ADDITIONAL DATA ON THE CFC CONCENTRATION AND CORRESPONDING GROUND WATER AGE IN THE FRESH GROUNDWATER OF LATVIA

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One of the main issues in groundwater studies is groundwater age, also known as residence time. This is important for investigating the groundwater filtration rate and to solve variety issues of groundwater use, management and protection.

During this project the CFC concentration is now analyzed in 39 samples – 19 samples in year 2010 and 20 new samples in 2011 (Table 1, Fig. 1. shows locations). Previous studies have shown that Latvian CFC method is appropriate for aquifers to an average depth of 30-50 m (Gosk et al 2006) therefore new samples from year 2011 are taken from average depth of 37 m although depth changes from 6 m to 128 m and one sample is taken from surface water (Baltezers basin). CFCs concentrations were analyzed in the laboratory at GEUS after Busenberg and Plummer (Busenberg & Plummer, 1992) described method by gas chromatography equipped with an EDC detector. Interpretation of the results was carried out by laboratory expert Troels Laier. Many samples are taken from on place at different depth to obtain better view of residence time distribution and therefore these new samples from 20 wells are located in 8 places (Fig. 1.).

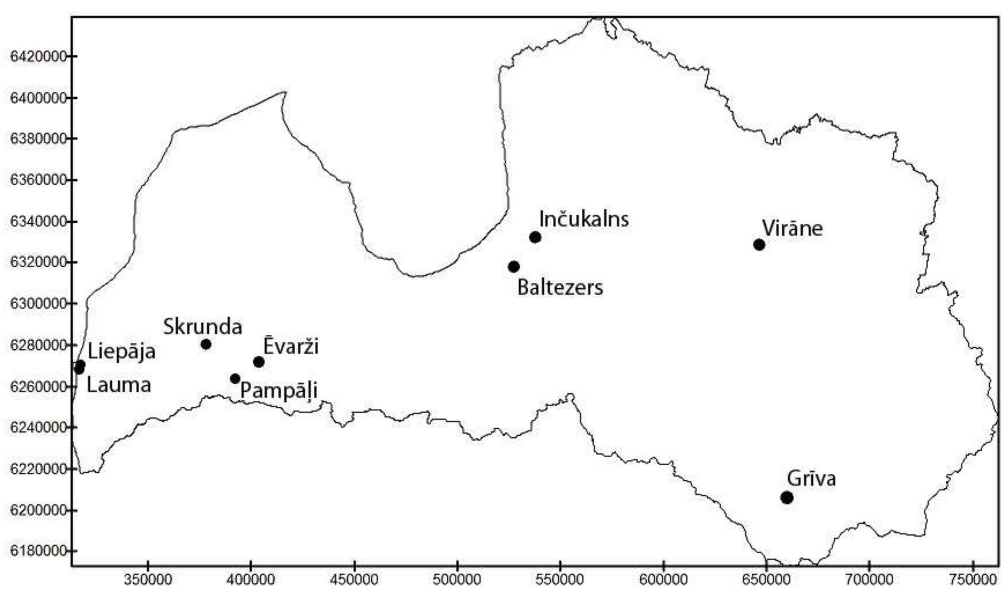

Fig. 1. Map showing locations of sampling wells

New samples are taken both from the unconfined aquifer and the first confined aquifer, the sampling interval for CFC analysis varies from 6-14 m up to 108-128. It is stated that most of determined groundwater from both - confined and unconfined aquifer - has residence time of 35-60 years according to CFC concentration (Fig. 2.).

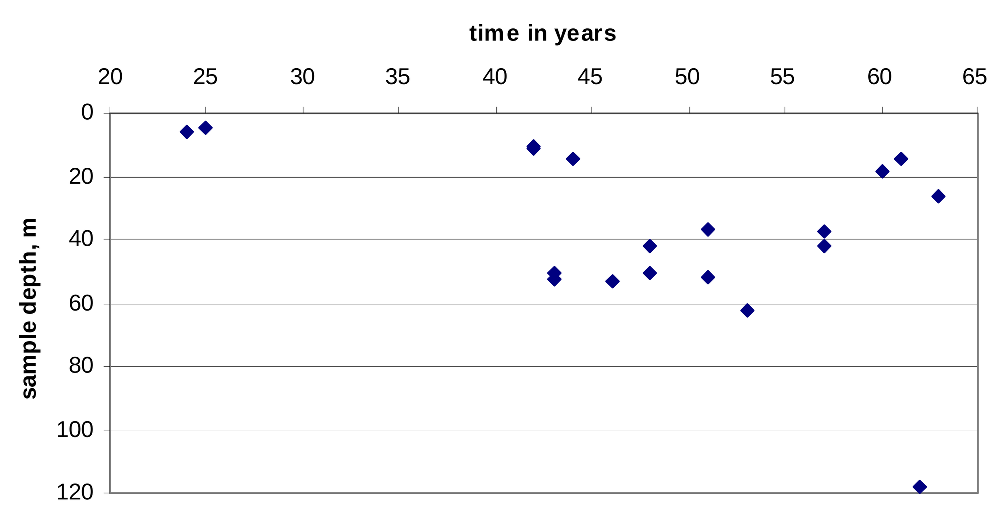

Fig. 2. Water residence time at different depths

Table 1
Results of CFC analysis in fresh groundwater during year 2011

Age-dating of groundwater using the CFC-method - Latvia May-Sept. 2011

Geological Survey of Denmark and Greenland
23-12-10

Location/ Well No.	Depth metres	Ampoul No.	Sampling Date	Hour	Concentration in water pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Partial press. (calc.) in atmosphere, pptv CFC-11	CFC-12	CFC-113	CFC model infiltation year CFC-11	CFC-12	CFC-113	Remarks	CFC age
Murjani-99	9-12	1	04-05-11	12.40	8.5	92.6	12.3	2.6	127.2	9.0	1953.5	1969.5	1973.0		
		2	04-05-11	12.47	7.0	81.8	4.1	2.2	112.2	3.0	1953.0	1968.5	1965.0		c 40
Murjani-101	36-38	1	04-05-11	13.53	8.4	30.7	35.4	2.6	42.2	26.1	1953.5	1961.0	1980.5	CFC113 co-elute with other species	
		2	04-05-11	14.03	5.9	28.8	28.7	1.8	39.5	21.1	1952.5	1960.5	1979.0	CFC113 co-elute with other species	c 50
Lauma-465	40-44	1	17-05-11	12.45	7.2	42.2	78.5	2.2	57.9	57.8	1953.5	1963.5	1987.0	CFC113 co-elute with other species	
		3	17-05-11	13.07	0.0	42.2	80.3	0.0	58.0	59.1	<1945	1963.5	1987.5	CFC113 co-elute with other species	c 50
Liepaja-XIVg	43-58	1	17-05-11	15.22	7.3	41.4	11.2	2.3	56.8	8.2	1953.5	1963.5	1972.0	CFC113 co-elute with other species	
		2	17-05-11	15.31	10.9	41.8	14.3	3.4	57.4	10.5	1954.5	1963.5	1974.0	CFC113 co-elute with other species	c 50
Liepaja-XI	46-57	1	18-05-11	9.50	19.4	26.8	8.9	6.0	36.8	6.5	1956.5	1960.0	1970.5	CFC113 co-elute with other species	
		2	18-05-11	10.02	11.3	25.9	14.5	3.5	35.6	10.6	1954.5	1960.0	1974.0	CFC113 co-elute with other species	c 50
Pampali-47	35-40	1	18-05-11	14.05	1.1	13.8	9.1	0.3	19.0	6.7	1948.5	1955.5	1970.5	CFC113 co-elute with other species	
		2	18-05-11	14.15	7.6	11.3	19.7	2.4	15.5	14.5	1953.5	1954.0	1976.5	CFC113 co-elute with other species	c 55
Evarzi-43	24-29	1	18-05-11	16.47	12.3	5.6	17.0	3.8	7.7	12.5	1955.0	1950.0	1975.5	CFC113 co-elute with other species	
		2	18-05-11	16.59	9.9	2.2	13.3	3.1	3.0	9.8	1954.0	1946.5	1973.5	CFC113 co-elute with other species	c 60
Evarzi-49	48-53	1	18-05-11	18.45	17.4	70.6	0.0	5.4	97.0	0.0	1956.0	1967.5	<1959,5	CFC113 co-elute with other species	
		2	18-05-11	18.57	20.5	96.8	0.0	6.3	132.9	0.0	1957.0	1970.0	<1959,5	CFC113 co-elute with other species	c 40
Skrunda-8	15-22	1	13-06-11	15.25	23.0	10.1	62.7	7.1	13.9	46.1	1957.5	1953.5	1985.5	CFC113 co-elute with other species	
		2	13-06-11	16.37	17.4	4.8	65.9	5.4	6.6	48.5	1956.0	1949.5	1985.5	CFC113 co-elute with other species	c 60
Skrunda-9	4-8	1	13-06-11	14.10	338.6	318.4	39.5	105.0	437.2	29.1	1974.0	1987.0	1981.5		
		2	13-06-11	14.22	347.9	324.6	38.3	107.8	445.6	28.2	1974.0	1987.0	1981.5		c 20
Incukalns-358	108-128	1	16-06-11	12.32	8.0	5.2	70.1	2.5	7.1	51.6	1953.5	1949.5	1986.0	CFC113 co-elute with other species	
		2	16-06-11	12.42	5.7	5.2	67.2	1.8	7.1	49.4	1952.5	1949.5	1986.0	CFC113 co-elute with other species	c 60
Incukalns-359	46-59	1	11-07-11	15.30	78.5	82.0	7.9	24.3	112.6	5.8	1964.5	1968.5	1969.5		
		2	11-07-11	15.40	76.8	83.1	6.7	23.8	114.1	5.0	1964.0	1968.5	1968.5		c 40
Baltezers-basin	0.00	1	11-07-11	11.32	409.6	229.1	55.5	127.0	314.5	40.8	88.0/06	*)	modern		T=23C
Baltezers		2	11-07-11	11.43	421.9	231.3	51.4	130.8	317.6	37.8	89.0/02	*)	91.5/03		modern
Zakumuiza-3	10-12	1	11-07-11	14.12	30.5	91.9	14.4	9.4	126.1	10.6	1959.0	1969.5	1974.0	CFC113 co-elute with other species	
		2	11-07-11	14.27	27.5	91.1	11.4	8.5	125.1	8.4	1958.5	1969.5	1972.5	CFC113 co-elute with other species	c 40
Virane-32	51-55	1	10-08-11	13.29	17.3	56.3	86.2	5.4	77.4	63.5	1956.0	1965.5	1988.0	CFC113 co-elute with other species	
		2	10-08-11	13.43	14.7	52.9	62.2	4.5	72.6	45.8	1955.5	1965.0	1985.0	CFC113 co-elute with other species	c 45
Virane-36	13-16	1	10-08-11	15.51	23.1	8.5	99.5	7.2	11.6	73.2	1957.5	1952.0	1989.5	CFC113 co-elute with other species	
		2	10-08-11	16.07	19.9	3.9	91.4	6.2	5.3	67.3	1957.0	1948.5	1988.5	CFC113 co-elute with other species	c 60
Baltezers47N	61-64	1	24-08-11	10.33	12.5	21.7	85.6	3.9	29.8	63.0	1955.0	1958.5	1988.0	CFC113 co-elute with other species	
		2	24-08-11	10.52	8.6	24.2	88.2	2.7	33.3	64.9	1954.0	1959.5	1988.0	CFC113 co-elute with other species	c 50
Griva-233	3-6	1	24-08-11	10.38	496.2	310.4	143.8	153.8	426.1	105.8	1978.0	1986.5	*)	N2O	
		2	24-08-11	10.53	504.2	316.6	104.7	156.3	434.6	77.1	1978.0	1986.5	1990.0	N2O	c 25
Griva234	13-16	1	11-09-11	12.50	77.6	72.9	147.7	24.1	100.1	108.7	1964.0	1967.5	*)	CFC113 co-elute with other species	
		2	11-09-11	12.58	87.1	72.7	178.2	27.0	99.8	131.2	1965.0	1967.5	*)	CFC113 co-elute with other species	c 40
Griva-235	40-44	1	11-09-11	14.35	8.2	7.3	49.3	2.5	10.0	36.3	1953.5	1951.5	1983.5	CFC113 co-elute with other species	
		2	11-09-11	14.43	6.4	16.8	45.4	2.0	23.0	33.4	1953.0	1956.5	1983.0	CFC113 co-elute with other species	c 55

"Concentration in water" are measured CFC-concentrations
"Partial pressure" is the calculated CFC-concentration in the atmosphere at the time of infiltration
"CFC-model infiltration year" obtained by comparison with atmoshpere CFC-curve for individual CFCs
"Remarks" eg. Other halocarbons observed in the chromatogram
High concentration of N2O interfer with CFC-12, therefore extra purge is needed to remove N2O from the trap
*) CFC higher than maximum equlibrium concentration with modern atmosphere

Ages that are obtained from every CFC concentration in ideal conditions should be the same but as seen in table 1, many of samples have unequal CFC ages. In most cases CFC-113 age is younger that CFC-11 and CFC-12 ages. Consideration of age determined from multiple CFC ratios provides dating options when one of three CFC compounds has been contaminated degraded or otherwise altered from its original concentration at or after recharge (International Atomic Energy Agency, 2006) as it seems to be.

It is possible to date groundwater using CFC mixing ratio between two of them. This approach has several limits for dating groundwater. The CFC-11/CFC-12 ratio has a dating range of approximately 1947 through 1976. The rapid growth of CFC-113 concentration in air from the late 1970s to the early 1990s permits dating, using either the CFC-113/CFC-12 or CFC-113/CFC-11 ratio from approximately 1975 into the early 1990s (International Atomic Energy Agency, 2006).

Ratio between every CFC in samples is plotted in Fig. 3. Year for each sample is an average year of two corresponding CFC concentrations.

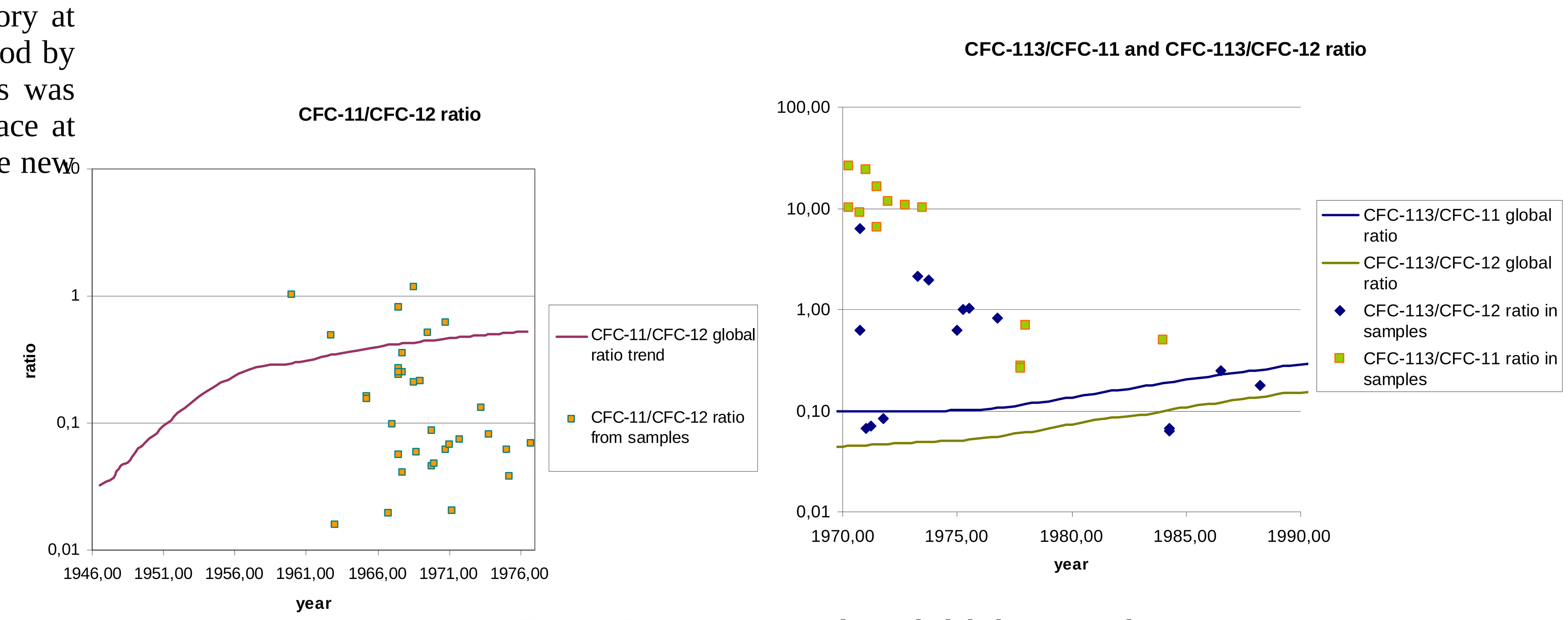

Fig. 3. CFC's ratio in samples and global ratio trends

Figure 3 shows that only small part of samples have equal CFC concentration and CFC ratio ages. Most of CFC-113/CFC-11 ratio are much greater than it should be while CFC-11/CFC-12 ratio tend to have lower value than global atmospheric ratio although last one is nearest to the global ratio trend and it could mean that CFC-11 and CFC-12 are better age dating indicators but with exceptions.

Particular situation is formed in Ēvarži wells where water residence time according to CFC-11 and CFC-12 concentration dating in depth of 24 – 29 m is ~63 years but at depth of 48 – 53 m water age is 43 years (distance between these two wells is only 10 meters) (Fig. 4.).

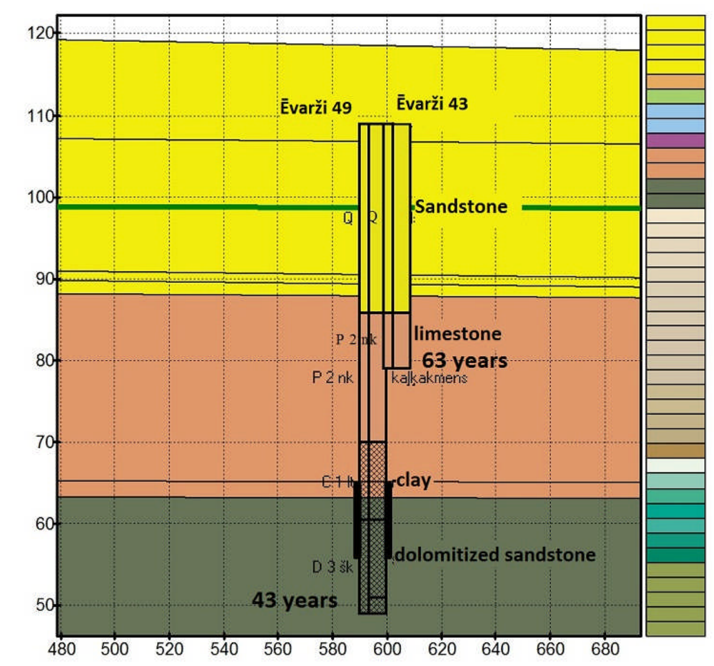

Fig. 4. Water residence time in Ēvarži 43 and Ēvarži 49 boreholes

Ēvarži 43 sample is placed between fractured limestone but deeper sample from Ēvarži 49 borehole is placed in dolomitized sandstone and it seems incorrectly (Fig. 4.). Solution for this situation is ratio age: according to International Atomic Energy Agency (International Atomic Energy Agency, 2006) stated principles for dating by CFC's ratios, CFC-11/CFC-12 dating ratio for Ēvarži 43 sample shows age of 38 years and it is close to the CFC-113 concentration age (36 years) and it is younger than deeper sample. According to these facts it is possible that CFC-11 and CFC-12 concentrations are degraded in this sample.

Mixing CFC ratio dating approach can help to obtain better results of groundwater recharge ages in case of CFC concentration degradation. More detailed investigation for CFC concentration age and CFC mixing ratio ages is necessary to ensure that wrong result will not be acquired. Wide scattering of CFC-113 related ratio dating as well as remaining CFC ratios shows that some of CFC almost in all cases are affected after recharge.

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