HYDROCARBON CONTAMINATION IN WATERS AND SEDIMENTS OF THE PERTUSILLO FRESHWATER RESERVOIR, VAL D'AGRI, SOUTHERN ITALY

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Presented at the 17th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region (MESAEP), September 28 - October 01, 2013, Istanbul, Turkey

ABSTRACT

In order to determine hydrocarbon contamination of drinking water in the Southern Italian region of Basilicata and to identify its source, we sampled water and subaqueous surface sediments from Lake Pertusillo, a freshwater, highly dynamic, artificial reservoir located entirely within the largest oil field in Italy (Val d'Agri, Basilicata). Monitoring by the Basilicata Agency for Environmental Protection (ARPAB) is infrequent and insufficient to determine temporal variability of water quality. In the present study, metals and hydrocarbons were identified and quantified in 4 water samples and in 10 subaqueous grab sediment samples. Our data were integrated with other 7 sediment samples collected by ARPAB. Total hydrocarbon concentrations ranged from 97 to 6458 μg/l in water samples and from 6.6 to 559 mg/kg in sediment samples, with values exceeding the threshold limits of Italian legislation, when present. The areal distribution of hydrocarbons in subaqueous surface lake sediments reveals a strong asymmetry between the northeastern and southwestern subaqueous lake margins. Higher levels of hydrocarbons were recorded along the northeastern side of Lake Pertusillo, at the mouth of stream tributaries and of the Agri River. 25 oil-producing wells are located on the northeastern side of Val d'Agri. River runoff represents thus an important pathway for hydrocarbons in the freshwater reservoir. Hydrocarbon concentrations along the southwestern subaqueous side of the reservoir were marked by lower values; the corresponding subaerial margin is more populated and urbanized than the northeastern one, with no oil-producing operations. There is evidence that urban runoff of street or agriculture waste is the less important hydrocarbon source, since the northeastern industrialised subaerial margin is much less populated and urbanized than the opposite one. Temporal high variability of water quality, asymmetric hydrocarbon distribution in sediments of subaqueous lake margins, and the occurrence of well-defined hydrocarbon-rich beds, indicate that most hydrocarbon deposition in Pertusillo reservoir was episodic, from the catchment basin trough northeastern lake tributaries and Agri River. This scenario is compatible with sources mainly related to oil industry of Val d'Agri.

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KEYWORDS: Val d'Agri, Southern Apennines, oil pollution, hydrocarbons in sediments.

1. INTRODUCTION

Water quality is becoming a major issue in countries affected by hydrocarbon extraction [1-5]. The increasing demand for oil and gas worldwide is driving petrochemical companies to target fragile ecosystems, at times lobbying governments for less stringent environmental regulations, often stirring controversies with local populations on issues related to health and environmental consequences. In this study we assess the impacts of oil drilling on drinking water quality in the Val d'Agri area in Basilicata, Southern Italy (Fig.1). Basilicata is the Italian region with the largest oil production and at the same time one of the most important sources of freshwater for the country. The Val d'Agri oil field (Fig. 2), owned by the Italian company ENI, produces about 85,000 barrels of crude oil per day with 25 active wells [6] located on the northeastern side of the valley (Fig. 3). Oil extraction activities started in the nineties and wastewater reinjection in 2001. The 660 km^2 oil field hosts 23 water bodies, more than 650 springs with a mean spring discharge from carbonate aquifers of about 3550 liters/sec, and the Pertusillo reservoir with a capacity of 155 Mcm (Fig. 4). The latter provides water intended for human use to Basilicata and Puglia southern Italian regions. According to ARPAB's classification Lake Pertusillo freshwaters are of class A2, and must be subject to physico-chemical treatments and disinfection prior to distribution and consumption by the public. Waters from Lake Pertusillo are thus sent to the nearby Missanello water treatment plant for purification. The latter does not treat nor eliminate hydrocarbons.

The responsibility to monitor water quality in the Lake Pertusillo reservoir rests with the Agenzia Regionale per la Protezione dell'Ambiente di Basilicata (ARPAB), the Basilicata Agency for Environmental Protection. ARPAB did not record nor analyze hydrocarbon levels in the Pertusillo reservoir until May 2011 [7], when we looked for hydrocarbons and local media reported our preliminary results. ARPAB monitoring began in June 2011, but its frequency is insufficient to detect temporal variability of water quality in such a dynamic body of water. Our 4 samples were the first to reveal high levels of total hydrocarbon (THC) in the Pertusillo freshwaters [8-10]. We further investigated THC in the Pertusillo sediments, since the latter act as ‘‘chemical archives” and geochronometers of contaminant deposition in the environment, providing valuable information in resolving pollution sources and sinks [11-12].

FIGURE 1 - Location of the Val d'Agri, Basilicata, Southern Apennines of Italy.

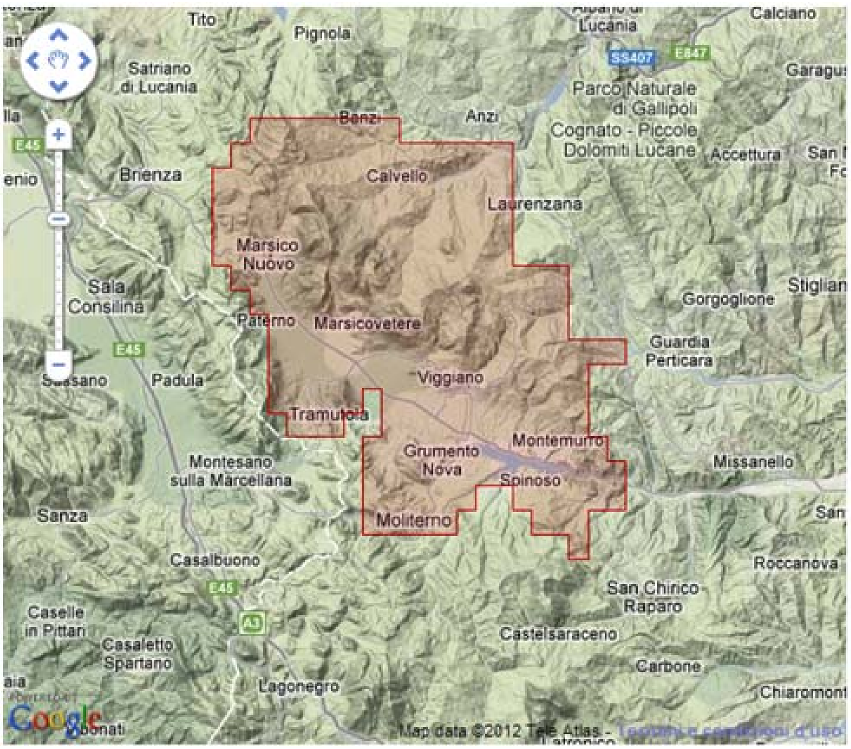

FIGURE 2 - Location of the Val d'Agri oil concession, that comprises the Pertusillo freshwater reservoir [6].

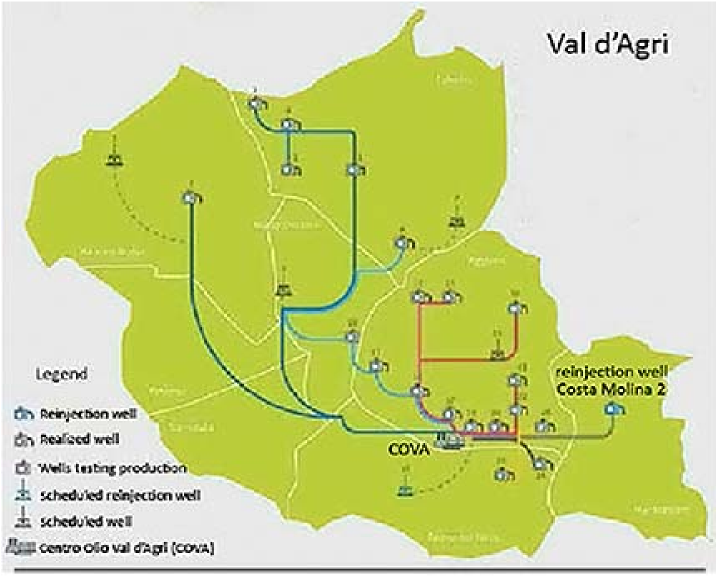

FIGURE 3 - Location in the Val d'Agri of oil wells, wastewater reinjection wells (Costa Molina 2), Centro Olio Val d'Agri (COVA) and pipelines. (Modified from ENI, 2013).

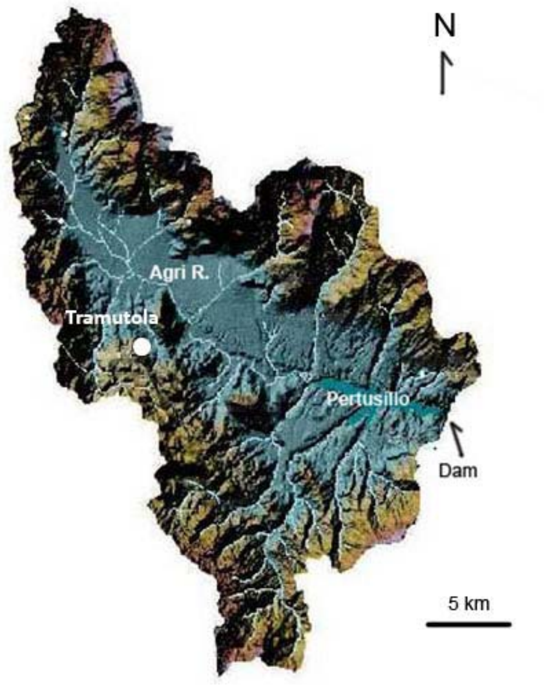

FIGURE 4 - Val d'Agri digital map showing the Agri River and the 22 tributaries merging into the Pertusillo freshwater reservoir. The map shows also the location of Tramutola, a village where a natural spring of water, oil and gas occurs.

2. STUDY AREA

The Val d'Agri [13-18] is a Pleistocene intermountain basin located in the axial part of Southern Apennines (Basilicata, Southern Italy; Fig. 1). It is a NW-elongated alluvial plain of 140 km^2, drained by the Agri River and its tributaries, and filled by up to 500 m of Pleistocene coarse- and fine-grained lacustrine and alluvial sediments, where minor porous aquifers occur [19-20]. Important karstified and fractured aquifers occur in the pre-Quaternary bedrock of the valley margins [21]. These include a carbonate platform unit of Late Triassic–Tertiary age, thrusted over a coeval basinal carbonate, siliceous, marl and siliciclastic rocks and their Miocene synorogenic cover. These units are situated over a buried layer of Mesozoic-Tertiary shallow-water carbonates, measuring roughly 6-7 km in thickness, and overlying Pliocene foreland rocks, which represent the western extension of the Apulian carbonate platform [22-26].

The Val d'Agri oil field comprises the Agri River alluvial plain, and includes its northeastern mountainous flank and small areas of its southern flank. Two carbonate reservoirs (TREND 1 and TREND 2) occur at an average depth of 3-4 km in the Mesozoic rocks of the Apulian carbonate platform, much deeper than the aquifers that are penetrated by oil drills. Lake Pertusillo is located at the southeastern end of the alluvial plain, roughly 2.5 km SE from the "Centro Olio Val d'Agri" (COVA): an oil facility that separates and desulfurizes oil, gas and water (Fig. 3). Several water pollution episodes have been reported in the past, such as the occurrence of benzene, toluene, manganese and sulfates exceeding the threshold values imposed by Italian legislation in the COVA ground-waters [27] that flow towards the Pertusillo reservoir [28].

3. METHODS

Waters and sediments were sampled from January 2010 to October 2012, when the Pertusillo reservoir was affected by severe pollution resulting in a die-off of a large number of carps and red algae infestations in eutrophicated waters. Four water samples (Pw1-Pw4) were collected at a depth of about 3 meters from the lake water surface with PET bottles, placed in a lightproof insulated box containing ice-packs, and transported to the laboratory. Sediment samples were collected from 10 stations (Ps1-Ps10) using a Van Veen grab sampler, stored in glass containers and frozen with ice packs on return to the laboratory. Sampling stations are shown in Fig. 5; geographic coordinates are listed in Table 1.

In the first and preliminary water sample Pw1, collected by Radicali Lucani Association, total hydrocarbons (THC) were not looked for. In water samples Pw2-Pw4 THC were measured using a gas chromatographer equipped with a FID (flame ionization detector), using method APAT Rap. 29/2003 met. 5160B2. Metals were measured with ICP- OES DUO, using methods APAT CNR IRSA 3010 Man 29 2003 + APAT CNR IRSA 3020 Man 29 2003. Other parameters were also analyzed with the following methods: pH - APAT CNR IRSA 2060 Man 29 2003; conductibility - APAT CNR IRSA 2030 Man 29 2003; COD - APAT CNR IRSA 5130 Man 29 2003; biochemical oxygen demand (BOD5) - APAT CNR IRSA 5120 Man 29 2003; total surfactants - APAT CNR IRSA 5170 Man 29 2003 + APAT CNR IRSA 5180 Man 29 2003; chloride content - APAT CNR IRSA 4020 Man 29 2003; Ammonia - APAT CNR IRSA 4030 A2 Man 29 2003; nitrate nitrogen - APAT CNR IRSA 4020 Man 29 2003; nitrite nitrogen - APAT CNR IRSA 4050 Man 29 2003; sulfates - APAT CNR IRSA 4020 Man 29 2003; total phosphor - APAT CNR IRSA 4110 A2 Man 29 2003; dissolved oxygen was measured in the laboratory using an ossimeter. In sediments THC were evaluated according to

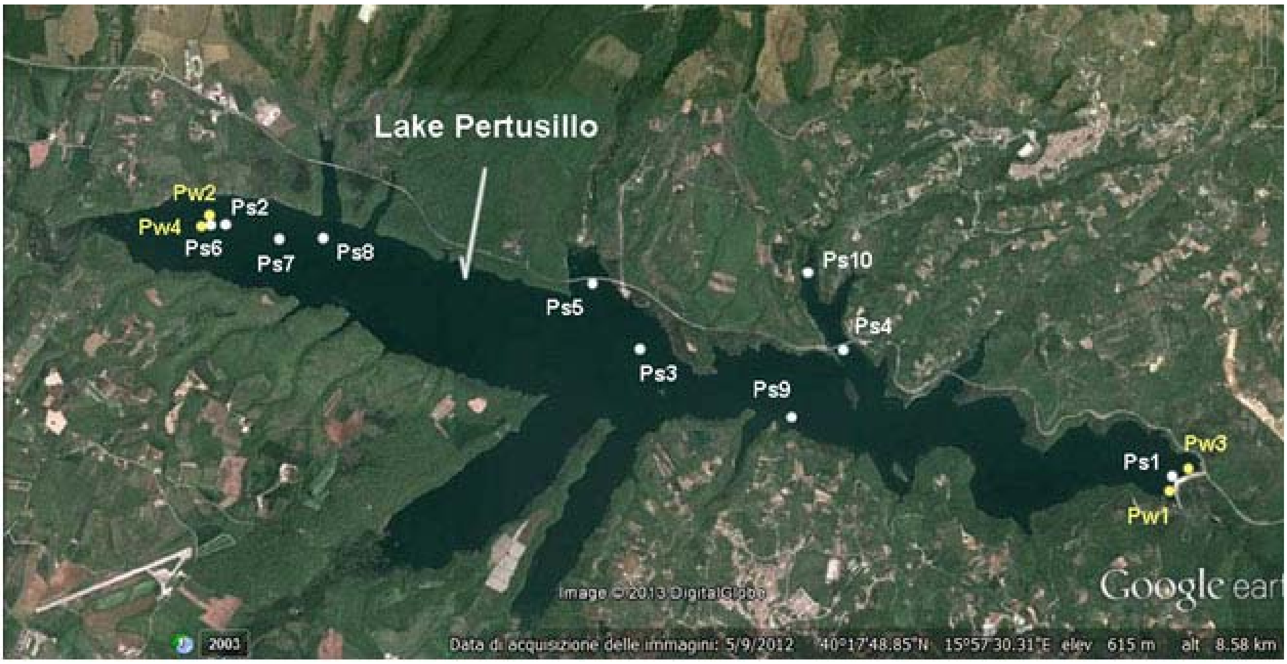

FIGURE 5 - Location of water (Pw) and sediment samples (Ps) in Lake Pertusillo. Courtesy of Google Maps.

TABLE 1 - Latitude, longitude and sampling date of water (Pw) and sediment (Ps) samples in the Pertusillo reservoir.

SAMPLE	LATITUDE	LONGITUDE	DATE
Pw1	40°16’31.25”N	16°0’1.86”E	21 January 2010
Pw2	40° 17’ 31.97”N	15°55’16.72”E	20 May 2011
Pw3	40°16’35.49”N	16°0’6.67”E	22 July 2011
Pw4	40°17’30.38”N	15°55’7.67”E	28 May 2012
Ps1	40° 16’33.27”N	16° 0’3.39”E	06 July 2011
Ps2	40° 17’30.03”N	15° 55’19.96”E	13 October 2011
Ps3	40°17’2.97”N	15°57’22.43”E	13 October 2011
Ps4	40°17’3.51”N	15°58’23.85”E	12 July 2012
Ps5	40°17’18.45”N	15°57’9.45”E	12 July 2012
Ps6	40°17'30.52"N	15°55'13.75"E	12 October 2012
Ps7	40°17'25.46"N	15°55'37.03"E	12 October 2012
Ps8	40°17'25.85"N	15°55'50.55"E	12 October 2012
Ps9	40°16'48.58"N	15°58'8.32"E	12 October 2012
Ps10	40°17'21.30"N	15°58'13.25"E	23 October 2012

methods EPA 5035 A 2002 + EPA 8260 C 2006 and UNI EN 14039 2005, and metals by ICP-OES DUO, according to methods UNI EN 13657:2004 + UNI EN ISO 11885:2009.

4. RESULTS

4.1. Waters

Preliminary data are listed in Colella [8-10] and are analyzed in conjunction with data collected for this work. Microbiological and physico-chemical parameters as well as hydrocarbon concentrations taken from water samples Pw1-Pw4 are summarized in Tables 2 and 3. All measured values are compared with threshold values imposed by Italian legislation for drinking water according to D.Lgs. 31/2001 and for class A2 water according to D.Lgs 152/2006. Threshold limits for THC in D. Lgs. 31/2001 are lacking; previous legislation - now repealed - DPR 236/1988- set a threshold limit for THC in drinking water of 10 μg/l. The latter is now regarded as a precautionary limit for drinking water, as recommended in 2002 by the Italian Institute for Health, the Istituto Superiore di Sanità [29] and by the Agenzia Regionale per la Protezione dell'Ambiente di Toscana, the Tuscan Agency for Environmental Protection (ARPAT). The threshold for THC in class A2 water according to D.Lgs 152/2006 is 200 μg/l.

THC concentrations from water samples taken from the Pertusillo reservoir are shown in Table 3. In the three of the four collected samples where hydrocarbons were looked for, levels exceed the 10 μg/l precautionary limit. In two of the four collected samples, the class A2 threshold of 200 μg/l was exceeded as well. The measured THC concentrations were 6458±645 μg/l in sample Pw2; 265±26 μg/l in sample Pw3 and 97±10 μg/l in sample Pw4. Metal concentrations are within quality standards for class A2 waters (Table 3), except for iron and manganese. Aluminum concentrations range from <1 to 5,308 μg/l exceeding the 200 μg/l threshold limit of aluminum for drinking water set by D.Lgs 31/2001.

4.2 Sediments

The lithology of the Pertusillo subaqueous surface sediments includes mud, muddy sand and granule. Grain size and chemical composition show large areal variability, due to the complex sedimentation pattern in Lake Pertusillo, with longitudinal input from the Agri River and lateral input from several tributaries on both its northeastern and southwestern flanks. Sediment samples collected from Lake Pertusillo show similar compositional anomalies to those reported for water samples in Table 3. Results are summarized in Table 4. Since Italian legislation lacks reference values for THC and metal concentrations in lake sediments, the usual threshold value that is commonly referred to is that for soils, of 60 mg/kg according to D. Lgs. 152/2006 (Alleg.5, P.IV, T.V, Tab.1A). Our results show that 60% of sediment samples (Ps1, Ps4-Ps8) carry THC concentrations in excess of the above reference value of 60 mg/kg.

Table 4 shows that THC areal distribution in reservoir sediments is highly variable, with values ranging from 6.6 to 559 mg/kg. Fig. 6 shows the location and THC values

TABLE 2 - Physico-chemical and microbiological parameters of Pw1 and Pw2 water samples of the Pertusillo reservoir compared with threshold values of Italian legislation for drinking waters (D. Lgs.31/2001) and Class A2 waters (D.Lgs. 152/2006).

Microbiological - Physico-chemical elements	Measure unit	Sample Pw1	Sample Pw2	Drinking waters (D.LGS. 31/2001)	Water class A2 (D. Lg.s.. 152/2006)
pH		7.3	8.16 +/-0.12	6.5 – 9.5	5.5-9
Conductivity	micro-S/cm	320	392.4 +/-6,8	2500	1000
Chlorides	mg/l	9.9	9.17 +/-0.98	250	200
Sulfates	mg/l	82	13.90 +/-0,93	250 l	250
Nitrates	mg/l	1.83	2.27 +/-0,95	50	50
Nitrites	mg/l	0.07	2.27 +/-0,95	0,50	
Ammonia	mg/l	0.08	<0,4	0,50	1.5
Phosphor	mg/l	Not measured	<0.05		
Dissolved oxygen	mg/l	Not measured	6.60 +/-0.66		
COD	mg O2/l	Not measured	7.2 +/-0.7		
BOD5	mg O2/l	Not measured	2.70 +/-0.81		<5
Total surfactants	mg/l	Not measured	<0.08		0.2
Total coliforms	UFC/100ml	Not measured	140	0	5000
Fecal coliforms	UFC/100ml	20	30	0	2000
Streptoc./Enter.	UFC/100ml	14	16	0	1000
Eschericia coli	UFC/100ml	<4	80	0	
Toxicity		Not measured	0		

TABLE 3 – Total hydrocarbon and metal concentrations in Pertusillo water samples Pw1-Pw4, compared with threshold values set by Italian legislation for drinking waters (D. Lgs. 31/2001) and for class A2 waters (D. Lgs. 152/2006). * Repealed DPR 236/1988.

Metals	Pw1 (μg/l)	Pw2 (μg /l)	Pw3 (μg /l)	Pw4 (μg /l)	Drinking waters (μg /l) D.Lgs.31/2001	Waters Class A2 (μg/l) D.Lgs.152/2006
Aluminum	Not measured	5308 +/-287	48	<1	200	
Antimony	Not measured	<0.5	<0.5	<1	5	
Silver	Not measured		<0.5	<1		
Arsenic	Not measured	<0.5	<0.5	<1	10	50
Barium	3000	76 +/-2.8	<0.5	28.0 +/- 4.5		1000
Beryl	Not measured	<0.5	<0.5	<0.4		
Boron	Not measured	33.3 +/-8.3	<0.5	3.24 +/-0.91	1000	1000
Cadmium	<1	<0.5	<0.5	<0,5	5	5
Cobalt	<0.5	<0.5	<0.5	<1		
Chromium	Not measured	7.20 +/-0.43	<0.5	<1	50	50
Iron	30	5720 +/228	64.3	<1	200	2000
Manganese	Not measured	160 +/-8	1080	1.51 +/-0.71	50	100
Mercury	Not measured		<0,5	<0,1	1,0	1,0
Molybdenum	Not measured	2.10 +/-10	<0,5	<1		
Nickel	<6	5.30 +/-0.53	0,5	<1	20	
Lead	<100	13.5 +/- 4	0,5	<1	10	50
Copper	< 40	9.10 +/-0.54	<0,5	<1	1000	50
Selenium	Not measured	<0.5	<0,5	<1	10	10
Tin	Not measured	1.400 +/-0.098	<0,5	<1		
Thallium	Not measured	0.5	<0,5	<0.2		
Tellurium	Not measured	<0.5	<0,5	<1		
Vanadium	Not measured	7.50 +/-0.38	<0,5	<1	50	
Zinc	Not measured	31.8 +/- 1.5	<0,5	<1		5000
TOTAL HYDROCARBONS	Not measured	6458 +/- 645	265 +/-26	97.0 +/-9.7	---------- (10*)	200
Hydrocarbons C<12	Not measured		<10	21.0 +/-2.1		
Hydrocarbons C>12	Not measured		265 +/- 26	76.0 +/- 7.6		

of our 10 sediment samples and other 7 samples collected by ARPAB; the location of the ARPAB sample near Rifreddo Stream is uncertain.

Similar to water samples, higher THC levels occur in sediment samples collected at the mouth of the Agri River and at stream mouths on the northeastern side of Lake Pertusillo, marked by the presence of oil wells (Fig. 6). The highest recorded value of THC (559 mg/kg) was measured in sample Ps4 where the Spetrizzone and Scannamogliera streams merge in a narrow embayment of Lake Pertusillo. These streams debouche into Lake Pertusillo after having drained a small area where the Costa Molina 2D wastewater reinjection well and several oil, gas, and produced water pipelines are located. THC levels decrease significantly in sediment samples collected along the southwestern subaqueous side of the reservoir, with values ranging from 5 to 37.5 mg/kg. No oil wells are present on the southwestern side of the reservoir.

Metal content in the Ps1-Ps10 sediment samples are also shown in Table 4; similarly for THC, higher concentrations occur at the Agri River and at stream mouths on the northeastern side of Lake Pertusillo.

While collecting data at station Ps10, near the confluence of the Spetrizzone and Scannamogliera streams (Figs. 5, 6), we also observed the emission from the underground of reddish fluids flowing into Lake Pertusillo (Fig. 7). Sample Ps10 (Fig. 5, Table 4) was collected at this site.

TABLE 4 – Total hydrocarbon (THC) and metal concentrations in Pertusillo sediment samples Ps1-Ps10. These values are compared with the threshold value of the Italian legislation for soils (D. Lgs. 152/2006, Alleg. 5, P. IV, T. V, Tab.1A), since Italian legislation is lacking such values in lake sediments.

METALS	Ps1 mg/kg	Ps2 mg/kg	Ps3 mg/kg	Ps4 mg/kg	Ps5 mg/kg	Ps6 mg/kg	Ps7 mg/kg	Ps8 mg/kg	Ps9 mg/kg	Ps10 mg/kg	D. Lgs. 152/2006 P.IV,T.V, Al. 5, Tab.1A
Aluminum	514 +/-55	7182 +/-538	8549 +/-641	4879 +/-305	4630 +/- 290	6734 +/-421	6078 +/-360	5840 +/-365	5123 +/-321	11970 +/-749	
Antimony	<0.034	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	10
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Arsenic	<0,5	2.00 +/- 0,22	1.38 +/0,15	1.19 +/- 0,14	1.27 +/- 0,15	2.37 +/- 0,28	2.04 +/- 0,24	2.31 +/- 0,28	2.19 +/- 0,26	2.18 +/- 0,26	20
Barium	3.02 +/- 0,36	40.7 +/4,9	35.3 +/4,2	35.0 +/4,3	36.8 +/4,5	33.3 +/4,21	31.8 +/3,29	31.8 +/3,9	23.6 +/2,9	53.9 +/6,6	
Beryl	<0.5	<0.5	<0.5	<0.5	<0.5	0.545	<0.5	<0.5	<0.5	<0.5	2
Boron	1.17 +/- 0,18	16.9 +/2,5	13.8 +/2,1	8.5 +/-1	7.1 +/-0,9	15.5 +/-1,7	13.2 +/- 1,5	14.4 +/1-6	13.1 +/- 1,5	13.7 +/- 1,6	
Cadmium	<0.5	0.80 +/- 0,18	0.74 +/- 0,15	0.65 +/0,11	<0.5	0.80 +/- 0,12	0.68 +/- 0,11	1.04 +/- 0,15	0.94 +/- 0,14	0.75 +/- 0,12	2
Cobalt	<0.5	4.66 +/- 0,70	3.77 +/- 0,57	2.56 +/- 0,31	2.34 +/- 0,29	5.15 +/- 0,62	4.27 +/- 0,52	4.76 +/- 0,67	4.02 +/- 0,49	4.36 +/- 0,53	20
Chromium	0.75 +/0,11	11.9 +/- 1,8	9.4 +/1,4	7.4 +/- 0,9	6.02 +/-0,74	9.4 +/1,1	7.87 +/- 0,96	7.09 +/- 0,86	7.4 +/- 0,9	11.9 +/- 1,4	150
Iron	515 +/-29	7429 +/-1114	11010 +/-1651	4862 +/-1024	4399 +/-926	6920 +/1458	6472 +/1363	4557 +/-960	6033 +/-1271	7044 +/-1484	
Manganese	8.17 +/- 0,82	241 +/- 24	143 +/- 14	104 - /+12	84 +/-10	186 +/- 22	136 +/- 16	99 +/- 11	108 +/- 12	203 +/- 24	
Mercury	<0.5	<0.5	<0.5	<0.1	<0.1	<01	<0.1	<0.1	<0.1	<0.1	1
Molybdenum	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	
Nickel	0.70 +/- 0,10	12.7 +/- 1,9	10.9 +/- 1,6	7.01 +/- 0,83	5.9 +/-0,7	11.0 +/- 1,3	9.4 +/- 1,1	9.2 +/- 1,1	6.97 +/- 0,83	12.4 +/- 1,5	120
Lead	<0.5	6.32 +/- 0,63	4.67 +/- 0,47	4.27 +/- 0,52	3.96 +/0,49	6.91 +/- 0,83	5.61 +/- 0,86	3.99 +/- 0,49	5.42 +/- 0,66	6.33 +/- 0,76	100
Copper	0.593 +/- 0,089	14.9 +/- 2,2	9.2 +/- 1,4	8 +/-1	7.49 +/0,93	13.1 +/- 1,6	9.9 +/- 1,2	9.2 +/- 1,1	6.11 +/- 0,77	16.2 +/- 1,9	120
Selenium	<0.005	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3
Tin	<0.5	<0,5	<0.5	<0,5	<0.5	<0.5	<0,5	<0,5	<0.5	<0.5	1
Thallium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1
Tellurium	<0.5	0.76 +/- 0,15	0.67 +/- 0,13	<0.5	<0.5	0.91 +/-0,11	0.73	0.8	0.704	0.594 +/-0,12	
Vanadium	0.533 +/0,080	13 +/-2	10.6 +/- 1,6	9.1 +/- 1,1	7.92 +/0,97	15.6	13.1 +/- 1,6	11.3 +/- 1,4	10.9 +/- 1,3	15.0 +/- 1,8	90
Zinc	2.31 +/0,35	37.7 +/- 5,6	27 +/-4	27.2 +/- 2,7	27.5 +/-2,7	44.5	35.7 +/- 3,4	22.2 +/- 2,3	27.6 +/- 2,7	68 +/-6	150
TOTAL HY-DROCARBONS	134 +/- 13	7.7	5.6	559 +/- 55	122 +/-12	127 +/- 12	233 +/- 23	62.6 +/- 6,3	37.5 +/- 3,8	48 +/- 4,8	60
C < 12	<1	<1	<1	5.8 +/1,5	5.2 +/1,4	2.54 +/- 0,93	2.4 +/- 0,29	3.7 +/- 1,1	1.85+/- 0,61	3 +/-1	10
C 10 – C 40	134 +/-13	7.7 +/- 6,5	5.6 +/- 4,6	553 +/- 89	117 +/-23	124 +/- 24	231 +/- 39	59 +/- 15	36 +/- 12	45+/-13	50

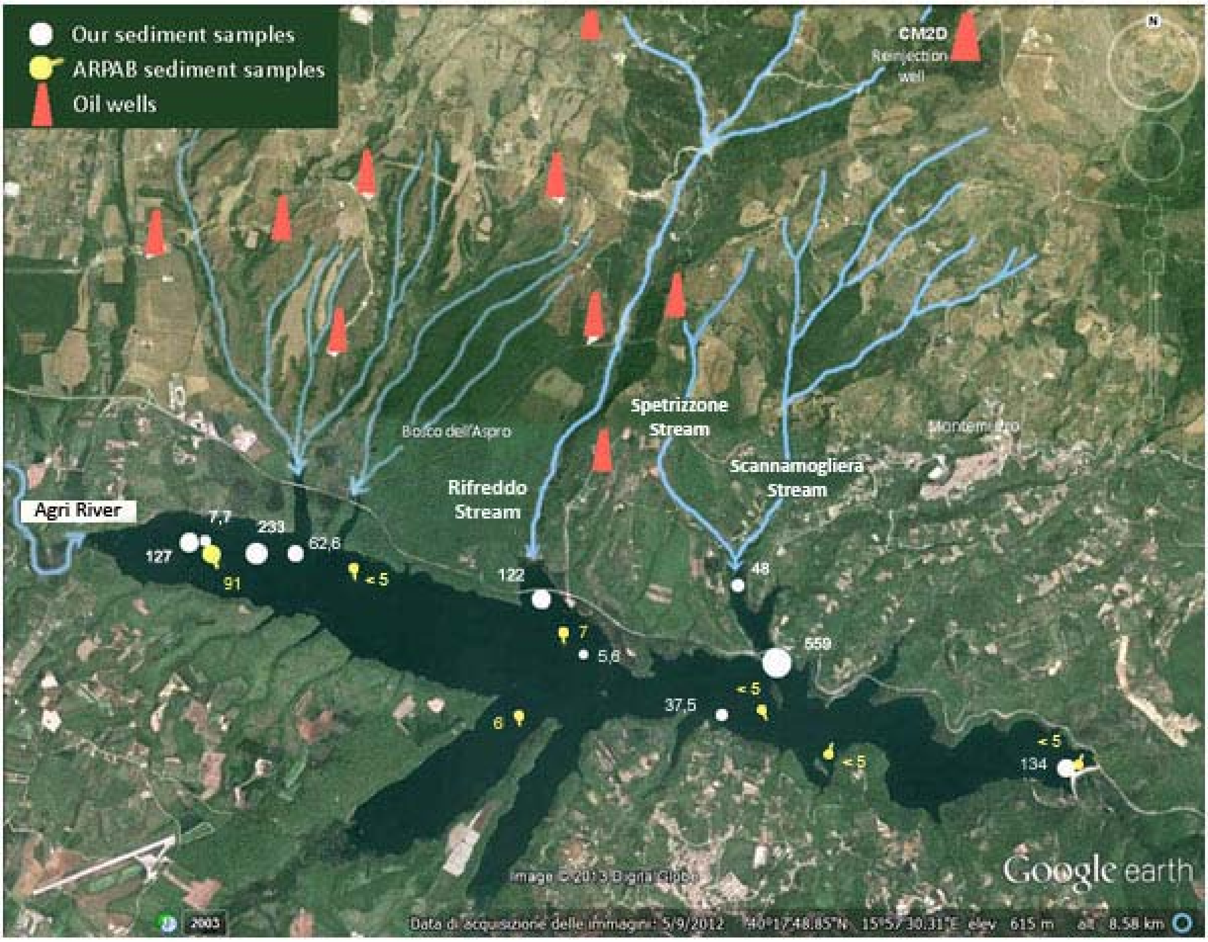

FIGURE 6 - Areal distribution of total hydrocarbons in subaqueous surface sediments of Lake Pertusillo. Dots show the location of our (white) and ARPAB's (yellow) sediment samples. The numerical values shown are concentrations of hydrocarbons in mg/kg. Courtesy of Google Maps.

FIGURE 7 - Reddish fluids flowing from the underground in a stream that debouches in Lake Pertusillo.

5. DISCUSSION AND CONCLUSIONS

Total hydrocarbon (THC) concentrations in water samples collected from Lake Pertusillo ranged from 97 to 6458 μg/l, with three of four samples exceeding the precautionary value for drinking waters and two measurements exceeding the threshold value for Class 2 waters. In sediment samples THC varied from 5.6 to 559 mg/kg with 60% of our measurements exceeding the reference threshold value.

Our results show: i) the marked asymmetric distribution of THC in lake subaqueous surface sediments, with the more polluted area adjacent the northeastern side where oil wells are present; ii) higher hydrocarbon concentrations at stream mouths of the northeastern lake margin and of the Agri River; iii) the highest THC value at the confluence of two very small streams (Spetrizzone and Scannamogliera), that drain into Lake Pertusillo from a small area characterized by oil and wastewater reinjection wells, as well as several pipelines of oil, gas and reinjection waters originating from the Centro Olio Val d'Agri.

Hydrocarbon contamination of the Pertusillo freshwater reservoir could be ascribed to several potential sources. It could be of natural origin, possibly from the Tramutola spring from which a mixture of water, oil and gas naturally flow into the environment (Fig. 2); it could be due to unauthorized domestic and/or agricultural discharges or to surface runoff from other contaminants; or finally to oil related activities such as spills during the transport of crude oil, illegal discharges of waste, accidents to oil wells and reinjection wells, leaks from pipelines and/or well casings.

Our sedimentological study indicates that most of the THC in the Pertusillo reservoir is due to episodic depositional events, as suggested by the high water quality variability and by the presence of hydrocarbon-rich thin beds in some muddy clods sampled by grab. The occurrence of higher THC concentrations at stream mouths, suggests intermittent discharges of land-derived pollutants both from the longitudinal input of the Agri River and from the lateral input of stream tributaries on the northeastern side. This scenario is incompatible with a prevalent natural input from the Tramutola oily waters that flow into the Agri River north of Lake Pertusillo. The longitudinal input of the river is inconsistent with the asymmetric hydrocarbon distribution between the two sides of the lake, and does not explain the occurrence of high THC concentrations in lateral streams and in narrow lake embayments, such as those measured at stations Ps4 and Ps5.

It is also unlikely that unauthorized domestic and/or agricultural discharges, or other surface runoff of anthropogenic contaminants, would have contributed significantly to hydrocarbon contamination on the northeastern side of the Pertusillo reservoir, since this side of the lake has only one small village and is much less populated and urbanized than the opposite one, with three villages.

Our analysis suggests that it is highly likely that hydrocarbon contamination in the Pertusillo reservoir originates from oil extraction and related processing, storage and disposal activities. Several pollution episodes support this hypothesis: the occurrence of high concentrations of manganese, benzene, toluene and sulfates, as measured by ARPAB [27] in June 2011 in ground-waters at the Centro Olio Val D'Agri that flow towards lake Pertusillo [28], the several episodes of crash of trucks that discharged oil on soils or directly in the Agri River, as documented by local media, the oil spills at COVA [30], and the problems of Costa Molina 2D reinjection well in the past [31].

ACKNOWLEDGEMENTS

This study was realized by Prof. Albina Colella, with the collaboration for field sampling of Giuseppe di Bello, Roberto Tedesco and Giovanni Boezio, and was financially supported by University of Basilicata and by local environmental associations. The analysis of water sample Pw1 was financed by Radicali Lucani Association. The study benefited of helpful discussions with Prof. Maria Rita D' Orsogna, that was supported by the National Science Foundation through grant DMS-1021850 and by the ARO through the MURI grant W911NF-11-1-0332.

The authors have declared no conflict of interest.

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Received: June 04, 2014
Accepted: June 18, 2014

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