600 km². Located in the region of the Southern Caucasus, the country is predominantly mountainous having the Greater Caucasus, Lesser Caucasus, Talish and North Iranian mountains surrounding the Kur lowland, which stretches from the central part of the country to the east and southeast. The Kur lowland is the main agricultural area of Azerbaijan supporting mainly cereal crops, vineyards and cotton. The climate in Azerbaijan varies from semi-arid and dry steppe to a moderate, cold and mountainous tundra types in the Caucasus. Average precipitation for the period 2008-2012 is 447 mm year⁻¹ (FAO 2011; Kosarev and Kostianoy 2005). The annual average air temperature is approximately 14 °C in the Kur-Araz lowlands and 0 °C in the mountains (Verdiyev 2009).

The chemical industry has long been concentrated on the Apsheron peninsula that extends into the Caspian Sea, particularly Baku, the capital of Azerbaijan, and Sumgayit, a small town located ~35 km north of Baku. These cities were major centres of the FSU's chemical industry and remain major centres for the oil/petrochemical industry within Azerbaijan to this day. Industrial effluents and domestic wastewater of both cities, coupled to operations associated with the chemical industry, have resulted in POPs pollution entering the coastal environment and posing a risk to both humans and wildlife (Bickham et al. 2003; Matson et al. 2005a; Swartz et al. 2003).

Farming practices and use of pesticides

Relative to other republics within the FSU, Azerbaijan had a well-developed agricultural infrastructure. However, extensive agricultural development and unsustainable land use practices resulted in environmental pollution through uncontrolled application of fertilisers and pesticides (World Bank 2006). The mostly cultivated areas are located in the central part of the country along the Kur River, i.e. Kur lowland, and presumably, the part of the country with the highest pesticide use.

OCPs were widely used in agriculture, particularly for cotton and cereal production as well as in vineyards. Alt-stadt (1992) reports that in the 1970s, 5.5 million tonnes of cotton were produced in Azerbaijan compared to 2.4 million tonnes in the 1960s. In the 1970s, with abstraction of water from the Araz and Kur rivers for the improvement of irrigation, Azerbaijan produced 7.4 million tonnes of grapes, or 3.6 times more than in the previous 25 years (Altstadt 1992).

The data of the Statistical Committee of Azerbaijan (StatCom 2012) provide information about total area of land used for crop production in the period 1965–2009. The average cotton and vineyard cropland area in 1965–1994

was 257 kha. For the later period of 1998–2009, the area of land subject to cotton cultivation and vineyards had decreased to 36 kha in favour of increasing wheat cultivation, and this resulted in a total cultivated agricultural area in the country to be ~1,705 kha by 2009 (StatCom 2012). According to Avazova (1993), the total area of arable lands in Azerbaijan in 1983–1992 comprised ~2,412 kha, of which ~1,389 kha was cultivated under agricultural crops. These data for agricultural cultivated land area matched the data of the Statistical Committee of ~1,302 kha in the same period.

However, the extensive usage of fertilisers and pesticides to boost production of cotton and grapes has resulted in both health and environmental concerns (Fedorov and Yablokov 1999, 2004). For example, concerns over pesticide exposure in the late 1980s focused on the harm to agricultural workers and animals kept near vineyards (Altstadt 1992). Aerial application of many pesticides was commonly undertaken mainly due to the absence of efficient land-based delivery systems. This method of application implies the wider dispersal of pesticides compared to direct seed treatment and other application methods, and is likely to have resulted in the wider contamination of the environment (Voldner and Li 1995).

A large number of pesticides have been applied in Azeri agriculture but have not been monitored (Fedorov and Yablokov 2004). Pesticides widely applied in Azerbaijan in 1983-1991 include, but are not limited to: organochlorine (hexachloran (HCH), endosulfan, and dichlorodiphenyltrichloroethane (DDT), until 1985; kelthane, until 2000); organophosphorous (methyl parathion 40 %, dimethoate 40 %, phosalon 35 %, butifos 70 % and malathion 50 %); organomercury (chlorethylmercury under the commercial name 'granozan'); organonitrogen (atrazine, simazine and isophene); carbamate (carbaryl under the commercial name 'sevin'); polychlorocamphene (polydofen) and other formulations (Avazova 1993; Fedorov and Yablokov 2004; Mustafayev et al. 2005). Polychlorinated cyclodienes, such as aldrin, endrin, dieldrin and chlordane were neither produced nor used in Azerbaijan, except for small amounts imported for experimental purposes in the mid-1960s. Mustafayev et al. (2005) reports that in 1988, the list of imported pesticides included technical HCH (1,542 tonnes) and kelthane (287 tonnes). Of this, only 326 tonnes of technical HCH and 40.2 tonnes of kelthane were actually used, as indicated in Table 1 (Avazova 1993)

In the early 1990s, the agriculture of Azerbaijan dramatically deteriorated due to the undeclared war by neighbouring Armenia, resulting in the break-up of Azerbaijan from the Soviet Union, and the dismantling of the state-owned agricultural cooperatives. However, since this period, the revival of the oil and gas industry has resulted in an improvement of the economy, including agriculture. In 1997, the Government of Azerbaijan initiated the privatisation

 Table 1
 Usage (tonnes) of organochlorine pesticide formulations in the agriculture of Azerbaijan 1983–1992 (Avazova 1993)

Year	DDT, 5.5 %	Technical HCH, 12 %	Kelthane, 20 % (dicofol)	Thiodan, 35 %, 50 % (endosulfan)
1983	25	541	209	_
1984	2.5	524	45.4	_
1985	0.3	517	42.0	_
1986	-	465	24.2	314
1987	-	400	38.1	414
1988	_	326	40.2	521
1989	_	185	57.4	116
1990	_	135	23.5	44
1991	_	75.0	12.9	3
1992	-	—	-	0.5

The percentage next to the commercial name of each pesticide indicates the content of the active ingredient and the type of formulation. For example, 'thiodan 50 %' is a powder formulation while 'thiodan 35 %' is a concentrated emulsion, both containing 50 % and 35 % of endosulfan as an active ingredient by weight, respectively (Avazova 1993; Fedorov and Yablokov 2004)

programme of agricultural lands, resulting in the transfer of 95 % of the national lands to private citizens. The collective and state farms that were common in the Soviet era have been dismantled and transferred to private ownership. During the same year, the government passed 'The Law on Pesticides and Agrochemical Substances'. The control over registration, import, storage, use and disposal of pesticides has now been transferred to the State Phytosanitary Control Service under the Ministry of Agriculture of the Republic of Azerbaijan

The legacy of past pesticide use is most apparent through the occurrence of abandoned agrochemical storage and distribution facilities/warehouses set up during the Soviet collective farm period. These sites were later used as repositories for unused and old agrochemical stocks and represent current 'hot spots' of contamination (referred to here on in as 'obsolete pesticide stocks') across Azerbaijan. At these facilities, the pesticides are often stored together with mineral fertilisers (Cobban 2011). Transport, packaging, labelling and handling of pesticides generally did not conform with international standards, so that pesticides were supplied in 100-200-L containers or 20-50-kg bags (Fedorov and Yablokov 2004). Such an inefficient system of pesticide storage and distribution resulted in a high loss of chemicals and subsequent environmental pollution (UNEP 2002).

In 1989–1990, to address the issue of unused and banned pesticides, or 'obsolete pesticides', according to the definition of the UN Food and Agriculture Organisation's (FAO) (FAO Pesticide Disposal Series 2 1995), the authorities of

the former Soviet Azerbaijan created a concreted burial site 53 km from Baku in the village of Jangi, where, according to estimates, ~8,000 tonnes of obsolete pesticides were stored in 183 concrete bunkers, each 30 m³ in volume. However, from 1996 the burial site was abandoned with no supervision. Subsequently, chemicals have been removed leading to the potential for dispersal in the local environment. In 2007, the burial 'polygon' (a term used in FSU countries for obsolete pesticide burial sites) came under the control of the Ministry of Agriculture. The site was refurbished, and ~2,500 tonnes of pesticides were re-collected and buried back under the concrete bunkers (UNECE 2011; Alasgarova 2008). The estimated amount of pesticides in the burial site ready for disposal is indicated in Table 2.

The contaminated soils at agricultural areas in and around obsolete pesticide stocks still represent 'hotspots' of pesticide emission to the environment (Aliyeva et al. 2012).

Chemical industry

Azerbaijan was a key centre of the chemical industry of the FSU, including production of chemical pesticides (Li et al. 2004, 2006a). Twenty-three factories producing industrial and agricultural chemicals were concentrated in Sumgayit city and provided a variety of products including organo-chlorine pesticides and other agricultural, domestic and industrial chemical products (Bickham et al. 2003).

DDT and HCH were officially banned in 1970 and in 1990 respectively, however, their use continued throughout the FSU after these years (Fedorov and Yablokov 2004; Feshbach and Friendly 1992; Bodo 1998). A number of recent studies indicate the presence of these compounds and their metabolites in various environmental compartments and biota in the Caspian Sea region (Bodo 1998; Ibadov et al. 2009; Kajiwara et al. 2008; de Mora et al. 2004; Suleymanov et al. 2008; Swartz et al. 2003; Tolosa et al. 2004; Zhulidov et al. 2000; Hall et al. 1999; Matson et al. 2005a; Matson et al. 2005b; Bickham et al. 1998; Bickham et al. 2003)

 Table 2
 Estimated total quantity of select OCP formulations in obsolete stocks in Azerbaijan. Initial inventory compiled by the State Phytosanitary Control Service, Ministry of Agriculture of Azerbaijan (Alasgarova 2011)

Description	Amount (tonnes)
5.5 % DDT	~2,500
Tech. HCH (hexachloran)	~7.1
Thiodan (endosulfan)	~2.5
60 % Polydofen ^a	~400
Others	~2,400

^a Polydofen-60 is a mixture of 20:40 of DDT/toxaphene in a diesel fuel solvent (Melnikov 1974)

Data on the production and use of pesticides was censored during the Soviet era and information on environmental levels of these pollutants is limited, making it difficult to access Azerbaijan's contribution to regional contamination. However, attempts to quantify production and use estimates as well as emissions in the post-Soviet area have been undertaken in a number of studies (Breivik et al. 1999; Breivik et al. 2006; Li et al. 1996, 2004, 2006a; Pacyna et al. 2003). For this review, national data from the archives of the Ministry of Agriculture of Azerbaijan on the use and production of pesticides in Azerbaijan during the Soviet era were obtained (Alasgarova 2008). While it is difficult to ascertain the accuracy of these data, they do represent the only information on volumes of chemicals used and produced in the country, and allow us to assess potential emissions, as well as the environmental fate and transport of pesticides.

Production and use of DDT

The production of DDT in the FSU commenced from 1946, with production facilities in Moscow, Vurnary, Dzerjinsk, Chapayevsk and Novocheboksarsk, all now in the Russian Federation, and Sumgayit, in Azerbaijan (Fedorov and Yablokov 1999; Li et al. 2006a). All these cities are located in the catchment of rivers draining to the Caspian Sea.

DDT production in Azerbaijan began in 1958 at the Sumgayit Plant of Surfactants with a production capacity of 60 ktonnes year⁻¹. Roughly, 24 ktonnes of 71–80 % DDT was imported to Sumgayit in 1958–1980 for re-processing to the final formulation of technical 5.5 % DDT dust. According to the description of the final formulation, it was permissible that additive talc contain 4.4 % of technical HCH was included. Until 1980, the factory produced in total 481 ktonnes of the final formulation 5.5 % DDT dust, with the time-series of production provided in Fig. 1 (Mustafaev 2005).

The distribution of 5.5 % DDT usage throughout Azerbaijan was predominantly in the cotton growing areas along the Kur– Araz lowland. In 1965–1982, the highest usage rates were recorded in the cotton growing areas of Salyan and Sabirabad, followed by Beylagan, Barda and Aghjabadi (all located in the Kur–Araz lowland). Available data indicate the total application of DDT in 1965–1982 on cotton and vineyards to be 285 ktonnes. Of this, only 8.5 tonnes was used in vineyards and restricted to the 1965–1977 period only (Alasgarova 2008).

Figure 1 provides some evidence that the DDT ban in the USSR in 1970 had some effect on DDT production in Azerbaijan, as production volume fell rapidly to ~10 ktonnes a year by 1973, although usage in agriculture appears to have remained stable at ~25 ktonnes a year until 1974. It is possible that DDT was also imported to cover domestic shortages. In later years, particularly after 1974, there appears to be a growth in the production rate, while the usage declines. This suggests that after 1974, when domestic demand decreased, Fig. 1 Production of 5.5 % DDT in 1958-1980 (480,549 tonnes) and usage on cotton and vineyards over the period 1965-1982 (284,986 tonnes) in Azerbaijan (Mustafaev 2005; Alasgarova 2008)

1972

1974

1976

1978

1980

982

Amount of 5.5% DDT produced in Azerbaijan in 1958-1980, ktonnes (Mustafayev, 2005b) Usage of 5.5% DDT in cotton and vineyard areas in 1965-1982, ktonnes (Alasgarova, 2008)

1970

1968

production continued with DDT likely to have been exported or possibly stored for future use.

40

30

20

10

0

1958

ktonnes

1960

1962

196

vear -1

Li et al. (2006b) estimated historical usage of DDT in FSU in 1946–1990 to be 250–520 ktonnes in total by applying the pattern of HCH usage. The estimate of DDT usage for Azerbaijan has been provided by Li (personal communication) for the period 1946–1987 in the range 934–1,940 tonnes, with the note that for a national study such as this, the estimates may not be accurate.

As illustrated in Fig. 2, the estimated usage by Li (personal communication 2010) is markedly lower than the usage data reported by Alasgarova (pers.comm. 2008). According to Li, the highest total usage of DDT in Azerbaijan in 1946-1987 comprised 1,940 tonnes, which is almost 147 times lower than the data provided by Alasgarova for the period 1965–1982. Nonetheless, regardless of the discrepancy in the total usage amount over this period, both datasets follow a similar trend that shows a marked decline by the mid 1970s onwards. Both Li and Alasgarova provide data for the formulation of total DDT and not the active ingredient.

The difference in usage quantities could be explained by the fact that these estimates are based on data from various sources which vary significantly and are usually provided without detail and do not take into account geographical differences in use across the former USSR. For example, Fedorov and Yablokov (1999) reports that DDT usage in the period 1950-1970 in the FSU exceeded 20 ktonnes a year,

however, there is no indication whether this figure is for each of the selected republics with the highest use, or for the entire FSU. To clarify this, we examined usage in other republics/ regions of the FSU, which provide guite similar levels of usage to Azerbaijan (Kundiev and Kagan 1993). Pokarzhevskii and Florinskii (1994) report that in 1970, supplies of DDT to agriculture comprised of: ~40 ktonnes of 5.5 % DDT dust. ~18 ktonnes of 30 % DDT powder. and <5 ktonnes of 75 % DDT powder, that in total makes ~60 ktonnes. Zhulidov et al. (2000) reports that in 1976–1979 in the Volga river basin the usage of DDT active ingredient was in the range 0.25-338 tonnes year⁻¹, while in the river Don basin the usage was 22.4-326 tonnes year⁻¹, and in the river Kuban basin the rate ranged between 24.8-31.6 tonnes year⁻¹, respectively. Similarly, Samersov and Skuriat (1996) reports that in Belarus the use of DDT in 1970 to 1973 was 82-507 tonnes year⁻¹, with no use recorded after 1974. Assuming that 5.5 % DDT was the major formulation, then these usage numbers of the active ingredient indicate that between 5 and 10,000 tonnes year⁻¹ of DDT formulation was in use in the FSU republics. While we recognise that these data sources have their limitations, they do allow us to assume that the usage of ~20,000 tonnes a year provided by Fedorov and Yablokov (1999) can be applied to each of the FSU republics where intensive agricultural activity took place.

Using the data from the Statistics Committee of Azerbaijan (StatCom 2012) on the area of land under cotton cultivation,

Fig. 2 Trend of DDT use (tonnes) in Azerbaijan over the period 1965-1982 based on data by Li (2010, personal communication, estimated high total usage 1,940 tonnes) and Alasgarova (2008, personal communication, documented total usage 284,986 tonnes)



and the annual usage data of DDT on cotton provided by Alasgarova (2008), then the average application rate of 5.5 % DDT for the period 1965-1982 is estimated as ~4.2 kg ha^{-1} of active ingredient (details of how this figure arises is provided in Table 3). By taking this approach, it is possible to verify the usage data of Alasgarova by comparing the application rate in Azerbaijan to data from other republics of the FSU over broadly the same time period. Again, as a comparison, the annual usage rate of 10 % DDT in Uzbekistan rice fields in the 1960s was 60-120 kg ha⁻¹ (Kundiev and Kagan 1993). This matches the range of 107-133 kg ha⁻¹ estimated for Azerbaijan over roughly the same period, as shown in Table 3. In Kazakhstan, the application rate of DDT in the 1960s was reported as 0.3-2 kg ha⁻¹ of active ingredient (Kundiev and Kagan 1993), which is lower but still supports our estimate for Azerbaijan of 5.9-7 kg ha⁻¹ of active ingredient. It is reported that after the ban of DDT in 1970 it was in use in the FSU in reduced volumes until 1985 (Kundiev and Kagan 1993; Fedorov and Yablokov 1999; Bodo 1998; Li et al. 2006b).

Fedorov and Yablokov (2004) provides a range of pesticide active ingredient application rates in some FSU Republics in 1980–1984 and reports that within the FSU Republics, Azerbaijan had the highest rate of total pesticide usage of up to \sim 238 kg ha⁻¹ of active ingredient. Although this figure lacks sufficient supporting evidence, we assume that it represents the usage rate of the sum of pesticides used in the period 1980–

1984 in all cultivated crops, where the DDT share would be in total ~0.3 kg ha⁻¹ of active ingredient, according to our estimate and due to reported decrease of usage rates (Table 3). No other data are available on the production of DDT in Azerbaijan after 1980 or its usage after 1985 (Djavadov 2001).

Production and use of HCH

In the 1980s, the number of pesticides allowed for application in the FSU was reduced and HCH became one of the most widely used pesticides. HCH was mainly produced by five chemical plants in the FSU, one of which was located in Sumgayit (Fedorov and Yablokov 2004; Li et al. 2004). Technical HCH or 'hexachloran', containing 12 % of the γ -isomer, was produced in the Sumgavit Plant of Surfactants from 1951. According to Fedorov and Yablokov (1999), the production capacity of HCH in Sumgavit was 100-300 tonnes year⁻¹, however, archived data show that production rates of more than a thousand tonnes a year occurred between 1956 and 1970 as illustrated in Fig. 3. There is no data on production rates of technical HCH after 1978. However, it is presumed that it was still being used according to records that detail an imported quantity of 1,542 tonnes in 1988. The total amount of technical-HCH produced in Azerbaijan in the period 1951-1978 was ~30 ktonnes (Mustafaev 2005)

Table 3 Estimated use of 5.5 % DDT active ingredient per hectare of land in cotton cultivated areas in 1965–1982

Year	Cotton cultivated area, kha (StatCom 2012) A	5.5 % DDT usage in cotton cultivated areas, ktonnes (Alasgarova 2008) B	5.5 % DDT application rate in cotton cultivated areas, kg ha ⁻¹ C (B/A)	5.5 % DDT active ingredient application, kg ha ⁻¹ 5.5 % of C
1965	215	22.974	107	5.9
1966	218	23.579	108	5.9
1967	210	25.341	121	6.6
1968	204	25.928	127	7.0
1969	198	26.221	132	7.3
1970	193	25.748	133	7.3
1971	206	26.228	127	7.0
1972	196	25.167	128	7.1
1973	198	26.342	133	7.3
1974	210	26.691	127	7.0
1975	212	15.362	73	4.0
1976	216	8.794	41	2.2
1977	218	4.028	18	1.0
1978	224	1.278	5.7	0.3
1979	241	0.437	1.8	0.1
1980	250	0.404	1.6	0.1
1981	283	0.245	0.9	0.05
1982	306	0.215	0.7	0.04
Average usage of 5.5 % DDT active ingredient, kg ha^{-1}				

Fig. 3 Production of technical HCH in 1951–1978 (~30 ktonnes) (Mustafayev, 2005b), estimated usage in 1950–1990 (~7 ktonnes) (Li, 20010, personal communication) and documented usage for 1983– 1991 (~3 ktonnes) (Avazova 1993)



The production of lindane in Azerbaijan occurred over a short period (1985 to 1988) due to a spate of industrial accidents which resulted in cessation of production. The total amount of lindane produced in Azerbaijan within this time is reported to be 181 tonnes with annual data presented in Fig. 4. All of the lindane was exported to Novomosskovsk, Russia (Mustafaev 2005),

The available data on the usage of technical HCH covers the period of 1983-1991 with some 3,093 tonnes used (Avazova 1993). It is plausible that the formulation was used in previous years; however, there are no data on the use of technical HCH before the 1980s. Nonetheless, Li (2010, personal communication.) estimated the usage of 7,020 tonnes of technical HCH and 144 tonnes of lindane in Azerbaijan for the period 1950-1990, with data displayed in Figs. 3 and 4. In Fig. 3 the total usage estimated by Li in 1983-1990 comprises 23 % of the total usage in the same period provided by Avazova (1993). Assuming this ratio remains constant through the previous vears too, we can estimate that usage of technical HCH in 1950–1990 could be ~30,522 tonnes. This figure matches the amount of technical HCH produced in Azerbaijan in 1951-1978. This raises a question whether technical HCH produced in Azerbaijan was eventually used for domestic purposes.

Fig. 4 Comparison of production data of lindane in 1986–1988 (Mustafayev, 2005) and usage data for 1950–1990 (Li et al. 2004) in Azerbaijan (tonnes) However, we recognise that this assumption requires supporting evidence and, therefore, should be considered with caution.

As a comparison to other republics/areas of the FSU, in Belarus, the use of 12 % technical HCH was 2,097 tonnes in 1974, which constituted 57.7 % of total pesticide usage. After 1975, the use of HCH gradually decreased until complete phase-out in 1993 (Samersov and Skuriat 1996). Zhulidov et al. (2000) reports that the total amount of HCH active ingredient used in the Volga river basin in 1987–1990 to be in the range of 25–295 tonnes, with an application rate of 0.00018–0.00214 kg ha⁻¹.

Toxaphene usage (60 % Polydofen)

Toxaphene used in the FSU was in a liquid mixture with DDT in a ratio 40:20. The formulation called 'Polydofen-60' also contained a fractional distillate of crude oil, petroleum solvent and additives (Melnikov 1974). DDT contained in Polydofen-60 formulation was not taken into account in the estimation of DDT usage.

Polydofen was produced in the FSU over the period 1968– 1982 in the Chapayevsk Plant of Agrochemicals (Samara oblast of Russia) and total production was 44,000 tonnes.



No information is available on the usage of polydofen in Azerbaijan, except the existence of an unused and repackaged quantity of ~400 tonnes stored in an obsolete pesticide site in the Ganja region, as well as an unknown quantity in the Salyan region (Alasgarova 2008; UNECE 2011).

Environmental surveys of soil and river-sediment contamination

Agricultural soil monitoring in 1982–1993 (Avazova 1993)

Avazova (1993) examined OCP levels in soils in the agricultural areas of Azerbaijan during 1983–1992, with sampling campaigns organised twice in the same location over a 10year period (each sampling was repeated in spring and autumn in the same year). Soil samples were collected in 23 regions of Azerbaijan and analysed for 12 compounds: DDT, dichlorodiphenyldichloroethylene (DDE), α -, β -, γ - HCH, endosulfan (thiodan), methyl parathion (metafos), dimethoate (phosfamid), 2,4-D, dalapon, sodium trichloro-acetate and treflan. In this paper, we report findings of the organochlorine pesticides only.

The research revealed that 12.6 kha of agricultural areas out of a studied area of 25 kha were contaminated with ΣDDT (n=50), at an average (range) concentration of 0.573 (0.058– 1.596) mg kg⁻¹, Σ HCH (n=39) at an average concentration of 0.028 (0.004–0.086) mg kg⁻¹, and endosulfan (n=28) at an average concentration of 0.052 (0.013–0.274) mg kg⁻¹. Mainly, contaminated areas included the cotton and grain growing regions, followed by vineyards and other crops. The study mentions that although DDT was applied only in cotton growing areas, the contaminated grain and other crop areas inherited DDT residues as the result of 'rotational cultivation' approach to land use, where, after a particular number of seasons, the land was allocated for cultivation by another crop. According to the study, 92 % of all contaminated lands fell within the Kur-Araz lowland. The results of this study are illustrated in Fig. 5, which shows the higher range of soil OCP concentrations are situated in the central agricultural region of Azerbaijan. The application rate of DDT in the agricultural areas in the 1980s, according to Avazova (1993) comprised 0.1-1.12 kg ha⁻¹ of active ingredient. This separate assessment of the use of DDT is comparable to our estimate of active ingredient use of 4.2 kg ha^{-1} in the period 1965–1982 (see section on Production & use of DDT), after which the usage of DDT declined.

The study reports temporal variations in the concentrations of OCPs in soil over each year of the programme. The significant prevalence of DDE was observed in some regions which could also be explained by the usage of kelthane, a pesticide widely applied in the FSU after the ban of DDT, which also degrades into DDE (Fedorov and Yablokov 2004; Avazova 1993). Kelthane used during FSU contained a larger amount of DDT impurity than the defined limit of $<1 \text{ gkg}^{-1}$ (EC Directive 90/533/EEC 15 October 1990). In Azerbaijan, kelthane was used predominantly in vineyards, fruit and cotton-growing areas. The supplies comprised ~200–300 tonnes a year over the period 1988–1996. In 2000, kelthane was removed from the list of registered agrochemicals permitted for use in Azerbaijan.

For the HCHs, α -HCH was the most abundant isomer with an average concentration of 0.014 (0.001–0.093) mg kg⁻¹ followed by β -HCH 0.014 (0.003–0.040) mg kg⁻¹, and γ -HCH 0.011 (0.001–0.067) mg kg⁻¹. This was explained by the higher proportion of α -HCH contained in the technical formulation. Higher levels of β -isomer were observed in some locations and can be explained by its recalcitrance in soils compared to other isomers. (Doelman et al. 1988).

The concentration of endosulfan (thiodan) was reported in the range of $0.007-0.527 \text{ mg kg}^{-1}$, with an increase in a number of regions at the end of the study period.

The declining trend of OCP concentrations was observed in the annual sampling data in regions of intensive DDT use, such as Neftchala and Salyan. For example, Fig. 6 illustrates the year on year decline for DDT in the region of Neftchala, located close to the delta region of the Kur River. For other compounds, like the HCHs, this decline is not so apparent. Figure 7, however, shows the time-series of selected OCPs in Salyan, located in the heart of the Kur–Araz farmland, where the OCP levels are higher than in Neftchala, and the decline in concentrations is not as apparent.

Recent monitoring of potentially contaminated sites for the Stockholm convention (Azerbaijan Government Monitoring Group 2005)

In 2005, the monitoring group of Azerbaijan for the UNEP Stockholm Convention analysed levels of OCPs and polychlorinated biphenyls (PCBs) in obsolete pesticide stocks and suspected contaminated agricultural sites. The analytical work was contracted to a local laboratory. Chemical analysis was conducted by GC-electron capture detector (ECD) and like the previous soil survey data (see previous section) these analyses were not subject to critical review and specified quality assurance and quality control (QA/ QC) protocols. High levels of OCPs were evident in 68 samples, of which 35 were samples from obsolete pesticide sites (remains of pesticides and/or pesticide mix with soil identified here as 'OS'), 19 soil samples were from agricultural areas ('AG') with known use of OCPs in the past and 14 soil samples were taken from selected agricultural sites with no official record of OCP use, although these sites had been heavily developed for agricultural purposes ('AGN').

All three categories of samples have many outliers and data were skewed significantly. Due to these outliers, the



Fig. 5 An outline map of Azerbaijan displaying average soil concentrations of Σ DDT, Σ HCH and endosulfan in agricultural areas during monitoring over the period 1983–1992 (Avazova, 1993). *Stars* indicate the locations of known obsolete pesticide stocks

median concentrations of OCPs showed a wide range: $0.63-32.8 \text{ mg kg}^{-1}$ in the OS group of samples, $0.008-0.43 \text{ mg kg}^{-1}$ in the contaminated agricultural sites AG, and $0.005-0.146 \text{ mg kg}^{-1}$ in the AGN group. Data for the different chemicals are presented in Table 4.

For the OS samples, the upper range of concentrations represent percent-level contamination for specific OCPs in the soil, specifically, for p,p'-DDE, β -endosulfan, endosulfan sulphate and α -HCH. It is plausible that this sample set also contained samples of the neat formulations rather than just soil. The very high levels of p,p'-DDE and endosulfan sulphate would suggest considerable 'weathering' of the soil samples. The identification of endosulfan sulphate by GC– ECD only, leads to some uncertainty regarding the presence of this chemical in these samples (Weber et al. 2010).

Included in Table 4 is the recent soil data from a survey by Aliyeva et al. (2012), with soils collected from across Azerbaijan in 2009. These contemporary concentrations are comparable to the AGN soils for the DDTs, but are generally lower than the AGN soils for the HCH isomers, possibly indicating a declining trend in concentrations of these chemicals over the last decade. Chemical analysis by Aliyeva et al. was conducted under carefully controlled QA/QC protocols with

Fig. 6 Time series of annual average concentrations of OCPs measured in soils in the Neftchala region over the period 1985–1992 (Avazova 1993)



Fig. 7 Time series of annual average concentrations of OCPs measured in soils in the Salyan region over the period 1985–1992 (Avazova 1993)



compound qualification and quantification conducted using authentic mass-labelled standards by GC-MS.

storm and sewage waters and 52 % of Georgian waters (Suleymanov et al. 2008).

Kur-Araz river studies

The Kur–Araz river system is the main source of drinking water for the population of Azerbaijan, and provides irrigation water for the Kur–Araz agricultural region of central Azerbaijan. The Kur–Araz river catchment includes parts of Turkey, Iran, Armenia and Georgia. Eighty percent of Azeri territory is located in the Kur–Araz watershed, while its tributaries provide natural drainage for 100 % of Armenia's OCP and PCB monitoring in river sediments has been conducted within the NATO Transboundary Water Resources, 'Monitoring of South Caucasus Rivers, SFP 977991 2002– 2008', and also within the Caspian Environment Programme (CEP 2005). The analytical part of both projects was implemented by the same local laboratory which implemented the soil survey (outlined in "Recent monitoring of potentially contaminated sites for the Stockholm convention (Azerbaijan Government Monitoring Group 2005)" section), using EPA methods 8081A, 8082, 3540, 3620, and GC/ECD as described elsewhere (Ibadov et al. 2009). Figure 8 illustrates the findings

 Table 4
 Median (range) of concentrations (milligramme per kilogramme) of OCPs at obsolete pesticide sites (OS), agricultural areas with known past use of OCPs (AG) and at former well-developed agricultural areas with unknown use of OCPs (AGN), (Azerbaijan Monitoring Group, 2005)

	OS ^a soil/pesticide	AG soil	AGN soil	Aliyeva et al. (2012) soil
<i>p,p'</i> -DDT	1.57 (0.004–1362)	0.031 (0.005–0.1)	0.005 (0.003-0.05)	0.006 (0.0005-0.5)
<i>p,p'</i> -DDE	32.84 (0.1-33229)	0.058 (0.003-0.9)	0.005 (0.002-0.03)	0.02 (0.0006-0.5)
α-Endosulfan	0.63 (0.01-202)	0.008 (0.002-0.1)	0.146 (0.006-0.3)	
β-Endosulfan	5.39 (0-11735)	0.027 (0.01-0.4)	0.004 (0.002-0.2)	
Endosulfan sulphate	32.33 (0.03-98686)	0.428 (0.14-17)	0.104 (0.02-1.9)	
α-НСН	16.98 (0.01-9925)	0.112 (0.01-11)	0.1 (0.02-7.3)	0.002 (0.0004-0.01)
β-НСН	4.92 (0.002–693)	0.046 (0.002-0.5)	0.02 (0.01-0.6)	0.005 (0.0004-0.02)
γ-НСН	4.67 (0.030-3733)	0.043 (0.001-1.3)	0.1 (0.01–9.4)	0.001 (0.0002-0.01)
Aldrin	1.82 (0.002–733)	0.025 (0.001-0.05)	0.3 (0.007-0.5)	

Also included is the recent study of background agricultural soil across Azerbaijan (Aliyeva et al. 2012)

^a Soil possibly mixed with technical product



Fig. 8 Concentrations of OCPs and PCBs along the Kur-Araz river system and coastal sediments. Stations 1–7: Kur-Araz river suspended particle sampling locations (CEP 2005); stations 8–12: river sediment

of both projects whereby Stations 1–7 were monitored by CEP (2006b) while stations 8–12 depict locations monitored within the NATO project (Ibadov et al. 2009).

Caspian Environment Programme (CEP 2005)

CEP reports the average concentration of Σ HCH in suspended particle samples to be 1.8×10^{-3} mg kg⁻¹, with the highest concentrations observed after the confluence of the Kur and Araz rivers. α -HCH, γ -HCH and δ -HCH were in the range of \langle MDL– 1.2×10^{-3} mg kg⁻¹, while β -HCH predominated at all the sampling stations 1×10^{-3} – 3.1×10^{-3} mg kg⁻¹, except stations 1 and 3. This is also reflected in soils taken previously by Avazova (1993) and Aliyeva et al. (2012). Higher levels of β -HCH were also reported in the study by de Mora et al. (2004) in Caspian Sea coastal sediments in Azerbaijan, Kazakhstan and Iran, except for Russia where γ -HCH dominated over β -HCH (de Mora et al. 2004)

The DDT profile was dominated by p,p' DDD (3.6× 10⁻³-12.5×10⁻³ mg kg⁻¹), followed by p,p'-DDT (4.2× 10⁻³-5.8×10⁻³ mg kg⁻¹). The concentration of p,p'-DDE was always <MDL. α - and β - endosulfan were <MDL-2.1×10⁻³ mg kg⁻¹ and <MDL-1.47×10⁻³ mg kg⁻¹ respectively, while high levels of endosulfan sulphate were observed in the range <MDL-13.1×10⁻³ mg kg⁻¹, higher in

and soil sampling locations (Ibadov et al. 2009), coastal sediment sampling (CEP 2006b)

the locations closer to the Kur river delta. The most OCP contaminated sediments were found to be at stations 4 and 5 which are located after the confluence of the Kur and Araz rivers, and before flowing into the Caspian Sea, as illustrated in Fig. 8.

The average concentration of Σ_{12} PCBs was 4.1×10^{-3} mg kg⁻¹. This is higher than PCB concentrations reported in Azeri shelf sediments of the Caspian Sea where the highest concentration was reported as 3×10^{-3} mg kg⁻¹ (de Mora et al. 2004).

NATO project (Ibadov et al. 2009)

River sediments and soil samples were also collected in several locations upstream of the Mingechevir reservoir and the Araz River before the confluence with the Kur. Stations 8–12 illustrated in Fig. 8 show data for HCHs, DDTs and PCBs in both river sediments and soil. In soil, α -HCH had the highest concentration (0.013–0.12 mg kg⁻¹), compared to β -HCH, which was <MDL in soil measured downstream of the Mingechevir reservoir and 0.012 mg kg⁻¹ in both sampling locations upstream of the Mingechevir reservoir. However, in the sediments, β -HCH mostly dominated over the other isomers. The highest concentrations of both α - and β -HCH were measured upstream of the Mingechevir reservoir (0.07 and 0.144 mg kg⁻¹, respectively), and at the confluence of the Kur and Araz rivers in Sabirabad (0.15 and 0.13 mg kg⁻¹, respectively). The concentrations of γ -HCH were <MDL in most of the soil and river sediment samples, except for a high concentration of 0.13 mg kg⁻¹ measured upstream of the Mingechevir reservoir.

Generally, concentrations of HCHs detected in the river study are lower than concentrations for the AGN soils (see previous section on soil monitoring), but higher than findings of CEP (2005) in suspended particles.

p,p'-DDT was \leq MDL in all soil samples downstream of the Mingechevir reservoir, but present in high concentrations in upstream locations (0.006 mg kg⁻¹ in soil, 0.03–0.06 mg kg⁻¹ in sediments). In contrast, *p,p'*-DDE was \leq MDL in the river sediments, but present in the range of 0.002–0.006 mg kg⁻¹ in soil upstream of the Mingechevir reservoir. The concentrations of DDTs are comparable to concentrations reported in soils but higher than findings of CEP (2005) in suspended particles.

Comparing the two studies of Ibadov et al. (2009) and CEP (2005), the concentrations of OCPs and PCBs in the locations downstream of the Mingechevir reservoir are much lower than those in the upstream locations. This implies that contaminated sediments are likely to be trapped in the Mingechevir reservoir, possibly reducing their transport to downstream areas.

Calculation of the flux of OCPs and PCBs to the Caspian Sea

Using the concentrations of OCPs and PCBs present in the water column (associated with suspended sediments) at the Kur–Neftchala station (Station 5), and water flow rate into the Kur delta in 2003 (Kur Surra averaging 315 m³ s⁻¹) (CEP 2005) the annual flux of OCPs and PCBs to Caspian Sea was calculated, as shown in the Table 5.

Table 5 presents the estimated annual flux of POPs based on CEP (2005) chemical data (see Fig. 8). Also included as a comparison are fluxes reported for the Volga River, which flows into the northern part of the Caspian Sea with a catchment of 1.4 million km², i.e. about 40 % of the total catchment area of the Caspian Sea. Approximately 80 % of the water inflow to the Caspian Sea comes from the Volga River compared to 6 % from the Kur River (Kosarev and Kostianoy 2005; de Mora et al. 2004). Zhulidov et al. (2000) indicated the importance of the riverine contaminant load when studying marine pollution of the Caspian Sea. The riverine fluxes of HCHs and DDTs to the Caspian Sea from the Volga River are provided in Table 5 for the periods of 1988-1996 and 1995-2000. The high OCP fluxes, particularly for the earlier period would agree with the elevated concentrations of γ -HCH observed in the northern part of the Caspian Sea compared to the central and southern parts (de Mora et al. 2004; CEP 2006a; Kosarev and Kostianoy 2005).

In a Caspian Sea sediment study conducted in the early 2000s, de Mora et al. (2004) showed the highest concentrations of Σ DDTs occurred in a location close to the Kur river delta.

The research by CEP which assessed the pollution status of the coastal zones of the Caspian and determined pollution fluxes from the main Caspian basin rivers (Volga, Kura and Terek) reports that Volga River is the most important source of OCPs into the Caspian Sea. However, the data here indicate that fluxes of HCHs and DDTs from these rivers have decreased in recent years (CEP 2007).

Caspian Sea studies

Research on POPs within the Caspian Sea environment has been reported for sea sediments (de Mora et al. 2004) and biota (Matson et al. 2005a; Matson et al. 2006; Kajiwara et al. 2003; Kajiwara et al. 2008; Swartz et al. 2003).

Kajiwara et al. (2008) determined that Σ DDTs was a predominant contaminant analysed in the blubber of Caspian seals (*Phoca caspica*) ranging from 3.1 to 560 µg g⁻¹ (lipid weight), followed by PCBs, 1.5–32 µg g⁻¹, HCHs, 0.11–17 µg g⁻¹ and chlordanes, 0.057–14 µg g⁻¹. The study suggested that high concentrations of OCPs and PCBs in these aquatic mammals might pose a risk of immunosupression (de Swart et al. 1996) as well as contributing to mass mortality episodes of Caspian Seals in 2000 and 2001.

PCB concentrations were reported to be comparable to those in Baikal Seals (*Phoca Sibirica*) from Lake Baikal (Nakata et al. 1995). The predominance of DDT and PCB residues in Caspian Seal (Kajiwara et al. 2002; 2008) is similar to those in other species of sturgeon fish (Kajiwara et al. 2003; Hosseini et al. 2008), sediments (de Mora et al. 2004) and seals (Hall et al. 1999)

In a sediment study off the coast of Azerbaijan, de Mora et al. (2004) reported OCPs in coastal sediments as p,p'-DDE ($0.11 \times 10^{-5}-1.3 \times 10^{-3} \text{ mg kg}^{-1}$), p,p'-DDD ($0.21 \times 10^{-5}-3.4 \times 10^{-3} \text{ mg kg}^{-1}$) and p,p'-DDT ($0.16 \times 10^{-5}-7.4 \times 10^{-3} \text{ mg kg}^{-1}$). The levels of γ -HCH were $1 \times 10^{-5}-0.24 \times 10^{-3} \text{ mg kg}^{-1}$ compared to α -HCH ($3.5 \times 10^{-5}-1.1 \times 10^{-3} \text{ mg kg}^{-1}$) and β -HCH ($4.8 \times 10^{-5}-1.6 \times 10^{-3} \text{ mg kg}^{-1}$). These concentrations are corroborated by another Caspian Sea sediment study within CEP (2006b) focused on the sediments in the vicinity of the Kur river delta, which are summarised in Fig. 8.

Health issues

In 1970s, the government of the Soviet Union launched an extensive and largely secretive research programme to study exposure of select groups of the population to pesticides used in agriculture, (Fedorov and Yablokov 2004). The study showed that in rural regions of Azerbaijan with a high

Table 5 The estimated fluxes (kilogrammes per year) of		Kur Estimated flux 2005, kg year ⁻¹	Volga		
particle-bound OCPs and Σ PCBs to the Caspian Sea from the Kur–Araz river			Estimated flux 1988–1996, kg year ⁻¹		Estimated flux 1995–2000 kg year ⁻¹
			OGNK/ GSN labs	Independent data	CEP, 2006
	α-HCH	1.0		3,800	5
	β-НСН	7.3			
Defe have 1 and an end of the	δ-НСН	2.5			
conducted at station 5, in June	ү-НСН	1.1		4,300	87
and August of 2005 (CEP 2005).	<i>p,p'</i> -DDD	38			
Also included are estimated total	<i>p,p'</i> -DDE	0.97	18,00 ^a	1,200 ^a	29.5 ^a
riverine fluxes of OCPs from the	<i>p,p'</i> -DDT	19	20,400 ^b	1,600 ^b	94 ^b
(Zhulidov et al. 2000) and in	α-Endosulfan	4.8			
1995–2000 (CEP 2006a)	β-Endosulfan	4.6			
^a DDE (the specific isomer was	Endosulfan sulphate	43			
not reported)	Aldrin	1.1			
^b DDT (the specific isomer was not reported)	ΣΡCΒ	92.5			

rate of pesticide use, children showed higher incidents of the following illnesses before the age 14: a 2.5-fold increase in iron-deficit anaemia, 1.6 fold increase in tuberculosis, 2-fold increase in viral hepatitis, acute infections of the upper respiratory tract, and a higher infant mortality rate.

In the Salvan region of Azerbaijan, human exposure of OCPs exceeded the public health standards of the FSU by 8-fold. Research by Baida (1983) in the Salyan region focused on various age groups and revealed that the most affected age group were adolescents of 11-14 years old and newborns <1 year in age. Five-year observations of the health conditions of these children in this region showed that continuous pesticide exposure caused endocrine disruption of children, an increase in the frequency of various diseases of children under the age of 15 years by a factor of 3.6, and an increase in the pathological disruptions of children 8-14 years old by a factor of 2.3, and an overall 3-fold decrease in the number of healthy children (Fedorov and Yablokov 2004). This research illustrates the risk to rural populations exposed to high pesticide use. Similar studies were conducted in Moldova, Uzbekistan, Armenia, Kirgizstan, Turkmenistan and the Ukraine (Fedorov and Yablokov 2004).

Recent research has investigated elevated levels of OCPs and PCBs in sediments and soils in the cities of Sumgayit and Baku, with regards to toxic effects on wildlife, particularly fish and amphibians (Bickham et al. 1998; Matson et al. 2005a; Matson et al. 2006; Swartz et al. 2003). Although it is difficult to link the wide range of toxic contaminants found in Sumgayit to observed effects, these studies show that despite the cessation of OCP production, Sumgayit remains a contaminant 'hotspot' affecting local habitats and wildlife. Human exposure and risk to these chemicals also, presumably, remains high. A situation that may also be the case around the obsolete pesticide storage facilities located in the main agricultural areas, as shown in Fig. 5.

Conclusions

Azerbaijan was a major producer and user of OCPs, particularly DDT and technical HCH which were both produced and used in large quantities within the country from the 1950s onwards. Government archives do contain data and information on the production and past use of OCPs as well as monitoring data for soils and sediments. In the case of DDT, however, there appear to be large discrepancies between government archives on countrywide usage compared to published scientific estimates. Comparing the usage rates of the active ingredient of the major DDT formulation ('5.5 % DDT') with other republics and regions of the FSU, then it is likely that the government usage estimates for Azerbaijan may well be accurate. For HCH use there is a reasonable agreement between government use data and international scientific estimates. It is likely that these types of datasets also exist for other republics in the FSU but are likely to exist in hardcopy form only and may be difficult to access.

The legacy of past OCP use is most apparent in the soils of the central Kur–Araz agricultural region, which have the highest concentrations compared to soils sampled in other regions within the country. The quality of these data are open to question however, as quality assurance and control protocols are not available, although data collected from a monitoring survey conducted in 2005 are in broad agreement to soil data derived

independently in 2009. Currently, the levels of OCPs in soils in some areas generally exceed concentrations reported in Eastern Europe and elsewhere. Furthermore, the occurrence of numerous obsolete pesticide stock sites, particularly in the main agricultural region are an area of concern, as selected pesticides in some cases are present at percent levels in nearby soils, although it is not clear whether these data reflect analyses of the abandoned formulations themselves or a mixture of soil and formulation. It is recommended that monitoring programmes are undertaken to assess the risk posed by these sites to the local environment, with both formulation (i.e. abandoned powders/ liquids) and soil samples collected and analysed separately. OCPs are present in sediment and suspended particle matter in the main Kur and Araz river systems, with some evidence to suggest that OCPs are entering catchment waters from countries 'upstream' of Azerbaijan. The highest particle-bound concentrations 'however' were present downstream of the Kur lowland agricultural region and it is likely that the Kur continues to provide contaminated sediments to the estuarine and coastal areas of the Caspian Sea, although local 'hotspots' such as the industrial city of Sumgavit (the former centre of the chemical industry) may also be a source of POPs to the coastal areas of the Apsheron peninsula. There appears to be fewer environmental data on PCBs, although these chemicals are present in the Kur river sediments and Caspian coastal sediments.

From the time-series of soil data accessed here, there is some evidence to indicate that OCP levels in soil, outside of the main agricultural region, have declined, given that many OCPs have not been used in Azerbaijan over the last 20 years or so. However, remaining residues in soil will continue to serve as a source to the overlying atmosphere for years to come, and along with pesticide use in neighbouring countries, the atmosphere is likely to serve as a source of these chemicals (through deposition) to the surface waters of the Caspian Sea and the wider region in general. Environmental surveys are recommended to assess the environment transfer of POPs within Azerbaijan, and determine the impact of contamination 'hotspots' in relation to OCPs levels present in agricultural soils.

Acknowledgments The PhD research of GA has been funded by the Ministry of Education of the Republic of Azerbaijan. The authors are grateful to Dr. Islam Mustafayev of Ruzgar non-government organisation, Prof. Mustafa Salakhov of the National Academy of Sciences of Azerbaijan, Dr. Shahin Panahov of UNEP-Ecores NatCom, Dr. Bahruz Suleymanov of AzEcoLab, and Mr Mammadali Dunyamaliyev, of the Ministry of Agriculture of the Republic of Azerbaijan. Finally, the authors would like to express their gratitude to Dr Yi-Fan Li of Environment Canada for providing DDT use estimates for Azerbaijan and for a helpful discussion on this subject.

References

Alasgarova K (2008) Usage of DDT in cotton growing areas of Azerbaijan in 1965–1982. Archive of the State Phytosanitary Control Service of the Ministry of Agriculture of the Republic of Azerbaijan (internal document, personal communication). Baku, Azerbaijan

- Alasgarova K (2011) List of pesticides imported to Azerbaijan in 2010 (internal document, personal communication). State Phytosanitary Control Service of the Ministry of Agriculture of the Republic of Azerbaijan, Baku
- Aliyeva G, Kurkova R, Hovorkova I, Klanova J, Halsall C (2012) Organochlorine pesticides and polychlorinated biphenyls in air and soil across Azerbaijan. Environmental Science and Pollution Research, Special Issue Brno Workshop 19:1953–1962
- Altstadt A (1992) The Azerbaijani Turks: power and identity under Russian rule. Hoover Institution Press, Stanford, ISBN 0817991824
- Avazova M (1993) Assessment of pesticide contamination in agricultural soils of Azerbaijan in 1983–1992 (unpublished report). Report of the Research Institute of Hydrometeorology and Melioriation of Azerbaijan (now a part of the Ministry of Ecology and Natural Resources of the Republic of Azerbaijan). In Azerbaijani language. Baku, Azerbaijan
- Azerbaijan Government Monitoring Group (2005) Report on POPs that are related to the United Nations Stockholm Convention on POPs. Ministry of Ecology & Natural Resources, Azerbaijan. Internal hardcopy report.
- Bickham J, Rowe G, Palatnikov G (1998) Acute and genotoxic effects of baku harbor sediment on Russian sturgeon Acipenser guildensteidti. Bull Environ Contam Toxicol 61 (4):512–518. doi:10.1007/s001289900792
- Bickham J, Matson C, Islamzadeh A, Rowe G (2003) Editorial: the unknown environmental tragedy in Sumgayit, Azerbaijan. Ecotoxicology 12(6):505–508
- Bodo BA (1998) An assessment of environmental and aquatic ecosystem contamination by persistent organochlorine pollutants (POPs) in the Russian Federation. UNEP and WHO GEMS/Water Collaboration Centre,
- Breivik K, Pacyna JM, Munch J (1999) Use of a-, b- and ghexachlorocyclohexane in Europe, 1970–1996. Sci Total Environ 239:151–163
- Breivik K, Vestreng V, Rozovskaya O, Pacyna JM (2006) Atmospheric emissions of some POPs in Europe: a discussion of existing inventories and data needs. Environ Sci Pol 9(7–8):663–674. doi:DOI: 10.1016/j.envsci.2006.09.001
- CEP (2005) Study and survey project to determine the fluxes of major contaminants from the Kura to Caspian Sea (Mingechaur reservoir to Kura river delta). Final Report of the project Ref. Rer/03/ G31(00034997), supported by UNOPS. Ecological Society 'Ruzgar', Azerbaijan Republic. Caspian Environment Program. http:// www.caspianenvironment.org/newsite/Activities-RiverPol.htm. Accessed 26 April, 2012
- CEP (2006a) Study and review for determination of major pollutants flow from the Volga cascade. Caspian Environment Programme. RER/03/G31 (00034997). http://www.caspianenvironment.org/ newsite/Activities-RiverPol.htm. Accessed 26 April 2012
- CEP (2006b) Scientific Sea Cruise 2005. Azecolab Azerbaijan. Small Contracts for Services. Caspian Environment Programme. Ref. RER/03/G31 (00034997). http://www.caspianenvironment.org/ newsite/Activities-SSC2005.htm. Accessed 26 April
- CEP (2007) Transboundary Diagnostic Analysis Revisit. 10 December 2007. Caspian Environment Programme. http://www. caspianenvironment.org/newsite/Data-MeetingReports.htm. Accessed 26 April 2012
- Cobban R (2011) EECCA Obsolete Pesticides Training and Repackaging Pilot Project - Azerbaijan. Mission Report 9th–16th March 2011. For the EECCA project team and UN FAO AGMP.
- de Mora S, Villeneuve J-P, Villeneuve M, Cattini C, Tolosa I (2004) Organochlorinated compounds in Caspian Sea sediments. Mar Pollut Bull 48(1–2):30–43
- de Swart RL, Ross PS, Vos JG, Osterhaus AD (1996) Impaired immunity in harbour seals (*Phoca vitulina*) exposed to bioaccumulated environmental contaminants: review of a long-term feeding study. Environ Health Perspect 104(Suppl 4):823–828

- Djavadov V (2001) Overview of the state of pesticide management in the Republic of Azerbaijan. C1.6. p449. Paper presented at the 6th International HCH and Pesticide Forum, 20–22 March, 2001, Poznan, Poland ISBN 83-913860-7-4 http://www.ihpa.info/ resources/library/. Accessed 6 April 2012,
- Doelman P, Haanstra L, Vos A (1988) Microbial sanitation of soil with alpha and beta HCH under aerobic glasshouse conditions. Chemosphere 17(2):489–492
- EC Directive 90/533/EEC (15 October 1990) European Council Directive 90/533/EEC of 15 October 1990 amending the annex to Directive 79/117/EEC prohibiting the placing on the market and use of plant protection products containing certain active substances. http://eur-lexeuropaeu/LexUriServ/LexUriServdo? uri=CELEX:31990L0533:EN:HTML. Accessed 1 May 2012
- FAO (2011) Aquastat-FAO's Information System on Water and Agriculture. Land and Water Division. http://www.fao.org/nr/water/ aquastat/data/query/index.html?lang=en. Accessed 26 April 2012.
- FAO Pesticide Disposal Series #2 (1995) Prevention of accumulation of obsolete pesticide stocks. ISSN 0009-0379. http://www.fao.org/ docrep/v7460e/v7460e00.htm. Accessed 26 April 2012
- Fedorov L, Yablokov A (1999) Pesticides—the toxic blow against the biosphere and man. Publishing House 'Nauka', Moscow, ISBN 5-02-00441-S
- Fedorov L, Yablokov A (2004) Pesticides: the chemical weapon that kills life (The USSR's tragic experience). Pensoft, Sofia-Moscow, 9546422053
- Feshbach M, Friendly A (1992) Ecocide in the USSR. BasicBooks, A Division of HarperCollins Publishers, Inc., New York, ISBN 0-465-01-781-9 (paper)
- Hall A, Duck C, Law R, Allchin C, Wilson S, Eybatov T (1999) Organochlorine contaminants in Caspian and harbour seal blubber. Environ Pollut 106:203–212
- Hosseini S, Behrooz R, Esmaili-Sari A, Bahramifar N, Hosseini S, Tahergorabi R, Hosseini S, Feás X (2008) Contamination by organochlorine compounds in the edible tissue of four sturgeon species from the Caspian Sea (Iran). Chemosphere 73(6):972–979
- Ibadov N, Suleymanov B, Abdullayev E, Abbasova D (2009) Organochlorine pesticides and polychlorinated biphenyls in Kura–Araz river. Kimya Problemleri (in Russian and Azerbaijani) 2:252–259
- Iwata H, Tanabe S, Sakai N, Tatsukawa R (2002) Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ Sci Technol 27(6):1080–1098
- Kajiwara N, Niimi S, Watanabe M, Ito Y, Takahashi S, Tanabe S, Khuraskin L, Miyazaki N (2002) Organochlorine and organotin compounds in Caspian seals (Phoca caspica) collected during an unusual mortality event in the Caspian Sea in 2000. Environ Pollut 117(3):391–402
- Kajiwara N, Ueno D, Monirith I, Tanabe S, Pourkazemi M, Aubrey D (2003) Contamination by organochlorine compounds in sturgeons from Caspian Sea during 2001 and 2002. Mar Pollut Bull 46 (6):741–747
- Kajiwara N, Watanabe M, Wilson S, Eybatov T, Mitrofanov I, Aubrey D, Khuraskin L, Miyazaki N, Tanabe S (2008) Persistent organic pollutants (POPs) in Caspian seals of unusual mortality event during 2000 and 2001. Environ Pollut 152(2):431–442
- Kosarev A, Kostianoy A (2005) The Caspian Sea environment, vol 5. The handbook of environmental chemistry, 2005th edn. Springer, Berlin, ISBN 10: 3-540-28281-5
- Kundiev YI, Kagan YS (1993) Pesticide usage in the former USSR: a report prepared for Environment Canada. Toronto, Ontario, Canada
- Li YF, Macdonald RW (2005) Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci Total Environ 342(1–3):87–106

- Li et al (1996) Global HCH usage with 1 degrees × 1 degrees longitude/ latitude resolution. Environ Sci Technol 12(30):3525–3533
- Li YF, Bidleman TF, Barrie LA, McConnell LL (1998) Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. Geophys Res Lett 25:39–41
- Li YF, Zhulidov AV, Robarts RD, Korotova LG (2004) Hexachlorocyclohexane use in the former Soviet Union. Arch Environ Contam Toxicol 48:10–15
- Li et al (2006a) Dichlorodiphenyltrichloroethane usage in the former Soviet Union. Sci Total Environ 1-3(357):138–145
- Li YF, Zhulidov AV, Robarts RD, Korotova LG, Zhulidov DA, Gurtovaya TY, Ge LP (2006b) Dichlorodiphenyltrichloroethane usage in the former Soviet Union. Sci Total Environ 357(1–3):138–145
- Lohmann R, Breivik K, Dachs J, Muir D (2007) Global fate of POPs: current and future research directions. Environ Pollut 150(1):150–165
- Matson C, Palatnikov G, Islamzadeh A, McDonald T, Autenrieth R, Donnelly K, Bickham J (2005a) Chromosomal damage in two species of aquatic turtles (*Emys orbicularis* and *Mauremys caspica*) inhabiting contaminated sites in Azerbaijan. Ecotoxicology 14(5):513–525
- Matson CW, Palatnikov GM, McDonald TJ, Autenrieth RL, Donnelly KC, Anderson TA, Canas JE, Islamzadeh A, Bickham JW (2005b) Patterns of genotoxicity and contaminant exposure: evidence of genomic instability in the marsh frogs (*Rana ridibunda*) of Sumgayit, Azerbaijan. Environ Toxicol Chem 24(8):2055– 2064. doi:10.1897/04-250r1.1
- Matson CW, Lambert MM, McDonald TJ, Autenrieth RL, Kirby CD, Islamzadeh A, Politov DI, Bickham JW (2006) Evolutionary toxicology: population-level effects of chronic contaminant exposure on the marsh frogs (*Rana ridibunda*) of Azerbaijan. Environ Heal Perspect 114(4):547–552
- Melnikov NN (1974) Chemistry and technology of pesticides (in Russian). Khimiya. UDK 632.95:54:66/M48, Moscow
- Mustafaev I (2005) Lindan and DDT in the environment and food products in Azerbaijan (in Russian). Project Report. International POPs Elimination Project (IPEN) and NGO RUZGAR. http:// www.ecoaccord.org/pop/ipep/mustafaev.htm, Baku
- Mustafayev I, Gurbanov E, Ramazanova Z (2005) Pesticides and the environment (in Azerbaijani language). International POPs Elimination Project and 'Ruzgar' Environmental Society, Publishing House 'Muellim'. Baku, Azerbaijan
- Nakata H, Tanabe S, Tatsukawa R, Amano M, Miyazaki N, Petrov EA (1995) Persistent organochlorine residues and their accumulation kinetics in Baikal seal (*Phoca sibirica*) from Lake Baikal, Russia. Environ Sci Technol 29(11):2877–2885
- Pacyna JM, Breivik K, Münch J, Fudala J (2003) European atmospheric emissions of selected persistent organic pollutants, 1970–1995. Atmos Environ 37(Supplement 1):119–131
- Pokarzhevskii AD, Florinskii MA (1994) HCH situation in Russian Federation. Paper presented at the 3rd HCH and Halogenated Pesticides Forum, 19–20 September, 1994, Bilbao, Spain http:// www.ihpa.info/docs/library/forumbooks/3rd/3rdForum_Bilbao_ Part1.PDF. Accessed 7 April 2012
- Samersov Y, Skuriat A (1996) Ecological aspects of use of pesticides in Belarus. p81. Paper presented at the 4th HCH and Pesticide Forum,15–16 January 1996. Poznan. Poland http://www. ihpa.info/docs/library/forumbooks/4th/4thHCHForumBook.pdf. Accessed 7 April 2012
- StatCom (2012) The State Statistical Committee of the Republic of Azerbaijan. http://www.azstat.org/statinfo/agriculture/az/001_1.shtml. Accessed 7 April 2012
- Suleymanov B, Ahmedov M, Humbatov F, Ibadov N (2008) Hazardous pollutant database for Kura–Araks water quality management. Transboundary Water Resources: a Foundation for Regional Stability in Central Asia. Springer, Dordrecht
- Swartz CD, Donnelly KC, Islamzadeh A, Rowe GT, Rogers WJ, Palatnikov GM, Mekhtiev AA, Kasimov R, McDonald TJ,

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Wickliffe JK, Presley BJ, Bickham JW (2003) Chemical contaminants and their effects in fish and wildlife from the industrial zone of Sumgayit, Republic of Azerbaijan. Ecotoxicology 12 (6):509–521

- Tolosa I, de Mora S, Sheikholeslami M, Villeneuve JP, Bartocci J, Cattini C (2004) Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. Mar Pollut Bull 48(Issues 1–2):44–60
- UNECE (2011) Environmental Performance Reviews Series No. 31, Azerbaijan. Second Review. ECE/CEP/158. New York and Geneva. United Nations Publication. ISBN 978-92-1-117035-1 http:// www.unece.org/index.php?id=17343. Accessed 26 April 2012
- UNEP (2002) Caucasus Environment Outlook. New Media. Tbilisi ISBN-99928-803-2-5 http://www.unece.org/fileadmin/DAM/env// epr/experts/Georgia/Caucasus%20Environment%20Outlook/ UNEP CEO 2002.pdf. Accessed 1 May 2012
- Verdiyev RG (2009) Computation and prediction of the flood runoff of the Eastern Caucasus River. Russ Meteorol Hydrol 34(1):46–50
- Voldner EC, Li Y-F (1995) Global usage of selected persistent organochlorines. Sci Total Environ 160–161:201–210

- Wania F, Mackay D (1996) Tracking the distribution of persistent organic pollutants. Environ Sci Technol 30(9):390A–396A
- Weber J, Halsall CJ, Muir D, Teixeira C, Small J, Solomon K, Hermanson M, Hung H, Bidleman T (2010) Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Sci Total Environ 408(15):2966– 2984. doi:10.1016/j.scitotenv.2009.10.077
- World Bank (2006) Azerbaijan Agricultural Market Study. Realizing Azerbaijans's comparative advantages in agriculture. Report no. 36283-AZ. World Bank, Environmentally and Socially Sustainable Development Unit (ECSSD). Europe and Central Asia Region. Washington http://web.worldbank.org/external/default/main? sortDesc=DOCDT&theSitePK=301914&cntry=82673& piPK=51189446&pagePK=51187344&menuPK=301942. Accessed 26 April 2012,
- Zhulidov A, Headley J, Pavlov D, Robarts R, Korotova L, Vinnikov Y, Zhulidova O (2000) Riverine fluxes of the persistent organochlorine pesticides hexachlorcyclohexane and DDT in the Russian Federation. Chemosphere 41(6):829–841