Does salt water intrusion constitute a mercury contamination risk for coastal fresh water aquifers?

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"Capsule": *Mercury pollution has been coupled with progressive salt water intrusion along coastal aquifers in Tuscany.*

Abstract

Four different sampling surveys were carried out in 1998 to evaluate the possible causes of severe mercury contamination involving many wells spread over a vast territory along the coast of southern Tuscany (Italy). Several samples of groundwater and coastal sea water were collected to determine the Hg, Cl, Ar, He and N contents. Anthropogenic or deep-seated sources of the Hg involved in the contamination event can be excluded. The observed coupling of Hg pollution with progressive salt water intrusion along the coastal aquifer indicates a close causal relation between these two phenomena. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The ever-growing demand for fresh water for a number of human purposes has become a world-wide cause of concern. Nowadays, groundwater reserves are exposed to intensive exploitation, which may create serious problems in coastal areas where some hydraulic connection exists between the water reservoirs and sea water (Van Dam, 1996). Hydraulic gradients following intensive withdrawal of fresh water in this type of aquifer can favor salt water intrusion, which in extreme situations can strongly affect the pumping wells (Fig. 1). The southern coast of Tuscany is also affected by this phenomenon (Pranzini and Bencini, 1996).

Drinking water standards established by authorities of developed countries (EU, USA, Canada) require that salinity values remain low (Tebbutt, 1992; WHO, 1993; Foster, 1995). Hence sea water intrusion may also rule out important water supplies.

Along the southern coast of Tuscany, several important aquifers are hosted by an Upper Triassic, very permeable formation, the so-called "Calcare Cavernoso" (Cavernous Limestone). In the Orbetello-Mt. Argentario area (Fig. 2), numerous wells withdraw large quantities of water, mostly for non-drinking purposes (agriculture, fish breeding, etc.). In February 1998, routine analyses of several of these wells revealed anomalous mercury (Hg) contents in the water, far beyond the upper limit for drinking water standards fixed by Italian law (1 μg/l). This compelled the quality control authorities and the water supply management to interrupt the pumping and distribution of drinking water from two of the three main wells employed for this purpose.

However, this is not an isolated case along the southern Tuscany coast, since about 50 km north, in the Gulf of Follonica, three wells for drinking water were closed in 1995 on account of Hg contamination. Curiously, in both cases Hg contamination was coupled with a steep increase in chloride values related to the intrusion of marine salt waters. In this paper, we will try to highlight the possible reasons for the observed Hg contamination and to evaluate possible relations to the intrusion of sea water.

2. Hydrological outline of the study area

Fig. 2 shows the Orbetello-Mt. Argentario area with the location of the main active pumping wells, including the Hg-contaminated ones which formerly contributed

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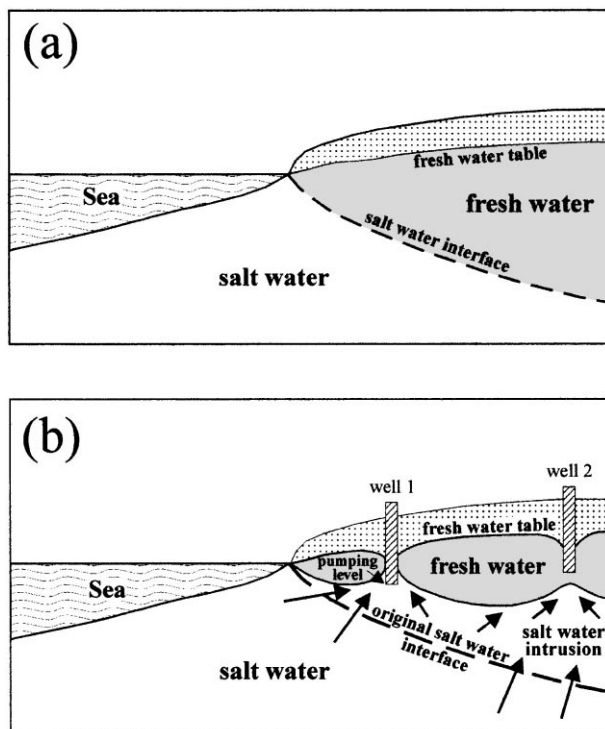
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Fig. 1. (a) Sketch of an unconfined coastal aquifer. (b) Salt wedge intrusion and contemporaneous thinning of the fresh water layer caused by overpumping.

to the drinking water system of this area. The figure also illustrates a model of the inland advance of marine water, as inferred from a geophysical survey carried out in 1991 (courtesy of Acquedotto del Fiora Special Agency). The salt water intrusion has been caused by overpumping of the wells (Fig. 1), at a faster rate than the natural aquifer replenishment, and the fresh water–salt water interface appears to be moving rather far inland (as indicated in Fig. 2). The waters of various wells close to the lagoon shore north of Ansedonia, for instance, show very high chlorine values (we measured contents from 2.5 to 10.8 g/l Cl), confirming on geochemical grounds the strong influence of marine waters (Table 1).

3. Sampling and analytical methods

During four different sampling surveys carried out in spring and summer of 1998, 51 samples of groundwater and marine coastal water were collected. The first sampling survey was devoted to the collection of water samples from various (17) wells (used for drinking water or for fish breeding) in order to assess the situation shortly after the discovery of the Hg contamination by the water quality control laboratory. A second survey was performed about a month later to re-sample the wells for a comparison with our previous results and

with those from the weekly monitoring by ARPAT (Environmental Protection Agency of Tuscany).

In a third survey in July, samples of marine water (10) were collected along about 40 km of coast, from south of Ansedonia to the mouth of the Albegna River, care being taken to avoid potential sources of pollution. Samples of water from the drinking wells were also taken once again.

Finally, water samples from three wells supplying drinking water (both Hg-contaminated and uncontaminated) were collected to determine the dissolved gas composition.

We collected the samples for Hg content determination in glass bottles (1000 cc), by drawing the water from the service tap of the well or by aspiration of the sea water (from about 30 cm below the surface). Immediately after collection, two sub-samples of 250 cc each were drawn from the 1000-cc water sample. To the first one, we added 1.25 cc HNO_3 for total Hg determination. The second consisted of a 0.2–μm filtered sample (Schleicher & Schuell pyrogen-free syringes) for an appraisal of the role of the particulate matter.

At the beginning of September, we collected samples for the determination of water-dissolved gases (Ar, He, N_2), employing appropriate Pyrex vials, according to the suggestion of Mazor (1977) and D'Amore and Nuti (1977).

The glass bottles used to collect groundwater and coastal marine water samples were previously kept in an oven for 24 h at 80°C and rinsed with a 5% HNO_3 solution of bidistilled water. Hg contents were determined with a Perkin Elmer 5000 AAS after Hg preconcentration on a gold trap, according to the method described by Duchi (1978). Briefly, the procedure consists of: (1) a reducing agent (stannous chloride or hydroquinone) is added to the acidified (0.5% HNO_3) water sample to convert Hg to the gaseous metallic form $Hg°$; (2) it is stripped in a prefiltered, controlled (120 cc/min) air flow passing through a gold trap (made of about 1 g of very small gold shavings in a Pyrex involucre); (3) the $Hg°$ is then desorbed from the gold amalgam at 600°C in a furnace and sucked into the AAS reading cell. This method is very effective mainly when very low Hg concentrations are to be determined. The precision of Hg determinations resulting from the analysis of 10 replicates of freshly prepared Hg standard solutions was within 8%. Ultrapure reagents (BDH) were used and working standards were prepared from BDH stock solutions.

Chlorine contents were determined with a Hach DR-4000 UV-VIS spectrophotometer following the Hach 8113 method. The accuracy and precision of the Cl analyses were both within 10%.

Gas analyses were performed at the Laboratory of Fluid Geochemistry, Department of Earth Sciences, University of Rome "La Sapienza". The determination
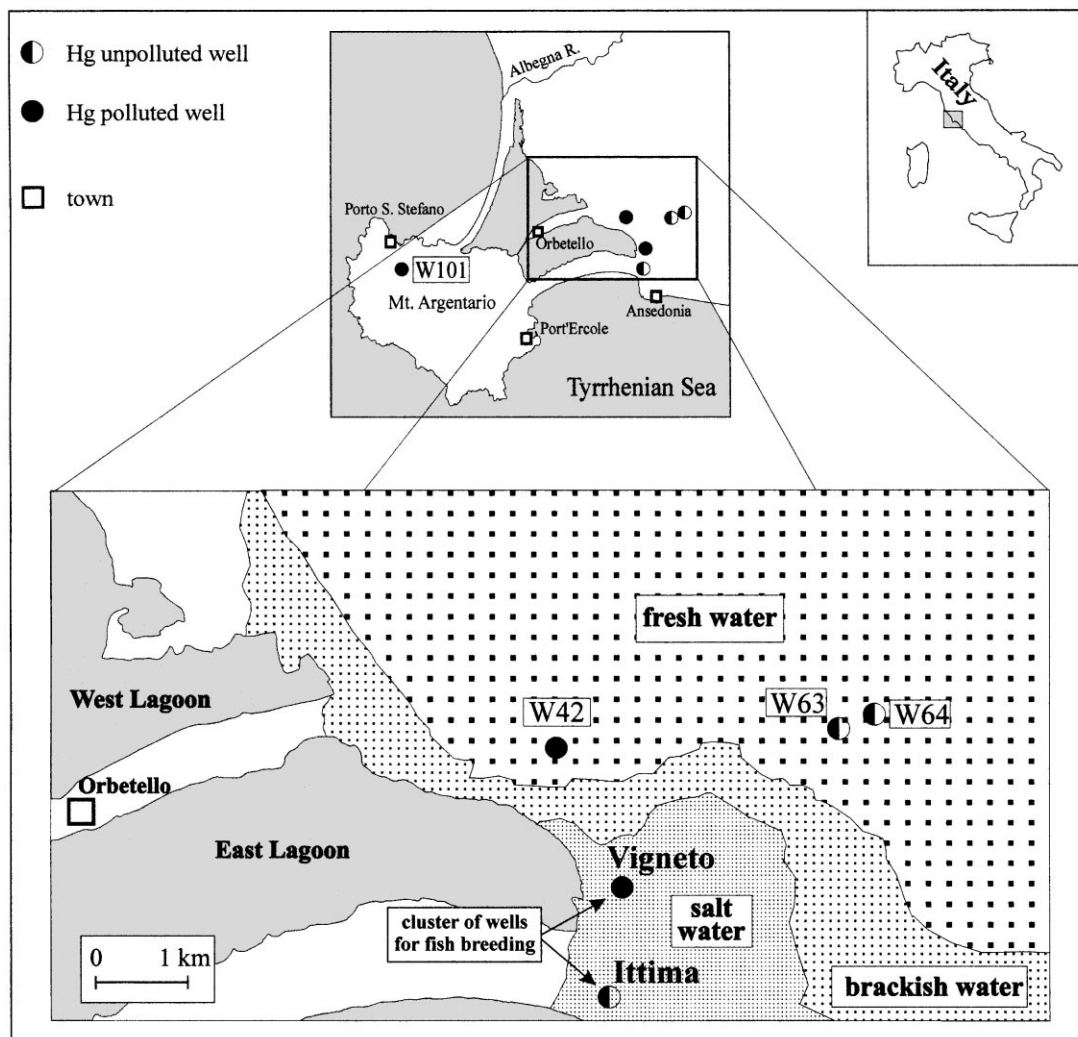
Fig. 2. Sketch map of the study area with the location of the main wells. The effects of the inland marine water intrusion are extrapolated from the data of a geophysical survey (carried out in 1991) and are referred to the absolute quota of about 1 m above sea level (courtesy of Acquedotto del Fiora Special Agency).

of helium (He) was performed with a Varian Inst. Mass 4 spectrometer. Sample analysis is based on the comparison of the peak height (Ph) for a known concentration (Ch) standard (air, which has a He content of 5220 ppb) and the peak height (Px) of the sample. Argon (Ar) and N_2 were determined by means of a quadripolar Sensorlab SX 200 VG mass spectrometer. A simultaneous analysis of masses 28 and 40 was carried out and the results were expressed as concentration percentage. Prior to running the samples, we tested a number of standards in order to verify the response of the instrument. The accuracy of the analyses was within 15%, while the precision varied from 5 to 8%, depending on the species.

4. Results and discussion

Total Hg contents in the contaminated wells are in the range 1–39.7 µg/l (Table 1). Water filtration was able to eliminate most of the contained element; thus, it appears in some way linked to the particulate phase. Experiments of Hg stripping by air flow, carried out on unacidified and unfiltered water samples, demonstrated that the Hg mostly occurs in the gaseous elemental form $Hg°$. The relationship with suspended matter can be explained by the low solubility of $Hg°$ in water and the tendency to escape the aqueous medium by sticking to the floating particles.

There is no obvious explanation for the Hg contamination of several wells spread over a relatively vast territory. However, this feature tends to exclude the hypothesis of an accidental anthropogenic input of metallic Hg to the environment. Such a hypothesis is even less likely when it is considered that the drinking water wells are located inside a protected area. Hence, we must seriously consider the alternative hypothesis of some natural mechanism able to add anomalous Hg aliquots to the groundwater of the area.

Table 1
Mercury and chloride contents in the wells of the study area

Well	No. samples	Time span[b]	Hg range (μ/l Hg)	Chlorine range (mg/l Cl)
W42 — Pitorsino 1[a]	39	Mar. 98–Jan. 99	2.4–5.0	370–486
W63 — Pitorsino 3[a]	4	Apr. 98	< 0.5–0.5	427–476
W64 — Giardino 2[a]	22	May 98–Jan. 99	< 0.5–0.5	339–492
W101 — Cannatelli[a]	6	Feb. 98–Apr. 98	3.2–39.7	198–691
Vigneto wells[a]	9	Mar. 98	0.5–3.2	10 300–15 700

Well	Apr. 98		May 98		Jul. 98	
	μg/l Hg	mg/l Cl	μg/l Hg	mg/l Cl	μg/l Hg	mg/l Cl
W42 — Pitorsino 1	2.82	412	3.14	415	3.00	390
W63 — Pitorsino 3	0.12	468	0.14	461	0.12	457
W64 — Giardino 2	0.09	345	0.11	475	0.11	390
W101 — Cannatelli	3.04	187	3.12	195	3.10	190
Vigneto wells						
W68	1.60	6790	2.43			
W69	1.12	8190	1.20			
W70	1.08	4220	1.06			
W71	1.53	5110	1.94			
W72	0.84	2510	1.02			
W73	0.93	3270	0.94			
W74	1.79	6400	1.68			
W75	0.71	3120	0.88			
W76	0.58	3800	0.65			
Ittima wells						
W77	0.20	10 840	0.22			
W78	0.17	9730	0.16			
W79	0.13	8720	0.14			
W80	0.16	7760	0.15			

[a] Data collected by ARPAT (Environmental Protection Agency of Tuscany).

[b] The quality control measurements have revealed small fluctuations of the Hg values, with an apparent slight decrease in time. However, this trend could be influenced by the fact that, after the discovery of the Hg pollution, the wells were subjected first to a marked reduction of pumping and later its complete cessation. The very high value (39.7 μg/l) measured in the water of the W101 well refers to a single measurement (the very first one, which signalled the Hg pollution and prompted the blanket controls) made after a period of inactivity of the well.

At least in theory, a main candidate could be a diffuse degassing phenomenon from deep-seated sources connected with the still active hydrothermal circulation which marked the recent geological history of this region (Calamai et al., 1970; Duchi et al., 1987). Moreover, world-class Hg ore deposits, linked to 0.5-Myr-old volcanism, are situated not far from the study area (Mt. Amiata ore field). It is well known that geothermal fluids are usually rich in highly volatile elements like Hg and that this element is mostly contained in these fluids in the elemental form Hg° (Robertson et al., 1977).

To test the hypothesis of an interference of deep fluids with the aquifer, we collected water samples from two locally important wells (W42-Pitorsino 1 and W101-Cannatelli), both contaminated by Hg, and from an unpolluted well (W64-Giardino 2), still connected to the drinking water system, in order to determine the contents of dissolved N_2, Ar and He.

The molar ratios of these gases can give precise indications of their origin (Mazor, 1977; Giggenbach, 1980;

Nicholson, 1993). Fig. 3 is a ternary plot which can help to identify the source of the gaseous phase. On the plot, the waters of the three wells are situated close to the air standard water (ASW) composition (gases in water equilibrated with atmospheric air at 20°C); thus, the gas mixing can be considered diagnostic of a meteoric origin quite free of deep-seated contribution. Moreover, it is highly significant that both contaminated and uncontaminated waters plot in the same region of the ternary diagram.

Another hypothesis of the ultimate origin of the Hg contamination can be proposed, namely that Hg could be leached (by the intruded marine waters) from the rocks hosting the aquifer. However, this theory is refuted by a number of facts. First, the host rock of the aquifer (Calcare Cavernoso) can hardly be envisaged as a valid Hg source since Baroni et al. (1994), in a study of Hg distribution in the rocks of Tuscany, found that these rocks have the lowest contents of the element (lower than the crustal average). Metal leaching from
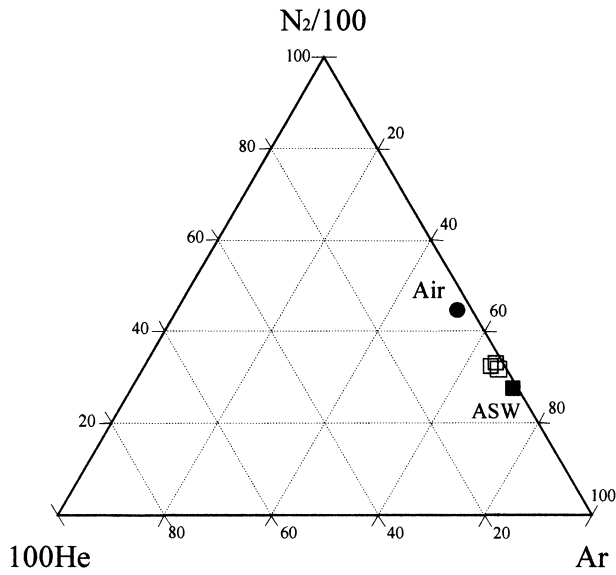
Fig. 3. Plot of the water-dissolved N₂, Ar and He contents in the wells of the Orbetello-Mt. Argentario area. Empty squares are the groundwater samples from the Pitorsino 1 (W42), Giardino 2 (W64) and Cannatelli (W101) wells. The solid square is the air standard water (ASW) composition (gases in water equilibrated with atmospheric air at 20°C). The solid circle represents the atmospheric air mixing for the considered gases.

blind Hg-ores appears theoretically possible, especially in a region such as southern Tuscany. We must stress, however, that the main Hg-bearing mineral is the sulfide, or cinnabar (HgS), which is known to be particularly stable in poorly oxygenated environments like the one we are dealing with. Furthermore, if we were to accept that this is the true mechanism, we would have to invoke the same solution to the problem at various times and at different places.

Nevertheless, our 'core problem' consists in explaining the Hg contamination by Hg°. Hence the mechanism
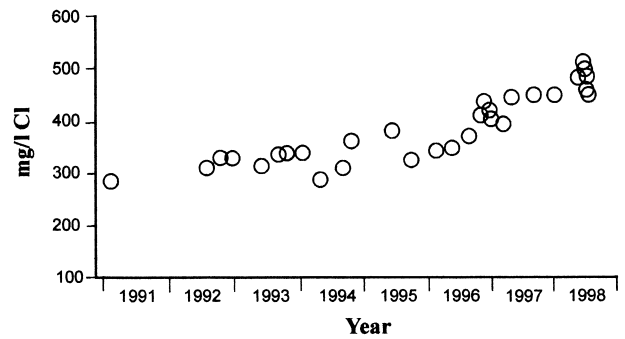

Fig. 4. Temporal trend of chlorine values in the W42 well (data from ARPAT).
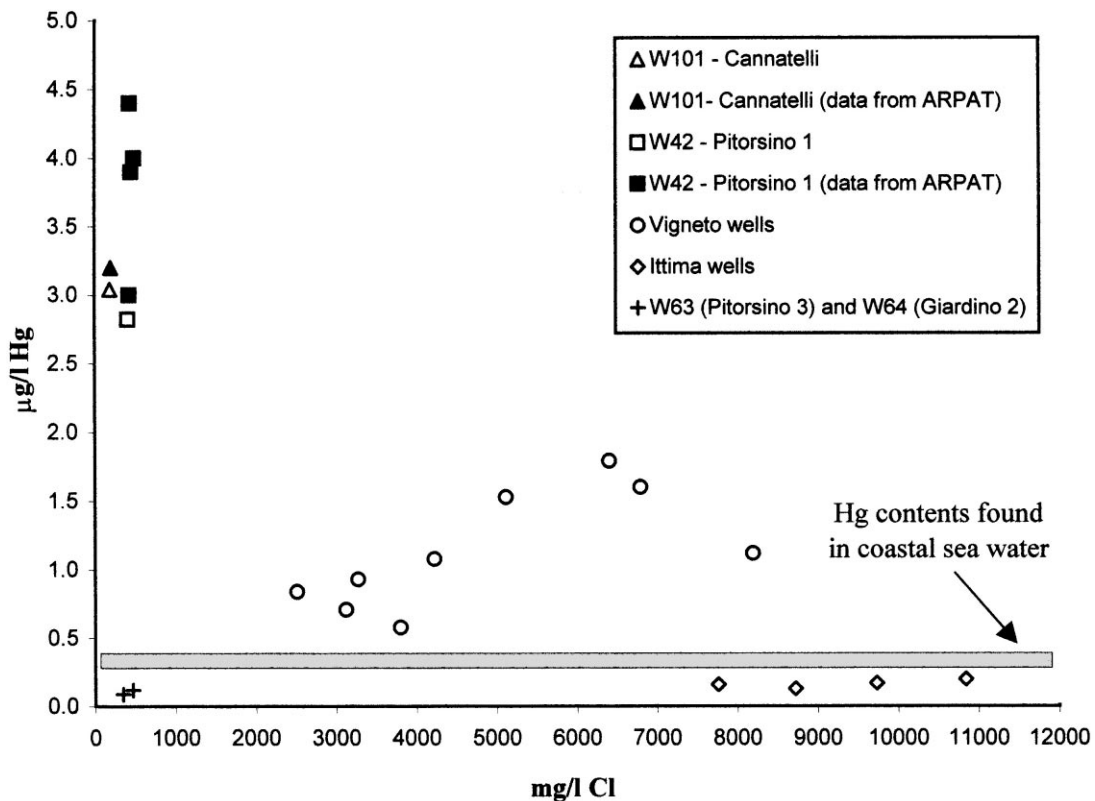

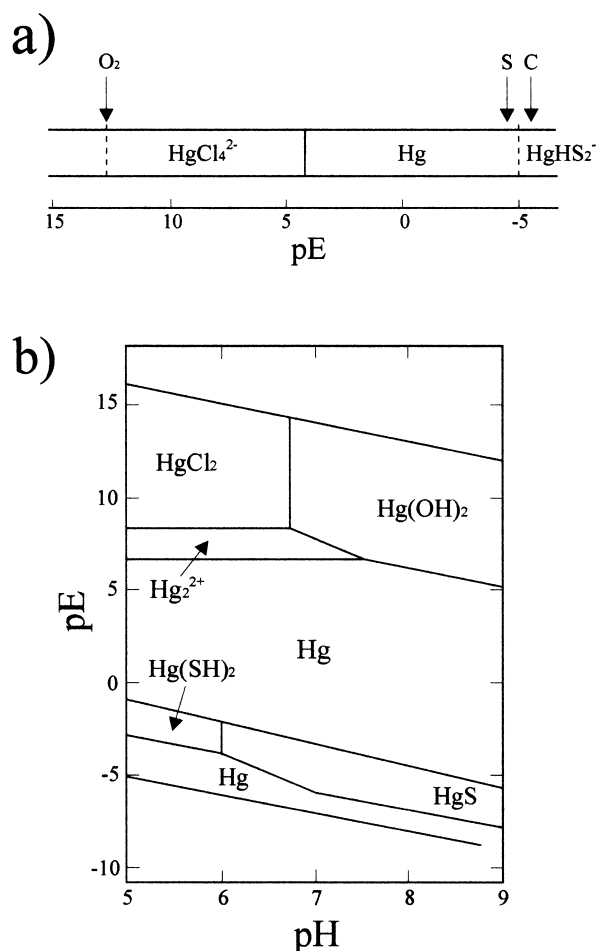Fig. 5. Chlorine versus mercury contents in the wells of the study area (samples collected in April 1998).

a)

b)

Fig. 6. Distribution of Hg species in aqueous solution at different pE values. (a) Predominance diagram of Hg species in sea water at pH 8.2. The arrow marked O_2 indicates the pE of oxygenated water. The anoxic system is shown by the arrows marked S and C, corresponding to a 10% reduction of sulfate (S) and bicarbonate (C) (modified after Turner, 1987). (b) Predominance diagram of Hg species at various values of pH and pE (modified after Allard, 1995; see also Pourbaix, 1966, and Dyrssen and Wedborg, 1991).

giving rise to the elemental Hg appears more important than the simple presence of this chemical species in marine water.

Having ruled out alternative hypotheses, we then considered the intrusion of sea water into the coastal aquifer as a possible factor involved in the observed Hg contamination.

As shown in Fig. 4, the routine water quality controls by ARPAT reveal a sharp and progressive increase of the chloride contents in fresh groundwater of this area. This is common to many wells along the coast and in various cases is coupled with the recording of Hg contamination.

The coastal sea water of this area has anomalous Hg contents with respect to unpolluted marine waters. The samples collected along this tract of coast have values between 0.2 and 0.3 μg/l, i.e. at least an order of mag-
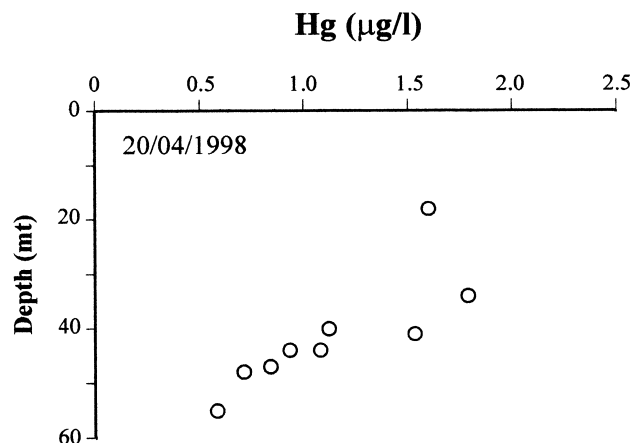
Hg (μg/l)

Fig. 7. Vigneto cluster of wells. Hg concentration versus depth of the pumping level of the wells.

nitude higher than normal sea water (Fergusson, 1990). This can be explained by the peculiar situation of southern Tuscany concerning the presence of Hg in the environment. The geochemical background of Hg in rocks of southern Tuscany is higher (0.218 ppm according to Baroni et al., 1994) than the average crustal value (0.080 ppm) reported by Greenwood and Earnshaw (1984). More importantly, the long history of mining (and roasting) of world class Hg-ores has given rise to the accumulation of huge piles of Hg-contaminated waste. The erosion and spreading of the contaminated materials gave rise to wide and profound geochemical anomalies of this metal around the mining centers (Riccobono, 1994; Protano et al., 1998). Subsequently, a significant amount of Hg likely reached the sea by means of the river drainage in this zone. Thus, the presence of anomalous Hg contents in the coastal sea water is not surprising.

Nevertheless, the simple intrusion of this kind of salt water into the aquifer and its partial mixing with fresh groundwater is insufficient to explain the rather high values of Hg found in various wells. Moreover, although there is a general correlation between Hg content and chlorine in the groundwater, it is not at all linear (Fig. 5).

Hg in marine water is largely present as chloro-complexes, $HgCl_4^{2-}$ being the most significant species at the chlorine ion concentration of sea water. However, thermodynamic calculations applied in the geochemical modeling of sea water/fresh water mixing processes suggest that a small change in redox conditions (i.e. slightly lower pE) can heavily bias Hg speciation (Turner, 1987). In particular, if the pE of sea water falls below a value of 4 (Fig. 6), the stability field of elemental Hg is greatly enhanced and the bulk of the element is converted to Hg°. A favorable environment for this conversion is surely represented by the root zone of an aquifer which coincides with a scantily oxygenated milieu. We believe that a simple mechanism of gaseous
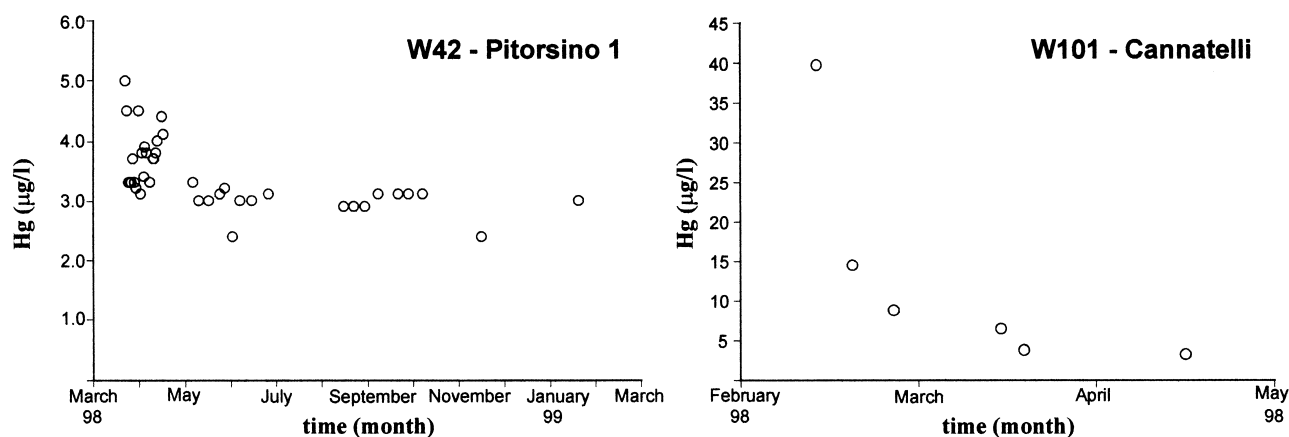
Fig. 8. Temporal trend of the Hg contents in two wells of the study area. Note the steep drop of values shortly after the contamination phenomenon was recognized. The trend of the W42 well could be influenced by a reduction of the pumping rate.

Hg° generation, when sea water enters a medium separated from the atmosphere, can be invoked to explain the curious overlap of salt water intrusion and Hg° contamination in the wells of southern Tuscany. The anomalous Hg contents in the sea water render the phenomenon even more apparent.

The ascent of Hg° toward the top zone of the aquifer may be linked to both the ultrafine suspended matter and the micro-bubbles of the dispersed gaseous phase caused by the depression from the pumping. We imagine this phenomenon as a kind of 'champagne plug effect'. Fig. 7 illustrates the relation between the depth of the pumping level and the Hg contents in water, in the cluster of wells at Vigneto (W68–W76) shown in Fig. 2. There is a strong progressive Hg accumulation from the bottom to the top zone of the aquifer. Such a situation corroborates the preceding interpretation.

Much work remains to be done to shed light both on some relevant details of the process we have described and on the crucial topic of the evolution in time of the Hg contamination. In this regard, our data (Fig. 8) indicate a decrease of Hg contents in time. A similar trend can be inferred from Fig. 5.

However, we wish to emphasize that if we are correct, even a slight increase of Hg content in the water of a coastal aquifer (and if mainly as elemental Hg°) could be a serious indication of the rupture of an equilibrium. Increased levels of Hg° could precede those of other chemical species in fresh water due to the interference of salt water intrusion. The magnitude of the phenomenon will be determined by the metal content in the salt water.

Acknowledgements

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