The Black Sea has lost more than a third of its habitable volume

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Credit: University de Liege

With rivers providing an abundant supply of fresh water, the upper

layers of the Black Sea are less dense than its saltier lower layers. A permanent boundary between the two prevents any vertical mixing. The oxygen, derived from the atmosphere and photosynthesis, remains restricted to these surface waters. However, this precious gas is essential to the development of the majority of living species. Recent research, carried out by the MAST (Modelling for Aquatic Systems) group at the University of Liège, has shown that this oxic boundary shoaled from 140 to 90 metres between 1955 and 2015. A compression of almost 40 % of the habitable space in the Black Sea, directly linked to its eutrophication and global warming. This phenomenon could be accompanied by major ecological and economic consequences. Furthermore, a high concentration of hydrogen sulfide, an extremely toxic gas, lies dormant in the deepest layers of the Black Sea. For the moment, there is no evidence of a correlation between the compression of the oxic zone and this gas rising. But if the stratification of the water column weakens, even locally, an imbalance could endanger the aquatic life in the surface layer.

Of all the planet's seas, the Black Sea has a very particular profile. Surrounded by land, it could even be mistaken for a great lake if it weren't for the fact that it is directly connected to the Mediterranean Sea through the Bosphorus Strait, a small one-kilometre-wide waterway. A sea surrounded by land that determines its special characteristics. "The main supply of water to the Black Sea comes from rivers. Especially the Danube", explains Arthur Capet, the first author of the publication on the decline of oxygen in the Black Sea and researcher at MAST, led by Marilaure Grégoire, FNRS research director. "This fresh water, which is less dense than sea water, colonises the upper layers of the water column without mixing with the lower layers." Because the lower layers are far more saline. The origin is to be found to the south-west of the Black Sea, in the Bosphorus. "Here, there is an exchange with the Mediterranean Sea in two layers. The fresh water at the surface flows out, and lower down, the salt water flows in and sinks directly towards the denser

levels."

The permanent stratification linked to salinity, the halocline, deprives the deep waters of oxygen. The marine food chain therefore develops above this boundary below which the waters are devoid of oxygen. "All the same, the Mediterranean inflow supplies a small amount of oxygen to the intermediary layers. Not only does it contain oxygen, but as it descends, it entrains surface water with it. However, this oxygen is very rapidly consumed as the organic matter decays." What happens is that the organic matter (plankton, algae, etc.), produced on the surface by photosynthesis, breaks down or is consumed and expelled by other species in the trophic chain. In both cases, this eventually sinks. Since it requires oxygen to break down, the few reserves that exist in the lower layers are exhausted.

"The oxygenated and therefore habitable area of the Black Sea is a very restricted space. This is the case horizontally, because the basin is almost completely closed, and also vertically, owing to this permanent stratification. Compared with other seas, this restricted volume is exposed to major external influences. It is therefore more sensitive and capable of evolving rapidly", Arthur Capet explains. It is this type of evolution that the researcher was able to observe. By compiling the data gathered over the past 60 years, he noted that the oxygen-rich top layer of the Black Sea had shrunk from 140 metres to 90 metres deep. Impressive figures that correspond to a more than 40 % decrease in the habitable volume.

Permanent stratification compared with seasonal stratification

The salt content favours the permanent vertical stratification in the Black Sea. In addition to this permanent stratification is a seasonal

stratification due to the temperature of the water. "In winter", Arthur Capet continues, "lower temperatures accompanied by higher winds make the surface water colder and richer in oxygen. However, cold water is denser than warm water. Therefore, this cold water sinks and takes the oxygen it contains with it. This creates a ventilation effect". It is this periodic phenomenon that supplies the deeper layers with oxygen. In the case of the Mediterranean, the surface waters cooled in winter sink to the bottom, supplying the entire basin with oxygen. However, in the Black Sea, these waters are blocked in the permanent halocline, even though they are colder than the deep waters. In terms of density, salt eventually wins over temperature. The cold waters end their journey here, and retain their oxygen. In summer, the surface waters warm up and no longer sink, thus creating a new stratification of the water column, the thermocline.

Several diagnostics to check the presence of oxygen

To diagnose this shrinking of the oxygen-rich top layer, Arthur Capet had to take into account two sources of variabilities that had to be distinguished to avoid biased conclusions. On the one hand, temporal variability, providing a view of the evolution in time of the presence of oxygen in the sea, and on the other hand, spatial variability. "Oxygen penetration isn't consistent in all areas. Especially close to coastlines, where the interaction between the current and the seabed induces increased vertical mixing, or close to the Bosphorus Strait. It was necessary to take into account every place where the measurements were taken to get a clear image of this evolution in time. And then there was another difficulty: the dominant currents in the Black Sea create forces that lift the vertical structure in the middle of the basin and lower it in the periphery. This mean that at the same depth, the water will be less dense close to the coast than in the middle of the basin." In other words, rather than forming a horizontal boundary, the halocline resembles a dome. To overcome this additional difficulty, the researcher quantified

the oxygen concentration by expressing the depth in metres on the one hand, and in terms of density on the other. Which then made it possible to find a consistent average for the whole of the basin and establish an accurate overall vertical profile for the water column.

The drivers behind this astonishing decline

Several historic databases contained information, collected during a number of campaigns, on oxygen distribution in the Black Sea. By compiling these figures and those collected by the ARGO www.argodatamgt.org buoys, which drift freely and send satellite information on the evolution of the temperature, salinity and oxygen, it was possible to compare more than 4000 profiles, taken between 1955 and 2015. By proposing an average of all these diagnostics and by inventorying the quantity of oxygen in the Black Sea, the final observation was very accurate and unequivocal. The oxygen penetration declined throughout the second half of the 20th century, shrinking from 140 metres in 1955 to a mere 90 metres in 2015.

There were two successive causes behind this gradual drop. A greater abundance of nutrients initially, then global warming. Up until the 1990s, the intensity of ventilationlinked to the dynamics of the cold waters didn't decrease. It even increased in certain years, during harsher winters. Therefore, there should have been a larger quantity of dissolved oxygen. However, its concentration continued to fall in the entire water column. It was necessary to look for the cause elsewhere than in the physical reaction linked to the climate. "In reality", Arthur Capet contextualises, "this shortage can be explained by the extensive eutrophication of the basin during this period. It corresponds to a major economic boom in the USSR, when huge farms and extensive cattle breeding were developed. What's more, this boom wasn't accompanied by environmental considerations." Fertilisers and organic waste linked to breeding found its way into the rivers and ended up in the Black Sea.

They had a very high nitrate and phosphate content which encouraged the primary production. "Just as the fertilisers encourage plants to grow, they also influence the production of algae. These algae consume oxygen when it decays or is consumed. A greater biomass therefore leads to a greater consumption of oxygen." In 1990, this influx of nutrients fell significantly. Once again, it seems that it was associated with a geopolitical and economic context, since it coincided with the fall of the Soviet empire and the economic difficulties encountered in the region. It is also the moment when the first wide-scale environmental measures were applied.

And yet, the level of oxygen didn't increase again. On the contrary, it remained the same for several years, when the winters were particularly cold, before decreasing again. This time, global warming was the culprit, by influencing ventilation. If the winters are warmer, a lower volume of dense water is generated, which reduces the oxygen content when these waters sink down to the halocline. "The phenomenon could well get worse. Before, this formation of cold water took place every year. And yet, the figures collected over the past ten years bear witness to an increasingly intermittent formation of cold water. We are currently in the process of analysing our results, but it would seem that this once annual ventilation now only takes place every two or three years. We still can't determine the consequences of this phenomenon, but in any case, we are witnessing a changing system."

Besides a less extensive and occasional mixing, this warming masks another effect leading to deoxygenation. One of the chemical properties of cold water means that it becomes saturated less quickly than warm water. The colder the water, the more it can contain dissolved gas, which obviously includes oxygen. As it heats up, the surface water is increasingly unable to accumulate oxygen. Subsequently, not only does oxygen no longer colonise the Black Sea at depth, but moreover, its concentration decreases in the entire water column. The deoxygenation

caused by the increase in the water's temperature is a global problem that concerns all the oceans. Today, the problem is taken very seriously by the scientific community.

Implications to be quantified

The study aims above all to quantify the physical processes linked to the water column by collecting and analysing the data. The dynamics seem to be properly understood now, in terms of both space and time. The big unknown remains the influence that these variations will have on the ecosystem. The models that enable the study of the different scenarios in the Black Sea must now be integrated with this new halocline, thermocline and oxycline data, so that their real impact can be more precisely predicted. However, several avenues can already be explored. "The Black Sea is clearly facing significant compression of its habitable area. The whole ecosystem is formed in this layer, from phytoplankton to predators, which evolve in the deeper waters. The entire trophic chain is organised in the water column according to the presence of light or nutrients. Previously organised over a depth of 140 metres, the interactions between these trophic groups must now find a new balance over a depth of 90 metres. There will be an ecological and economic affect. Fishing, which is one of the major activities in the region, will probably have to adapt to this reorganisation."According to the FAO, the catch amounted to 376,000 tons in 2013. Barely two times less than for the whole of the Mediterranean.

A toxic outsider

One final process deserves to be monitored. As previously mentioned, biomass consumes oxygen as it decays. When there is no more oxygen, this biomass continues to decay, leading to the consumption of sulfates by the bacteria and the production of hydrogen sulfide (H_2S), a highly

toxic gas. The permanent stratification of the Black Sea acts as a lid over the deep waters, in which this hydrogen sulfide has accumulated and reaches now unprecedented concentrations. Nothing currently proves that the shoaling of the oxygen penetration depthdirectly correspond to a shoaling of the hydrogen sulfide onset depth. "The depth at which the H2S appears doesn't exactly correspond to the depth at which the oxygen disappears. There is a whole series of intermediary processes in a median zone that is suboxic and devoid of hydrogen sulfide. We focused on oxygen and our study revealed a rise in the upper boundary of this zone, but not the lower one. We can assume that the stratification of the Black Sea will remain stable overall. But it's possible that if the H2S were to rise up, unstable climate or geological conditions would cause the hydrogen sulfide to pierce through the oxygenated layer. This could have major repercussions on aquatic life. In order to determine the situation and to solve the dynamics of the H2S, we must now model these processes, and quantify and inventory its concentration."

More information: Arthur Capet, Emil V. Stanev, Jean-Marie Beckers, James W. Murray, and Marilaure Grégoire, Decline of the Black Sea oxygen inventory, *Biogeosciences*, 13, 1287–1297, 2016

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