

# Gases released by water: impact on underground mines and on the surface

Giuseppe Sammarco<sup>1</sup>, Onofrio Sammarco<sup>2</sup>

<sup>1</sup> Richard Ginori 1735 S.p.A., Sesto Fiorentino, FI, Italy

<sup>2</sup> Bureau of Mines, Dept of Earth and Environment, Tuscan Region, Via Goldoni 6, 58100 Grosseto, Italy; e-mail [disminer@gol.grosseto.it](mailto:disminer@gol.grosseto.it)

**Abstract.** There are many areas in the world subject to CO<sub>2</sub> and, subordinately, H<sub>2</sub>S emissions that may be locally intensified by mining activities. Since these gases are highly soluble in water and are almost associated with it, this paper analyzes the mechanism of their release from the water and the factors that affect it. Above all it takes into account the effects of mining activities on this mechanism as well as the consequences of gas release on the mining work. It also analyzes all the other factors that concur with the foregoing to determine the spatial-temporal distribution of the gases in the atmosphere. By citing some specific cases it highlights the importance of promptly predicting and thereby preventing hazardous situations also through indirect detection of concentrations of dissolved gas.

## Introduction

Carbon-dioxide discharges are concentrated in the world along zones of seismicity that are also characterized by active or recent volcanic activity, such as the circum-Pacific belt, from southern South America to New Zealand and the alpine belt of Southern Europe and Asia Minor. The carbon-dioxide discharges generally seem to be derived from the metamorphism of carbonates and from mantle sources (Barnes et al. 1978). The high presence of carbonatic rocks and the high frequency of metamorphic events in the case of the first origin and the poor solubility of CO<sub>2</sub> in magma, in the case of the second origin, and the poor reactivity and water solubility of CO<sub>2</sub> in both cases explain the high quantities of this gas that are discharged into the atmosphere where, because of its high specific weight after discharge it tends to accumulate. In mines excavated in the above areas there may be gas emissions comprising mainly CO<sub>2</sub>, and then H<sub>2</sub>S. In general terms H<sub>2</sub>S should be considered a thousand times more dangerous than CO<sub>2</sub>. These gases reach the

mine either with the water that flows into it or alone after having been released from the water in which they were dissolved or had somehow reached. The fact that these gases are associated with water, a finding also confirmed by a census of gas emissions in the Peri-Tyrrhenian area of Central Italy (Duchi and Minissale 1995) that revealed the presence of water in 107 out of 109 emissions (Sammarco 2000 b), can be explained as follows: In general, the tectonic processes would generate not only metamorphism and hence, if carbonatic rocks are involved, CO<sub>2</sub>, but also fractures which can permit both the flow of gases to the surface as well as water circulation and the formation of aquifers even in the same areas where the CO<sub>2</sub> had accumulated. Carbon dioxide and hydrogen sulphide are much more water-soluble than the other gases that are frequently found in natural emissions (Table 1).

**Table 1.** Solubilities of gases in water at various temperatures when the partial pressure of the gas is 1 atm. (101, 3 kPa).

| Gas              | Solubility (g/l) |        |        |        |
|------------------|------------------|--------|--------|--------|
|                  | 10°C             | 20°C   | 30°C   | 40°C   |
| CH <sub>4</sub>  | 0.0308           | 0.0251 | 0.0208 | 0.0179 |
| CO <sub>2</sub>  | 2.3501           | 1.7208 | 1.3203 | 1.0025 |
| H <sub>2</sub> S | 5.2311           | 3.9737 | 3.1349 | 2.5547 |
| N <sub>2</sub>   | 0.0235           | 0.0195 | 0.0168 | 0.0148 |
| O <sub>2</sub>   | 0.0543           | 0.0443 | 0.0373 | 0.0330 |

For the reasons given above, this paper refers primarily to CO<sub>2</sub> and H<sub>2</sub>S gases which, since they are highly soluble in water are often released from it and are markedly affected by its dynamics. The paper primarily analyses the factors which by governing the mechanisms of gas release from water affect in the end the gas concentrations in the atmosphere.

The deductions presented here apply to the places in the above mentioned areas that are subject to CO<sub>2</sub> discharges and hence accumulations of that gas in the water and atmosphere especially if there are working mines in those places. In the areas where these workings develop they may cause marked increases in water and mainly gas permeability that can continue even for decades after the mine is abandoned, promoting the accumulation of those fluids in the areas.

## The mechanism of gas release from water: influences on and as consequence of mining.

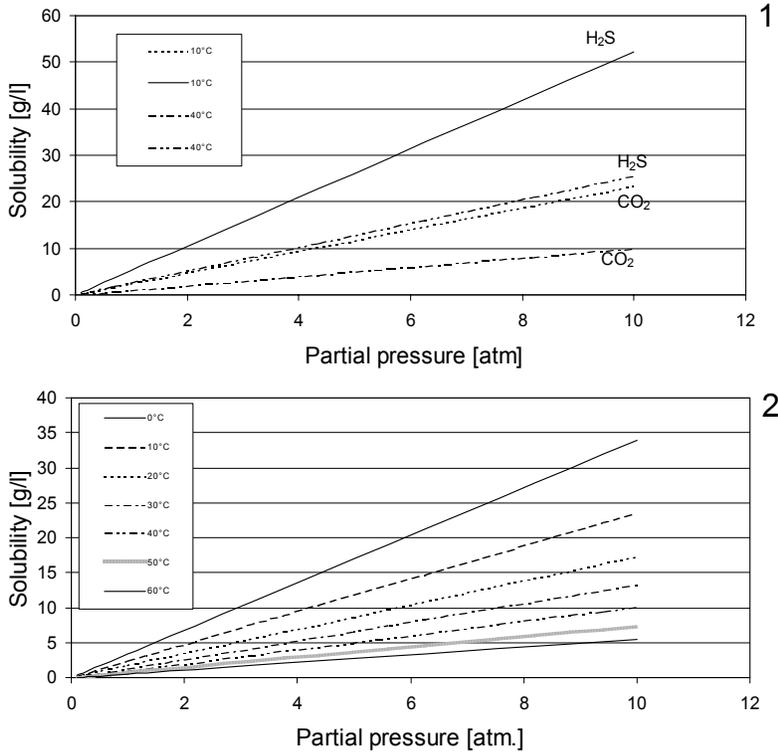
Bunsen coefficient values at various temperatures:

$$\alpha = v_0/Vp \quad (1)$$

where  $v_0$  is the S.T.P. volume of gas which at partial pressure  $p$  dissolves in the volume of water,  $V$ , and Henry's law

$$p = HC, \quad (2)$$

where  $H$  is the Henry coefficient and  $C$  is the concentration of gas dissolved in water at a given temperature and partial pressure  $p$ , make it possible to express the solubility of a gas in water as a function of temperature and partial pressure (Glasston 1963).



**Fig. 1.** Solubility of the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases in water as a function of the partial pressure at 10 and 40°C, (1). Solubility of  $\text{CO}_2$  in water as a function of the partial pressure at various temperatures (2).

Figure 1. shows the approximate solubility of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  as a function of the partial pressure and for two temperature values having considered the Henry's law valid for partial pressures exceeding 1 atmosphere (101.3 kPa), too, and for concentrations of non-diluted gases and solubility independent of the system's total pressure. Using the same approximations, figure 1.2 shows the solubility of  $\text{CO}_2$  alone, as a function of the partial pressure and for different temperature values (Perry and Green 1998; Stumm and Morgan 1996). It is obvious that before reaching saturation conditions, the more soluble the gas is in water, the bigger is the quantity of gas which can be dissolved.

Once saturation is reached, as shown specifically for CO<sub>2</sub> and H<sub>2</sub>S in figure 1.1, at constant temperature and at a given partial pressure decrease, as well as at constant pressure and at a given temperature increase, the more soluble the gas is in water, the higher will be the quantity of gas that is released. At a constant pressure and at a given temperature increase, the lower the temperature at which the increase begins, the greater the amount of the gas that is released (Fig. 1.2).

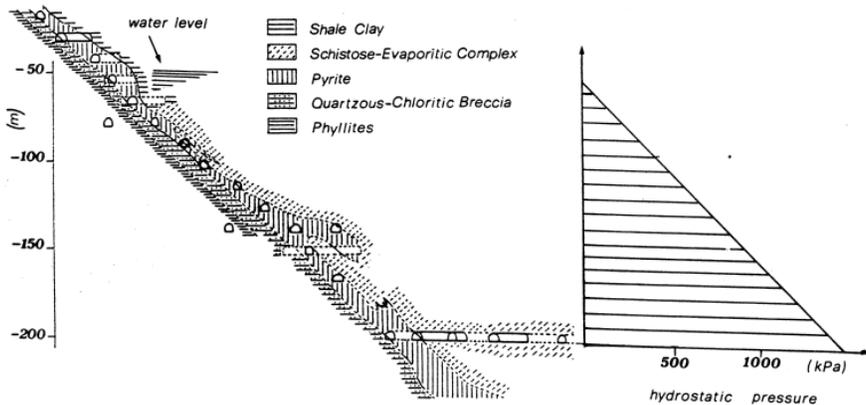
Both figures clearly show that significant amounts of both H<sub>2</sub>S and CO<sub>2</sub> are released as the temperature rises and, above all, partial pressure decreases.

There are various circumstances under which we can have water with dissolved gases. Just as there are many situations and modes with which the waters can be subject to pressure decreases and hence find themselves in conditions that will release gas.

In the case of surface water bodies, pressure decreases occur either in the backwater water when it is agitated or when its level drops, or in the water that is discharged from it. In this case the more the water is mixed where it flows the more is mixed and broken down where it falls or where there is great turbulence the more the pressure decreases. In these circumstances if the water contains dissolved gases they will be released according to ways which depend on those with which the pressure is reduced.

Pressure is reduced in subterranean water bodies when they are intercepted and exposed locally to the atmosphere, such as during mine excavations, or in environments with pressures lower than that of the water body at the point of interception, such as when drilling a bore-hole. As to the interceptions that occur when excavating underground mines, the following two alternatives can be cited.

1. Interception with a gallery of an unconfined or confined aquifer in formations with primary permeability.
2. Interception with mining work at several levels, of a water body in a karst cavity isolated from or somehow connected to superficial water bodies (Fig. 2).



**Fig. 2.** Hydrostatic pressure in a water body, on the right, intercepted at various altitudes by an underground mining, on the left.

In the first case as the water flows towards the gallery its pressure decreases with the pressure head and with a gradient that increase with the decreasing permeability of the formation and the decreasing distance from the gallery. If the water were to contain dissolved gases, because of these pressure decreases once it is saturated it would release gas which would flow together with the water in the gallery and by itself into the dry part of the formation, if it is an unconfined aquifer. In any case, the greater release of gas should occur when the water flows into the gallery because it is at the outlet where the greatest pressure reduction occurs. The gas that was released and flowed into the dry part of the formation would then enter the gallery with flow rate depending on the permeability of the formation and difference between the pressure of the gas in the formation and the pressure of the air in the gallery.

In the second case (Fig.2), as soon as the excavations have come close to the edge of the flooded cavity and compromise its integrity to the point of fracturing it and thus due to the hydrostatic pressure permit the water to flow into the mine, the water will immediately enter it. In this circumstance the water pressure in the cavity will start to decrease very slowly at a distance from the fracture that is little greater than its width (Nebbia et al. 1960), and decrease faster and faster as it gets closer to it, to finally reach atmospheric pressure at the outlet. If the water in the cavity were to contain dissolved gases, they would be released as soon as the pressure starts to decrease, and after up to the outlet in the same manner as which the pressure is decreasing. The gases released in this way could remain in part in the cavity and go back into solution or rise to the surface of the water and spread above it; in part they could be carried by the water that flows into the mine. In addition to the gases already released, the gases that are released from the water at the outlet and along its underground path will also enter the mine.

It is evident that as the hydrostatic pressure increases with depth, for a given amount of discharged water, the more the gallery is deep the more these gas releases will be intense. In the case of very high pressures, which could occur besides that owing to high hydrostatic heads also for high temperatures, these gaseous emissions could become explosive due to the rapid expansion of the gases. As examples we can mention instantaneous irruptions of water and gas and, for anomasia, phreatic explosions for which, however, the energy is provided mainly by the expansion of steam formed as a result of the pressure decrease.

## **Influences on the released gas emissions into atmosphere**

The actions of the factors that can affect the immission into and diffusion in the atmosphere of released gases depend on specific circumstances. Gas released by water can reach the surface atmosphere or the atmosphere in an underground mine directly or after having traversed permeable formations and/or cavities. Only in the latter case the flow rate of the gas that flows into atmosphere could depend significantly on atmospheric pressure: if the gas released by the water should enter

a cavity before going into the atmosphere, its flow rate when it finally does enter the atmosphere depends on the atmosphere pressure, as long as its pressure, upstream from the outlet of the cavity, is lower than twice the atmospheric pressure (Sammarco 1984, 2000). In this case the gas flow rate depends, in particular, on the atmospheric pressure, speed with which it varies, trend with which it has varied and size of the cavity (Sammarco 2000 b).

Actually, there could be increases in atmospheric pressure that would invert the flow between the cavity and the atmosphere causing air to enter the cavity, thus when the flow of gas would be restored, the gas would enter the atmosphere diluted with the air which would then contribute to reducing gas concentrations outside the cavity.

It is obvious that in the case of partially flooded cavities, increases and decreases in the water level will correspond, respectively, to decreases and increases in atmospheric pressure, even if the firsts will occur and influence these gas discharges with ways that could be quite different from those of the seconds.

There is no doubt that the manner in which this gas will appear on the surface or underground will also depend on the formations permeability to both water and gas. And the permeability changes with the geomorphology either owing to natural events or as a consequence of the mining work itself.

## **Gas concentrations in the atmosphere: effects of the combined action of the various influencing factors**

The factors reviewed are those that control the distribution and intensity of the emissions of gases released from water that reach the atmosphere either directly or via the formations into which they flow after release. High intensity emissions promote high concentrations of gas that may occur due to reduced dilutions which, in turn, may also be caused by equally reduced diffusion of the gas in atmosphere. On the surface gas diffusion depends on the morphology of the area around the discharge and meteorological factors, mainly winds; in underground mines it depends on the geometry of the mine network, microclimatic conditions and mainly ventilation. In both situations the specific weight of the gas or, in the case of mixtures, the specific weights of the various components also contribute to gas diffusion.

Due to the combined action of these factors the distribution of gas concentrations in the atmosphere can vary greatly from case to case. Sometimes they also vary greatly over time and in an unpredictable manner due to the significant and at times unpredictable changes that characterize some of these factors.

One example of the excessive variation of the gas concentrations in atmosphere is the case of two gas discharges into the atmosphere from bore-holes that connect the abandoned underground mine *Abbadia S. Salvatore*, where sulphydric waters flow too, with the surface. The gas, that also contains CO<sub>2</sub> (~96%) and H<sub>2</sub>S (~0,20%), released by these waters enters the mine cavity and the surrounding natural cavities, and reaches the surface via two bore-holes and the 7 meter high

vent pipe put on each. In this case the concentrations in atmosphere of the gases discharged from the two vent pipes depend on the piezometric situation around the mine, the water level in it, the atmospheric pressure, because the gas enters, after having been released from the water, the mentioned cavities prior to reaching the outside atmosphere, the evolution of those factors and primarily the winds.

Systematic readings of gas concentrations were taken over a period of 500 days at 12 points one meter from the soil, around each of the emissions, and situated on 4 orthogonal directions at distances of 1.50, 5.00 and 10.00 meters from each. Table 2 refers to the concentration of H<sub>2</sub>S in the atmosphere around one of the two bore-holes from which the gas exits at a mean flow rate of 150 l/s. The table shows the measuring points, the number of measurements taken at each point and the minimum, mean, maximum and standard deviation values of the concentrations found. The concentration distributions were anything but stationary. The high variability of the H<sub>2</sub>S concentrations at each point is due mainly to the just as high variability of the winds that have a strong impact on the diffusion of the gas.

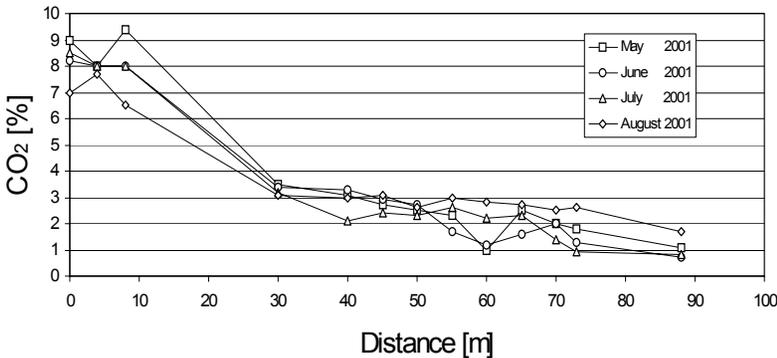
**Table 2.** Abbadia S. Salvatore Mine. H<sub>2</sub>S concentrations in atmosphere round Ermeta bore-hole: number of the look-outs in each point and minimum, maximum, average and standard deviation values of the H<sub>2</sub>S concentrations which have been observed in each of these points.

| Location        | Number | Minimum<br>(ppm) | Maximum<br>(ppm) | Average<br>(ppm) | Standard Deviation<br>(ppm) |
|-----------------|--------|------------------|------------------|------------------|-----------------------------|
| Dir. 1 at 1.5 m | 83     | 0.00             | 60.00            | 6.01             | 15.90                       |
| at 5.0 m        | 83     | 0.00             | 43.00            | 6.59             | 12.32                       |
| at 10.0 m       | 83     | 0.00             | 22.00            | 4.46             | 7.31                        |
| Dir. 2 at 1.5 m | 83     | 0.00             | 59.00            | 4.48             | 12.07                       |
| at 5.0 m        | 83     | 0.00             | 58.00            | 8.72             | 14.06                       |
| at 10.0 m       | 83     | 0.00             | 31.00            | 3.13             | 6.91                        |
| Dir. 3 at 1.5 m | 83     | 0.00             | 60.00            | 6.10             | 16.27                       |
| at 5.0 m        | 83     | 0.00             | 53.00            | 4.69             | 10.78                       |
| at 10.0 m       | 83     | 0.00             | 25.00            | 1.55             | 4.58                        |
| Dir. 4 at 1.5 m | 83     | 0.00             | 20.00            | 0.24             | 2.20                        |
| at 5.0 m        | 83     | 0.00             | 20.00            | 0.36             | 2.44                        |
| at 10.0 m       | 83     | 0.00             | 20.00            | 0.54             | 2.90                        |

A example of distribution of gas concentrations very different from those cited and that could be considered almost stationary given the slight variations in time that characterize it can be found in the distribution of the CO<sub>2</sub> concentrations 0.20 meters above a waterway, with a flow rate of approximately 300 l/s, that flowing along a gallery collects the drainage water of the Niccioleta mine. The readings were taken starting from the point where the water flows onto the surface. Only after the mine was abandoned the CO<sub>2</sub> was recognized in the water flowing at a rate exceeding 20 l/s. It probably comes from discharges of waters containing CO<sub>2</sub> or CO<sub>2</sub> discharges alone that probably developed following cave-ins in submerged parts of the mine. Figure 3 shows trends of the CO<sub>2</sub> concentration along the waterway obtained with monthly readings: the variations over time of those concen-

trations were very low in relation to the interval of time during which they occurred. The same figure 3 shows that in the section of the waterway that is between 8 and 30 meters from the outlet, where a small waterfall and high slopes occur, the concentration gradients are much higher than in other sections. The low variability over time of the trend of the concentration of CO<sub>2</sub> in atmosphere along the waterway depends on the very low ventilation around the surface of the water where the readings were taken.

Air velocity certainly has a determining influence on the distribution of gas concentrations. Therefore, on the surface where the winds are irregular in direction and intensity the concentration distributions will differ from one direction to another and will vary over time even in the same direction. In active underground mines, whereas, where air motion is guided by the same galleries and its speed is on an average constant except, for some transients (Sammarco 1971), the distribution of the gas concentrations will be essentially stationary if they are caused by gas discharges that do not change in position and in intensity, or that are controlled by adjusting the ventilation.



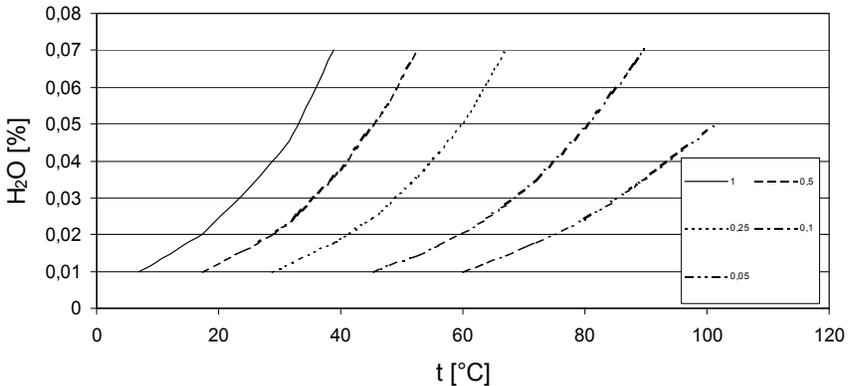
**Fig. 3.** Niccioleta mine. CO<sub>2</sub> released from the drainage: limited variability during the time of the CO<sub>2</sub> concentration in the air over the water course.

## Hazards and forecasts

When gas is released by water the consequent risks depend on specific circumstances. Here are a few examples.

If CO<sub>2</sub> were released with other gases, or if after release it is in an atmosphere with other toxic or anyhow harmful gases, in addition to a decrease in the oxygen concentration in the air, and the effects of each gas, there could be synergic effects as well, and unfortunately there is little knowledge about them.

In the case that the  $\text{CO}_2$  develops from water at a high temperature, in addition to favouring the development of the gas that temperature would intensify evaporation and the steam could come to be in air in not negligible concentrations in order to reduce, together with the  $\text{CO}_2$ , the oxygen concentration. In figure 4 that shows the volume concentration of steam as a function of the temperature at different values of relative humidity, it is possible to see that at temperatures above  $37^\circ\text{C}$  and relative humidity of 1, the steam concentrations exceed 6%. Hence the reductions in the oxygen concentrations are greater than 1%. It is obvious that since it is dealing with  $\text{CO}_2$  and not an explosive gas, these reductions increase rather than diminish the risk.



**Fig. 4.** Steam concentration in volume as a function of the temperature at various relative humidity values.

Another not uncommon case is that of accumulations of water subject to level changes and which contain  $\text{CO}_2$  or which this gas can be discharged into. In these circumstances the increase of the water mass and that of the hydrostatic pressure in the same mass increase the backwater's capacity to accumulate gas. If the water level of the backwater were to drop and/or the water flow into the valley the gas would be discharged into the atmosphere with considerable risks. The occurrence at the Selvena mine during a flood of its deepest parts is highly significant.

As the piezometric surfaces around the mine dropped, high concentrations of  $\text{CO}_2$  appeared in a tunnel above the drainage tunnel (Sammarco 2000 b).

The primary preventive measure is to ascertain whether there are situations that can generate risks. In the specific case it is first necessary to ascertain whether there is gas in the water that can develop. To facilitate and accelerate this check it would be advantageous to be able to determine the concentrations of dissolved gas indirectly by reading other quantities immediately readable and that could give a reliable indication of the concentration. We took over 30 mineral waters containing  $\text{CO}_2$  in solution, and correlated the concentration of  $\text{CO}_2$  dissolved in each with the concentrations of ions in solution and with the values of the electric con-

ductivity and of the pH. We found that high CO<sub>2</sub> concentrations in solution correspond to just as high conductivity values. For CO<sub>2</sub> concentrations exceeding 600 mg/l we found conductivity values, K, above 850 μ S/cm (fig.5) and pH values below 6.7.

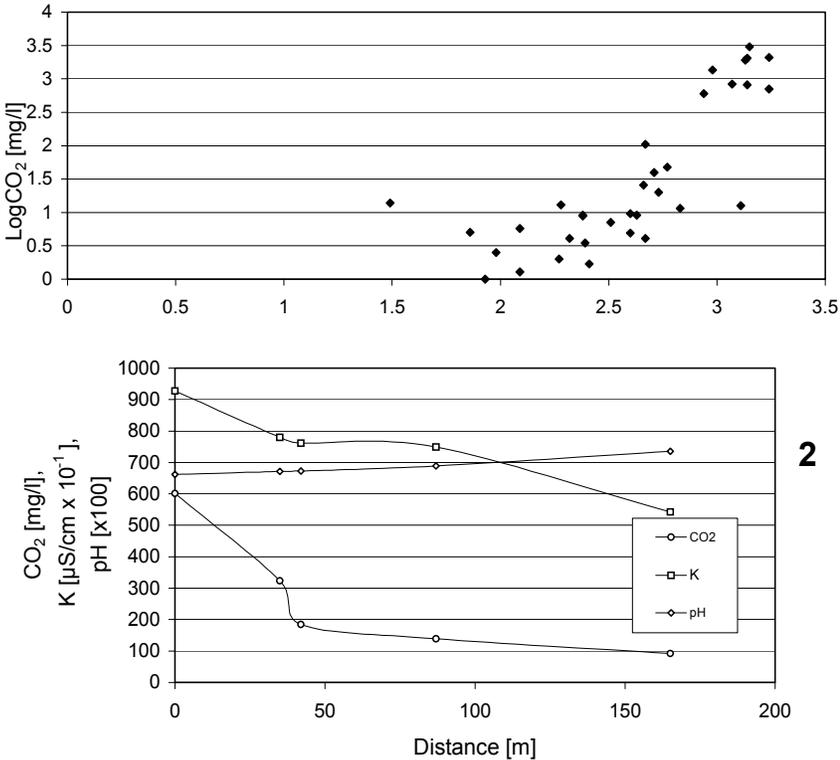
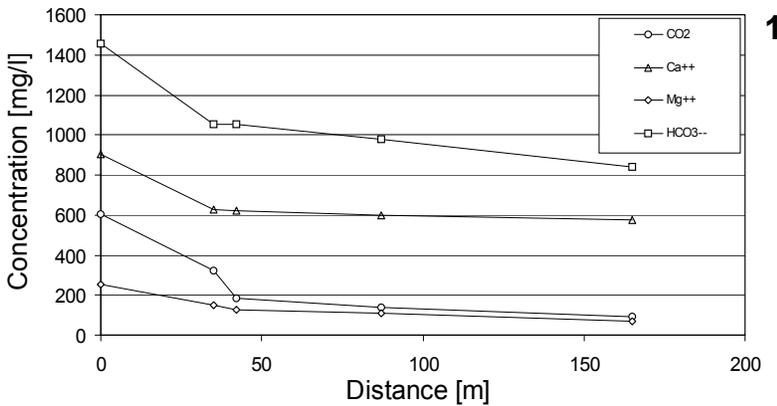


Fig. 5. Correlation between concentration of CO<sub>2</sub> dissolved and water conductivity.

Confirmations of these correlations are shown in Figure 5 that refers to the degassing of a thermal water raised to the surface by CO<sub>2</sub> gas. Degassing is obtained by making the water, which presents concentrations of free CO<sub>2</sub> of 602 mg/l at the outlet, run over 165 meters where small waterfalls are produced in the initial section. Figure 6 shows how in what manner decreasing the CO<sub>2</sub> in solution, decrease the calcium and magnesium concentrations, and, in particular, significantly decreases the conductivity and slightly increases the pH.

The pH and mainly electric conductivity monitoring can, with the appropriate precautions, be effectively utilized in determining whether or not there are excessive concentrations of CO<sub>2</sub> in solution or if a water containing this gas has been sufficiently degassed.



**Fig. 6.** Effects of the degassing of a thermal water: by decreasing the CO<sub>2</sub> dissolved in water, the Ca<sup>++</sup> and Mg<sup>++</sup> concentrations decrease, 1, pH increases and the conductivity decreases, 2.

## Conclusions

The gases covered by this paper are carbon dioxide and hydrogen sulphide. They are frequently found in geothermal fluids, and due to their high solubility in water as opposed to other gases, they are released from water with an as much high intensity when the factors that control their dissolution vary.

To predict and prevent excessive concentrations of gas in the atmosphere in the anything but rare cases, in which the gas reaches the atmosphere after having been released from water, we must take into account all the possible dynamics of the water as well as their repercussions on the release mechanism. We must never underestimate the possibility of a water body to accumulate gas when it extends and to return it when it diminishes. Nor should we underestimate its capacity to compress and expand the gas that was released and flowed into any cavities, when the water level respectively rises or lowers. All these factors must be considered along with the others that, at the end, affect gas concentrations in the atmosphere in order to combat those that contribute to increasing gas concentrations and favour those that tend to reduce them.

It is evident that in order to be able to control gas concentrations in the air it is important to be aware of them in water. With specific reference to carbon dioxide, concentrations of this gas in water, with appropriate precautions, can be readily checked by testing the electric conductivity of the same water.

## References

- Barnes I, Irwin W P, White D E (1978) Global distribution of carbon dioxide discharges and major zones of seismicity. *Open-file Rep 78-39*: 53-63
- Duchi V, Minissale A (1995) Distribuzione delle manifestazioni gassose nel settore peritirrenico toско-laziale e loro interazione con gli acquiferi superficiali. *Boll Soc Geol It* 114: 337-351 (in Italian)
- Enciclopedia des gaz – Gas encyclopaedia (1976). Elsevier Amsterdam – New York
- Glasstone S (1963) Trattato di chimica-fisica. Manfredi Milano: 870 (in Italian)
- Nebbia G, Ippolito G, Russo Spena A, Viparelli M (1960) *Idraulica Treves Napoli*: 512 (in Italian)
- Perry H R, Green W D (1998) *Perry's chemical engineers' handbook*. McGraw-Hill NY
- Sammarco O (1971) Le perturbazioni della ventilazione nelle miniere. *L'industria mineraria II XXII*: 467-476 549-559 (in Italian)
- Sammarco o (1984) L'influenza della pressione atmosferica sulle venute di gas in miniera. *L'industria mineraria III V*: 5-19 (in Italian)
- Sammarco O (2000) Water and gas emissions: dynamics and mutual influences. *Proc 7<sup>th</sup> International IMWA Congress, September, Ustron Poland*: 645-659
- Sammarco G, Sammarco O (2000) Gas da acque termo-minerali: modalità di liberazione, rischi e cautele. *Atti Problemi di geoingegneria: le risorse termo-minerali, Ottobre, Piacenza Italy*: 45-58 (in Italian)
- Stumm W, Morgan J J (1996) *Aquatic chemistry*. Wiley & Sons NY: 1022